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

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

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, feasibility of the adsorbed metals was estimated by DTTP 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 DTTP 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 electrodialysis [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 \( \text{SiO}_4 \) and \( \text{AlO}_4 \) 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 \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \) 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: \( \text{Na}_8\text{K}_8\text{Ba}_{0.84}\left(\text{Al}_{29.31}\text{Si}_{66.83}\text{O}_{172}\right)\cdot 19.56\text{H}_2\text{O} \) [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: \( \text{Pb} > \text{Cd} > \text{Cs} > \text{Cu} > \text{Co} > \text{Cr} > \text{Zn} > \text{Ni} > \text{Hg} \) [11]. Mier et al. [12] Studied the sorption of \( \text{Pb}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}, \) and \( \text{Cr}^{3+} \) on natural clinoptilolite and showed that equilibriums favorable for Pb, unfavourable for Cu, and of sigmoid shape for \( \text{Cr}^{3+} \) and \( \text{Fe}^{3+} \). 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...
under the same experimental conditions [18]. The mobility of metals in the environment is 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.

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 CaCl$_2$ solutions containing 50, 100, 150, 200, 250, and 300 mg/l as a chloride salts in 50-mL centrifuge tubes (pre-weighted) 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 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 I. This study showed that natural zeolite contained a complement of exchangeable sodium, potassium, and calcium ions. The zeolite contained high percentage of SiO$_2$, followed by Al$_2$O$_3$, K$_2$O, CaO, and negligible percentage of Fe$_2$O$_3$, TiO$_2$, MgO, and Na$_2$O. 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.

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 (Kd) 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 Kd value indicates high metal retention by the solid phase through chemical reactions, leading to low metal bioavailability. Similarly, a low Kd 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 (Kd) 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 Kd 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 Kd 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 Kd values with the increase metals addition. The Kd values increase with the decreasing concentration of metal ions. In other words, the Kd 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 Kd 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 Kd 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.
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 0.74Å\(^2\), whereas that of Cu is 0.72Å\(^2\). 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 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 Å) > Zn (0.74 Å) [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 \( \times 10^{-24} \) 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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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 pKfH, 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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Fig. 3. Average percentage of labile forms of total sorbed metals by zeolite.


He has published 11 paper in international journals. His research interests is Geochemistry of trace elements – Remediation of trace elements polluted soils and waters - Waste management- Chemistry of soil phosphorus.


He is not required for the military, Associate Professor, January 2010- till now, Department of Pesticides, Faculty of Agriculture, Kafrelsheikh University, Egypt. Assistant Professor, 2004–2009, Department of Pesticides, Faculty of Agriculture, Kafrelsheikh University, Egypt. Assistant Lecturer, 1999 –2004, Department of Pesticides, Faculty of Agriculture, Kafrelsheikh University, Egypt. Demonstrator, 1994 –1999, Department of Pesticides, Faculty of Agriculture, Kafrelsheikh University, Egypt.

He has Published 12 paper in international journals. His research interests are Analysis, fate and remediation technologies of Pesticide residues in different environmental matrices.

Farahat S. Moghanm was born at Kafr El-Sheikh, Egypt - 20/1/1976. Ph.D. in the field of the soil pedology (2009), Russia, Saint-Petersburg State Agrarian University.

He is not required for the military, 1- Demonstrator in soil dept. 1999-2003. 2- Assistant Lecturer, 2003 – 2009. 3- Research associate at Russia, Saint-Petersburg State Agrarian University 4- Assistant Professor, soil dept., Fac. of Agric., Kafir El-Sheikh Univ, 2010 - Present.

He has Published 5 papers in national and international journals and conferences. His research interests is Pedology (Remote sensing and GIS).