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Removing Cadmium and lead From Wastewater Using Natural Zeolite Isotherm models

[1]Mohamed A.A. Sayed, [2]Mohamed S. Khater

[1]Soil Sci. Dept., Fac. Agri., Cairo Univ., Giza, Egypt.
[2]National Institute of Leaser Enhanced Science, Cairo Univ., Giza, Egypt.

ABSTRACT

The adsorption behaviors with respect to the studied metals are investigated in the running work. A batch method has been employed, using Cd and Pb metal solutions ranging from 100 to 600 mg/L. The distribution coefficients (K_d) and adsorption percent were determined for the adsorption system as a function of sorbate concentration. In this study, the adsorption behavior of zeolites with respect to Cd, and Pb has been studied. In the uptake evaluation part of the study, adsorption ratios of metal cations on zeolite match to Langmuir, and Freundlich, adsorption isotherm data. According to the equilibrium studies, the selectivity sequence can be given as $Pb^{2+} > Cd^{2+}$. It was found that the uptake depend on hydrated ion diameter. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Key words: Zeolite – Cadmium – Lead – Langmuir – Freundlich – adsorption.

Introduction

With the rapid industrialization and economic development, heavy metals are continuing to be introduced to environment through point and non-point sources where metals are produced as a result of metal refinishing by products. Therefore, heavy metal contamination is still an environmental problem today in both developing and developed countries throughout the world (Dan'azum and Bichi. 2010; Inglezakis *et al*. 2003; Momodu and Anyakora 2010) They are also common groundwater contaminants at industrial installations. Numerous processes exist for removing dissolved heavy metals, including ion-exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis (Jeon *et al* 2001; Schnoor 1997) The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently (Gupta *et al* 2009) The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant removal efficiency. Activated carbon (Pollard *et al* 1992) clay minerals (de Aguiar *et al* 2002; Crini 2006) biomaterials (Crini 2005) zeolites (Babel and. Kurniawan 2003; Hedstrom 2001) and some industrial solid wastes (Wang and Wu 2006; Wang *et al* 2008) have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment. Since the original discovery of zeolitic minerals in a volcanogenic sedimentary rock, zeolitic tuffs have been found in many areas of the world. In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy (Bish and Ming 2001; Tsitsishvili *et al* 1992) It has been estimated that the world natural zeolite consumption is 3.98 Mt and will reach 5.5Mt in 2010 (Ozaydin *et al* 2006). 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 (Bailey *et al* 1999). The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion (Al) 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 (Na), potassium (K), or calcium (Ca)]. These cations are exchangeable with certain cations in solutions such as Pb, Cd, Zn, and Mn (Barer 1987) So, zeolites can transfer a heavy metal contamination problem of many thousands of liters to a few kilos of easily handled solid. Natural zeolites are classified as low-cost adsorbents because of their local availability and low-cost extraction and preparation. Natural zeolites also gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange ability and high surface areas. Zeolites offer a potential for a variety of industrial uses including molecular sieves, ion-exchangers, absorbers, catalysts, detergent builders (Haidouti 1997; Ouki and Kavannagh 1997; Panayotowa 2003) the removal of cations from acid mine drainage and industrial wastewater (Mondale *et al* 1995). Also,(Leppert 1990) reported that zeolites have strong affinity for heavy metal ions. The selectivity series of zeolite in the sodium form was determined by (Zamzow *et al* 1995) as follows: $Pb^{2+} > Cd^{2+} > Cs+ > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ (Zamzow and Schultze 1995). (Jama and Yucel 1990) observed that zeolite shows a very high preference for ammonium ions over sodium and calcium but not over potassium .

Corresponding Author: Mohamed A. A. Sayed, Soil Sci. Dept., Fac. Agri., Cairo Univ., Giza, Egypt.
E-mail:saskhater@hotmail.com

Heavy metals such as lead (Pb), and cadmium (Cd) are prior toxic pollutants in industrial wastewater, which become common groundwater contaminants and they tend to accumulate in organisms, causing numerous diseases and disorders (Inglezakis *et al* 2003).

As seen from the literature review, zeolites can be used for the removal of some heavy metals such as lead (Pb), and cadmium (Cd) from wastewater. In this study, the uptake properties of zeolite with respect to some heavy metal cations in solution were investigated.

Materials and Methods

2.1. Zeolite source and conditioning:

Zeolite was purchased from Sigma-Aldrich Chemical composition of zeolite samples was :

0.6 K2O : 4.0 Na2O : 1 Al2O3 : 2.0 A 0.1 SiO2 : x H2O , The pore size of zeolite was 3Å It lead to adsorb those molecules that have a critical diameter of less than three angstroms, while the particle size was < 45 μm .

2.2. Reagents:

Inorganic chemicals were supplied by Merck as analytical-gradere agents and deionized water was used. The metal ions studied were Cd^{2+} , and Pb^{2+}. Synthetic stock solution of cadmium and lead using their nitrates slates in deionized water was prepared.

2.3. Batch adsorption studies:

The removing of heavy metals by natural zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 5 g of adsorbent with 500 ml of solutions containing heavy metal ions of concentration from 100 to 600mg/L at constant temperatures (30 ± 0.1 C°) . The bottles were shaken in a shaker for 5.5 h the solutions were filtered through Whatman flitter paper (No.42) (Erdem *et al* 2004). The concentration of metal ions and filterable metal concentrations were determined by AAS (UNICAM 929 atomic Absorption spectrophotometer).

Results and Discussion

3.1 Effect of metal concentrations;

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

$$\%\ adsorption = \frac{C_i - C_f}{C_f} \times 100 \qquad \textbf{eq. 1}$$

where Ci and Cf are the concentrations of the metal ion in initial and final solutions respectively,

and

$$Kd = \frac{amount\ of\ metal\ in\ adsorbent}{Amount\ of\ metal\ in\ solution} \times \frac{V}{m} \qquad \textbf{eq.2}$$

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 (Khan 1995):

$$\%\ \text{adsorption} = \frac{100\ K_d}{K_d + V/m}$$

3.2. Adsorption of metals on natural zeolite:

The removal of Cd^{2+}, and Pb^{2+} onto zeolite as a function of their concentrations was studied at constant temperature (30 ± 0.1 C°) by varying the metal concentration from 100 to 600 mg/L while keeping all other parameters constant. The results are shown in Fig. 1 Percentage adsorption for Cd^{2+} and Pb^{2+} decreases with increasing metal concentration in aqueous solutions. 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: Cd^{2+}55%, Pb^{2+}96%. Fig.2 and 3 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.

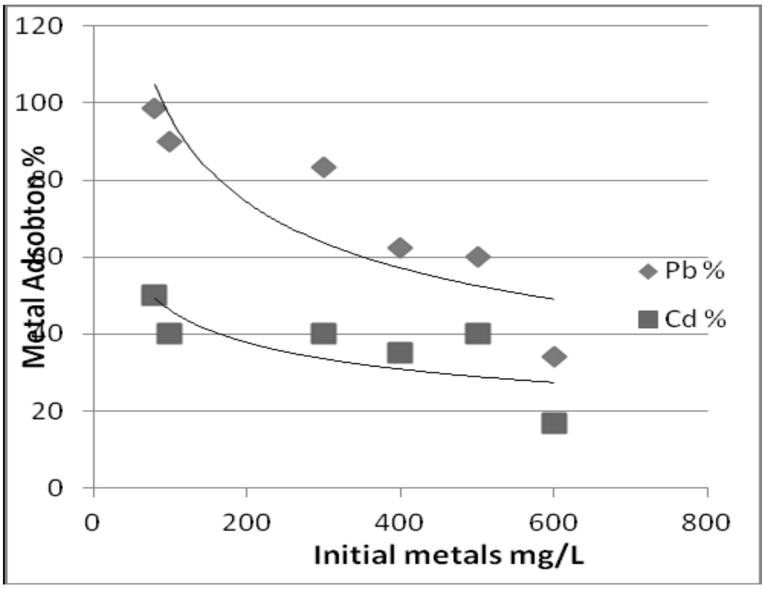

Fig. 1: Adsorption of metals ions by zeolite as a function of initial concentration at the optimum removal condition

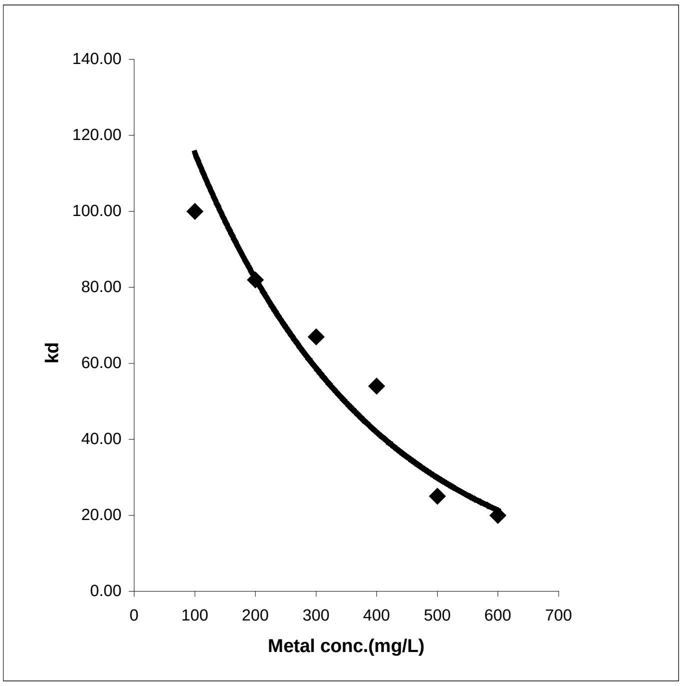

Fig. 2: Variation of Cd ion on natural zeolite as a function of initial concentration m = 1g , v = 100 ml time = 24 h.

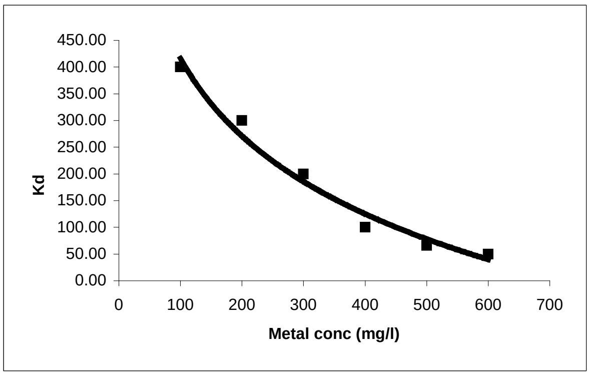

Fig . 3: Variation of Pb ions on natural zeolite as a function of initial concentration m = 1g, v=100 ml time = 24 h.

The heavy metal uptake may be attributed to different mechanisms of ion exch*a*nge processes as well as to the adsorption process (Akgul *et al* 2006; Aleksiev *et al* 2000; Erdem *et al* 2004; Harjula *et al* 1992; Tien 1994)

3.3. Isotherm Model:

Adsorption equilibrium measurements are used to determine the maximum or ultimate capacity. Adsorption equilibrium data are formulated into an isotherm model. The most commonly used models include Freundlich, and Langmuir isotherms (Hsia and Shin 2009) The sorption data have been subjected to different sorption isotherms, namely, Langmuir and Freundlich.

3.3.1. Langmuir Isotherm:

(Langmuir 1916) isotherm which models the monolayer cover age of the sorbent surface assumes that sorption occurs at specific homogeneous sorption sites within the sorbent and intermolecular forces decrease rapidly with the distance from the sorption surface. The model is also based on the assumption that all the sorption sites are energetically identical and sorption occurs on a structurally homogeneous sorbent (Prasad *et al* 2008; Gunay *et al* 2007; . Petrus and Warchol 2005; El-Kamash *et al* 2005 ; Bektas and Kara 2004). The equilibrium data for each metal cation Cd and Pb over the concentration range from 100 to 600 mg/L at◦25 ±0.1 C have been correlated with the Langmuir:

$C_e/C_{ads} = 1/Qb + C_e/Q$ **eq. 3**

where C_e is the equilibrium concentration of metal in solution, C_{ads} is the amount of metal ions sorbed per unit mass onto zeolite, Q and b are Langmuir constants related to sorption monolayer capacity and sorption energy, respectively. A linear plot is obtained when C_e/C_{ads} is plotted against C_e over the entire concentration range of metal ions investigated Figs. 4. The Langmuir model parameters and the statistical of the sorption data to this equation are given in Table 1. The Langmuir model effectively described the sorption data with R^2 values > 0.9 for lead and 0.78 for cadmium.

Table 1: Characteristic parameters and correlation coefficients of the experimental data according to Langmuir equation for Zeolite

Metal	Crystal radius (A)	Hydrated ionic radius (A)	Electronega tivity	Q(mmol/g)	b(L/mmol)	Correlation coefficient (R^2)
Cadmium	0.97	4.29	1.7	0.735	4.1	0.78
Lead	1.2	4.01	1.8	0.95	5.65	0.96

Table 2: Freundlich adsorption constants log K and 1/n for metal ions on zeolite at 25±0.1 ◦C.

Metal	Log K(mg/g)	1/n	Correlation coefficient (R^2)
Cadmium	0.63	0.68	0.73
Lead	0.85	0.78	0.78

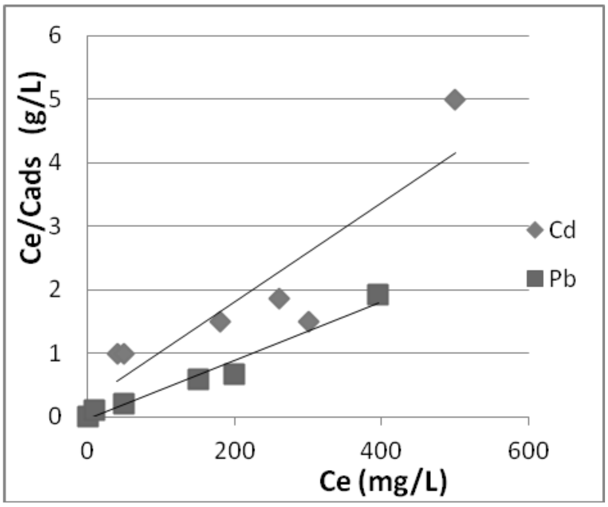

Fig. 4: Langmuir plots for metal ions adsorption onto zeolite

(Abd-Elfattah and Wada 1981) studied the selectivity sequence and estimated the competitive adsorption of several heavy metals. Most of the observed sequences are not correlated either with the sequence of ionic radii or with the sequence of electro negativity.

3.3.2. Freundlish Isotherm:

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. This isotherm developed by Freundlich (1926) describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity (Prasad *et al* 2008; Rao and Viraraghavan 2002; Hasany *et al* 2002). The equilibrium data for each metal cation over the concentration range from 100 to 600 mg/L at 30 ± 0.1 C$^{\circ}$ has been correlated with the Freundlich isotherm:

$Log\ C_{ads} = Log\ K + 1/n\ LogC_e$ *eq. 4*

Where C_e is the equilibrium concentration in mg/l and C_{ads} shows that the adsorption seems to follow Langmuir isotherm. A linear plot is obtained when log C_e is plotted against log C_{ads} over the entire concentration range of metal ions investigated and the values of *K* and *n* can be calculated from the intercept and the slope of this straight line, respectively (Figs. 5).

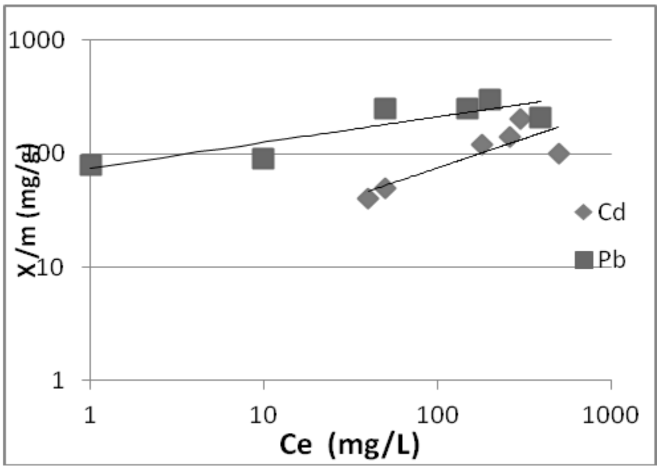

Fig. 5: Freundlich plots for metal ions adsorption onto zeolite

The result in Table 2 shows that all metals under investigation have a numerical value of 1/n< 1; value of *n* is greater than unity, suggesting that adsorption intensity is favorable at high concentrations but much less at lower concentrations. Values of *n* between 2 and 10 show good adsorption. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. The constants *K* and *n* were calculated for each cation (Hasany *et al* 2002).

Summary:

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 lowcost. Freundlich and Langmuir isotherm model are used to determine the maximum capacity Adsorption equilibrium. The Langmuir model described the sorption data with R^2 values 0.96 with lead and 0.78 with cadmium, while Freundlich R^2 values are 0.78, 0.73 with lead and cadmium respectively, so the amount of metal ions sorbet per unit mass onto zeolite (C_{ads}) follow Langmuir isotherm.

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