Removal of Cd²⁺ and Pb²⁺ Ions from Aqueous Solutions Using Iranian Natural Zeolite and Sepiolite

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Introduction

Industrialization and urbanization of societies have caused many environmental problems. Therefore, environmental protection has recently become highly important. Water resources are particularly of high risk of pollution from industrial waste disposal to river, surface, and ground water, and also from discharge of water to municipal waste water collection systems. These effluents usually contain a high concentration of heavy metals such as cadmium, lead, copper, and zinc which create many environmental problems due to their high toxicity.

Cadmium and lead are listed as dangerous heavy metals. These elements could contaminate soil and water resources in different ways. Remediation of soil and water contaminated with heavy metals is one of the important environmental policies in industrialized and developed countries. Many methods have been invented and used for waste water treatment such as chemical precipitation, reverse osmosis, and ion exchange, each with their own advantages and disadvantages. One of the methods developed in recent years is the use of inorganic adsorbents.

Different kinds of clay minerals such as smectite, palygorskite, sepiolite, Fe, Al and Mn hydroxides, and organic materials can be used for the sorption of heavy metals. This study has been carried out to compare the ability of Semnan zeolite and Yazd sepiolite in the removal of lead and cadmium from contaminated solutions and also to estimate the adsorption behavior of the zeolite and sepiolite minerals for cadmium and lead.

Materials and methods

Preparation of mineral samples

The clinoptilolite used in this research was collected from the Siah-Zagh mine of Semnan Province and the sepiolite sample from a mine in Yazd Province. Before use, the sepiolite and zeolite samples were passed through a 0.1 mm sieve (140 mesh). Some physicochemical properties of the minerals such as pH , cation exchange capacity (, and elemental analysis were determined by the use of pH meter device in saturation extract, by the method of saturation with sodium acetate, by the use of XRF, respectively. To determine the purity of minerals, the mineralogical composition of powdery zeolite and sepiolite samples was examined by an X-ray diffractometer (Philips PW-1840 model).

Adsorption experiments

0.5g of zeolite or sepiolite samples was mixed with 50 ml of solutions having different concentratins of Cd and Pb (0, 50, 100, 200, 400 and 600 mg/l) at pH =5. The suspensions were stirred for 24h at ambient temperature of 25±3°C and then centrifuged at 3000 rpm. The concentrations of Pb and Cd in the supernatants were determined by a GBC atomic absorption spectrometer (Savant AA). The quantity of Pb and Cd adsorbed by the minerals was calculated based on the difference between the initial and equilibrium concentrations of Pb and Cd in the solutions:

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$$C_S = \frac{(C_O - C_e) V}{W} \tag{1}$$

where C_S is the amount of Cd or Pb sorbed per unit mass of mineral (mg g^{-1}), C_0 and C_e are the metal concentrations (mg l^{-1}) in the initial and equilibrium solutions, respectively, V is the volume of solution added (l) and W is the air-dried mass of minerals (g).

All the experiments were performed in triplicate. The data obtained from lead and cadmium adsorption experiments were fitted to Langmuir and Freundlich equations. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$q = \frac{KCb}{1 + KC} \tag{2}$$

Where, K (l mg^{-1}) reflects the relative rates of sorption and desorption at equilibrium and is thus the bonding energy coefficient, b (mg.g^{-1}) is the maximum sorption capacity, q is the amount of Cd or Pb sorbed per unit mass of mineral (mg.g^{-1}) and C is the concentration of Pb or Cd in the equilibrium solutions (mg.l^{-1}).
The linear form of the Freundlich sorption isotherm is as follow:

$$\text{Log } q = \text{Log } K_f + 1/n \text{ Log } C \tag{3}$$

Where, C and 1/n are the intercept and slope of the Freundlich isotherm, respectively. K_f and n are Freundlich adsorption isotherm constants being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

Results and discussion
The CEC and pH (1:2 water: solid ratio) values of the natural zeolite and sepiolite samples were determined 177 and 8.5 cmol (+) kg^{-1} and 7.47 and 8.58, respectively.

The Effect of Initial Concentration
According to the results, the effects of all the experimental factors including the type of element, initial concentration, mineral type, and their interactions were statistically significant. In other words, all the experimental parameters could influence the process of lead and cadmium sorption. When the amount of sorbents (minerals) in contact with the contaminated solutions is fixed, the number of active adsorption sites on the sorbents is fixed. However, with an increase in the initial concentration of the solutions, the amount of cadmium and lead sorbed on the mineral surfaces decreased. The coefficient of variation in the Langmuir model was between 0.91-0.97. Accordingly, both models were able to describe the data but the Langmuir model showed better fit to the adsorption data of lead and cadmium. The maximum sorption capacities (b) of Cd and Pb onto the sepiolite and zeolite samples were found to be 50 and 52.6 and 19.2 and 29.4 mg.g^{-1}, respectively.

Using the Langmuir adsorption isotherm, Ponizovsky and Tsadilas (2003) reported that the maximum adsorption capacity of lead by a Bulgarian clinoptilolite was 36 mg.g^{-1}. Comparison of maximum adsorption capacity of lead in the present study (52.6 mg.g^{-1}) with that reported by Tsadilas-Ponizovsky (2003) shows the ability of Iranian sample to remove lead contamination. The Freundlich power constant (n) for zeolite and sepiolite to adsorb lead is 2.97 and 2.94, respectively, and to adsorp cadmium is 3.6 and 4.5, respectively. Based on the Freundich theory, the n values of 1 to 10 may indicate optimal adsorption of element on the mineral surfaces. Essington (2004) believes that the constant 1/n shows the heterogeneity of adsorbing surface. When this ratio reaches zero, the heterogeneity and diversity of the adsorbing places increase and when it gets close to 1, the adsorbent surface will be homogenous. In contrast, if the unit is equivalent to one, the Freundlich isotherm becomes linear and by increasing the concentration of pollutant the uptake increases linearly. It should be noted that the maximum adsorption of an element on the sorbent could not be predicted by the Freundlich isotherm.

Conclusion
The Langmuir model could describe the adsorption process better than the Freundlich model. The maximum adsorption capacities of Pb (II) and Cd (II) onto natural zeolite were 52.6 and 29.4 mg.g^{-1}, respectively. Where, the maximum adsorption capacities of Pb and Cd onto natural sepiolite were 50 and 19.2 mg.g^{-1}, respectively. The selectivity sequences based on the distribution coefficient were in lines with the values of the first hydrolysis constant of the metals. The highest K_f values were found for Pb followed by Cd. However, low K_f values were estimated for Cd. Therefore, Pb is more strongly sorbed by these minerals in comparison to Cd. The main mineral properties for the sorption of Pb and Cd onto the sepiolite and zeolite are the type of mineral, the level of pH, as well as the CEC.

Batch adsorption experiments together with our earlier results reveal that the removal of both lead and cadmium by zeolite and sepiolite involves the contribution of both adsorptions by ion exchange and precipitation.

The results of this study show that both zeolite and sepiolite can be used to prevent lead and cadmium enterance into the underground water. The results also illustrated that both adsorption and cation exchange reactions are contributing to the sorption of Cd and Pb ions onto sepiolite and zeolite. It seems that both sepiolite and zeolite minerals have a very high ability to remove Cd (II) and Pb (II) from aqueous solutions.

Keywords: cadmium, lead, removal, sepiolite, sorption, zeolite.