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Use of Jordanian natural zeolite as sorbent for removal of cadmium from aqueous solutions

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ABSTRACT

This study considers Jordanian zeolite as adsorbent for the removal of cadmium from aqueous solution. Zeolite collected from a geographic zone in Jordan valley was assesses for its ability to adsorb heavy metal after preliminary treatment. Kinetics and equilibrium of cadmium uptake by this new adsorbent were followed in this investigation. The experimental results showed that the adsorption of Cd^{2+} ions on zeolite sands was dependent on the pH and temperature. The uptake of cadmium ions increased with increasing pH, temperature and initial adsorbate concentration. Cadmium per unit adsorbent decreased with the increase in the amount of adsorbent used; while the percentage of cadmium removal increased with the increase in the amount of adsorbent. Addition of electrolyte, as NaCl, to zeolite-metal suspension decreased metal uptake by the zeolite.

Keywords: Natural zeolite; Cadmium; Adsorption

1. Introduction

Industrial wastewater is polluted with toxic materials such as heavy metals, phenols and dyes. Due to their adverse effects, removal of toxic heavy metals from wastewater is a matter of great interest in the field of water pollution. Numerous processes exist for removing dissolved heavy metals from aqueous and industrial solutions, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [1–4]. Adsorption is another well-known equilibrium separation process that is commonly used to remove heavy metals form wastewater systems. This is because of its simplicity, convenient operation and low cost application. Activated carbon is well know material for this objective, however, its relatively high cost largely restrict its use in developing countries. Thus, researchers started looking for other alternative adsorbents during last decades.

Due to the charged nature of the framework and its ability to form Bronsted acid sites, zeolites are useful for many applications [5]. For example, it has been used as an adsorbent of cationic surfactants [6]. Zeolites have been used in separation processes and purification processes like gas sweetening and air decontamination [7].

Zeolites are built from AlO_4 and SiO_4 tetrahedrons, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. The tetrahedrons can be connected in different ways, unified by common tops. Zeolite may be given by the general formula: (M^+_2, M^{2+})

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O.Al_2O_3.gSiO_2.zH_2O, where M^+ is usually Na or K, and M^{2+} is Mg, Ca or Fe.

Zeolite is one of the adsorbent groups that have often been tested for removal of heavy metals. Adsorption of metals by zeolite is attributed to ion exchange mechanism. Many examples are available in literature for such purpose. For example, the removal performance and the selectivity sequence of such mixed metal ions including Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+} in aqueous solution was investigated by adsorption process on pure and chamfered-edge zeolite 4A prepared from coal fly ash [8]. In another study, the adsorption behavior of natural clinoptilolite with respect to Co^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} has been studied; the objective was to purity metal finishing wastewaters [9]. Recently, adsorption of As(V) on iron-coated zeolite and of Ph^{2+} onto Algerian bentonite clay has been also investigated by Jeon et al. [10] and Dib and Boufatit [11]. Although there are more than thirty known natural zeolite, only seven occur in sufficient quantity; these include modenite, clinopilolite, chabazite, erionite, ferrierite, phillpsite and analcime [12].

Jordanian natural zeolites are products of alteration of volcanic basaltic glass found in a commercial value in the northeastern part of Jordan. It contains 35% to 60% zeolite [13,14]. The philipsite content in Jordanian zeolite tuff is greater than 40%. Its chemical composition is shown in Table 1. The structure of phillipsite consists of two channels, which have dimensions of 4.2Å× 4.4 Å and 2.8Å × 4.8Å.

In this work, the ability of local zeolite to remove cadmium ions from aqueous solutions is considered. Effects of such typical parameters on this adsorption process were investigated; these include contact time, sorbent and sorbate concentrations, pH, temperature, and addition of an electrolyte.

Table 1
Chemical composition of Jordanian fresh tuff, phillipsite rich and philipsite crystal [14]

Component	Fresh tuff (%)
SiO_2	44.43
Al_2O_3	13.16
TiO_2	3.02
FeO	3.53
Fe_2O_3	4.1
MnO	0.17
MgO	11.01
CaO	10.03
Na_2O	1.74
K_2O	1.24
P_2O_5	0.49
SO_3	ND
Loss on ignition	7.08
Total	100

ND = Not detected

2. Materials and methods

2.1. Materials

Fresh tuff zeolite was collected from the northeast part of Jordan. The chemical analysis of this mineral is shown in Table 1. They were crushed using mechanical crusher and ball mill. The powdered ore was sieved to obtain the following size fractions: smaller than 38 μm, 38–45 μm, 45–53 μm, 53–63 μm and greater than 63 μm. As most of the zeolite sample was in the range 38–63 μm, a mixture of such size fractions was used in the experiments. 25 g of each size fraction was treated separately with 0.1 N NaCl solution in order to enrich the surface of the zeolite. The suspensions were kept under mixing for 24 h; they were then washed twice by distilled water, dried at 100°C overnight, and then kept for further use in the sorption tests. Deionized water was used for preparation of the metal solutions and all chemicals were of analytical grade.

2.2. Sorption test

Batch adsorption tests were carried out to investigate the performance of zeolite toward the removal of Cd^{2+} ions from aqueous media. This was done by transferring a known quantity of the adsorbent into bottles containing 10 ml of aqueous solutions of Cd^{2+} ions of a predetermined concentration. The metal ion concentration employed was 20 ppm. The pH of the solution was in the range 2.1–6.4, in order to investigate the effect of this variable. The sample bottles were maintained in temperature-controlled water-bath shaker adjusted to certain temperature. At a predetermined time, samples were withdrawn after in order to study the kinetics of the adsorption process. The samples were subsequently filtered and the metal ion concentrations in the filtrate were measured using atomic absorption spectrophotometer (Spectro AA10, Varian). From the kinetics study, it was noted that no change in the Cd^{2+} ion concentration in the solution occurred after the first 2 h of the adsorption process. However, equilibrium isotherm test were conducted for 5 h to insure that equilibrium had been attained.

In each set of tests, one parameter was varied while all other parameters were kept fixed. Typical operating conditions used were as follows; adsorbent concentration: 5 mg/ml; Cd^{2+} ion concentration: 20 ppm; temperature, 25°C; pH: 6.4; contact time: 5 h. The cadmium uptake was calculated from difference between the concentrations before and after adsorption process divided by the amount of adsorbent used.

To determine the number of replicates that should be carried out in this study, a test with six identical systems containing 20 ppm of Cd^{2+} ions at a given pH and sorbent concentration was carried out. It was observed that the results of five of six samples were within 7%, while one of them was significantly out of the range. Considering this, each experiment was carried out in duplicate and the average results are presented in this work if they did not differ by more than 7%.

2.3. Equilibrium isotherm models

Many simplified models have been proposed to describe the equilibrium relation between the liquid phase concentration and the surface concentration of adsorbate at a given temperature. In this work, the Langmuir and the Freundlich isotherms were used to represent the experimental data.

The linearized form of the Freundlich model can be written as:

$$\ln q = \ln k_f + \frac{1}{n}\ln C \tag{1}$$

where q is the equilibrium solid-phase concentration (mg/g), k_f is the Freundlich capacity parameter, $1/n$ is the Freundlich intensity parameter, and C is the equilibrium liquid-phase concentration (mg/l). The model parameters k_f and $1/n$ can be calculated from the linear plot of ln q vs. ln C; they represent the slope and intercept of this plot, respectively.

The linearized form of the Langmuir model can be given by:

$$\frac{1}{q} = \frac{1}{A} + \frac{1}{AK}\frac{1}{C} \tag{2}$$

where K and A are the model parameters related to the maximum theoretical adsorption capacity and the energy of adsorption, respectively. Model parameters can be calculated from the slope and intercept, respectively, of the linear plot of $1/q$ vs. $1/C$.

3. Results and discussion

3.1. Effect of contact time

The kinetics of metal ion uptake are important for determining the time necessary to attain equilibrium and the nature of the sorption process; i.e. chemisorption or physical adsorption. The Cd^{2+} ion uptake by zeolite is shown in Fig. 1 as function of contact time using sorbent and Cd^{2+} concentrations of 5 mg/ml and 20 ppm, respectively. The rate of Cd^{2+} ion uptake is rapid during the first 2 min, and then is slowing down for the next 2 h attaining a plateau value. This indicates that the adsorption process was very fast and that Cd^{2+} uptake by this zeolite is covered by physical adsorption, i.e. simple van der Wall force of attachment at the surface of the adsorbent. Because there is no significant change in Cd^{2+} uptake after the first 2 h, later tests were conducted for 5 h to ensure equilibrium.

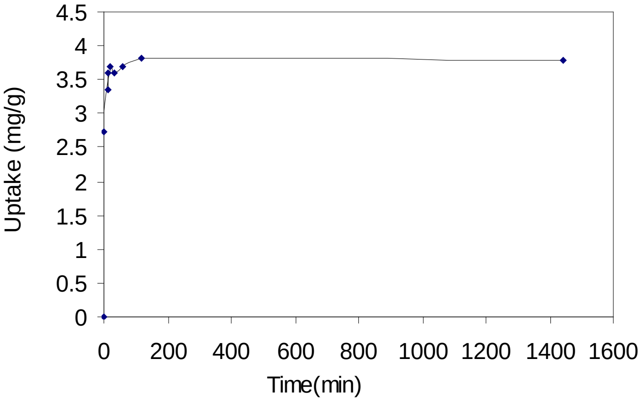

Fig. 1. The kinetics of Cd^{2+} ions uptake by zeolite. Zeolite concentration: 5 mg/ml; Cd^{2+} concentration: 20 ppm.

3.2. Effect of adsorbent concentration

The effect of adsorbent concentration on the equilibrium concentration Cd^{2+} ions was investigated using initial Cd^{2+} concentration of 20 ppm. The adsorbent doses employed varied from 5 to 25 mg/ml at a fixed temperature, pH, contact time and initial adsorbate concentration. Fig. 2 shows that the equilibrium concentration of Cd^{2+} ions in the solution decreased with the increase in adsorbent concentration; however, the amount metal being taken per unit amount of adsorbent, uptake, increased with the increase in adsorbent concentration. This is expected due to the increase in the number of sites available for adsorption with the increase in sorbent dose per same metal ions surrounding these sites.

The relationship between equilibrium concentration of Cd^{2+} ions and its uptake at different adsorbent concentration were also obtained through equilibrium isotherm. The collected experimental data were represented by linearized Langmuir and Freundlich isotherm models as shown in Figs. 3 and 4. The plots indicate that

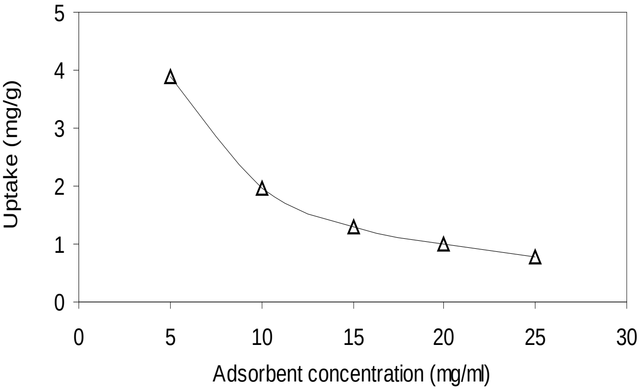

Fig. 2. Effect of adsorbent concentration on the uptake of Cd^{2+} ions.

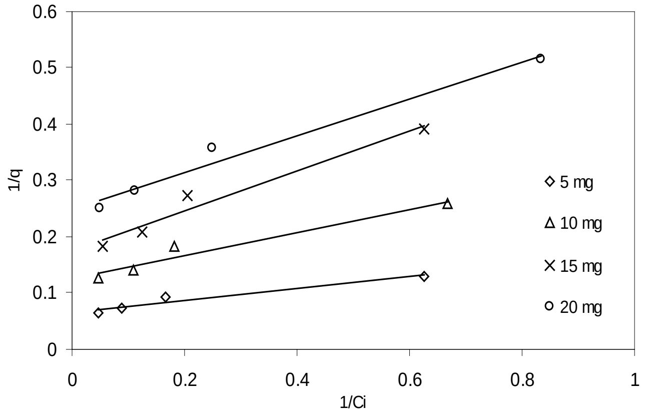

Fig. 3. Relationship between equilibrium concentration and Cd^{2+} uptake at various adsorbent concentrations. Symbols: experimental data; line: Langmuir model.

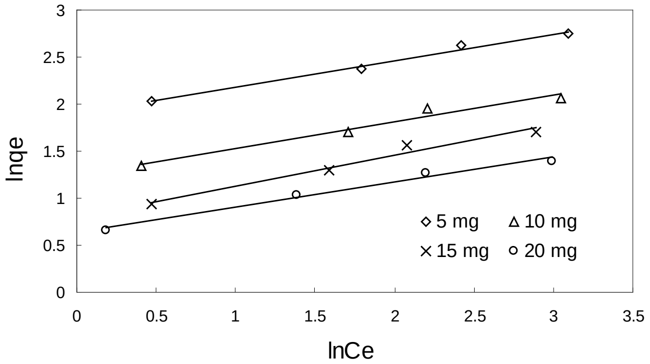

Fig. 4. Relationship between equilibrium concentration and Cd^{2+} uptake at various adsorbent concentrations. Symbols: experimental data; line: Freundlich model.

Table 2
Langmuir and Freundlich constants at different adsorbent concentration

Adsorbent concentration (mg/ml)	Langmuir isotherm			Freundlich isotherm		
	K	A	R^2	k_f	$1/n$	R^2
5	19.01	0.2213	0.9954	6.72	0.2783	0.9901
10	9.81	0.2379	0.9993	3.46	0.2846	0.9655
15	6.96	0.2367	0.9999	2.10	0.3259	0.969
20	4.49	0.4147	0.9999	1.89	0.2632	0.9825

both models fit the experimental data reasonably well. Applicability of Langmuir to the experimental data suggests monolayer coverage of copper ions on the surface of zeolite. Langmuir and Freundlich constants are displayed in Table 2. It is noticed that the adsorption capacity parameters (K and k_f) decreased with the increase in the adsorbent concentration (Table 2). This is consistent with the conclusion mentioned above. It can also be concluded from the results of Table 2, Freundlich parameter $1/n$, that adsorption is more intense at low adsorbent concentration than at higher adsorbent concentration.

Table 3
Effect of initial pH on uptake of Cd^{2+} ions from aqueous solution

pH	Uptake (mg/g)
6.4	4.20
4.9	3.93
4.03	3.95
3.75	3.87
3.17	3.76
2.1	0.37

3.3. *Effect of initial pH*

The effect of initial pH of the solution on the adsorption of Cd^{2+} ions was considered in this work. This was achieved by adjusting the initial pH of the system using either HCl or NaCl. Suspensions in the pH range from 2.1 to 6.4 were obtained. Each of these suspensions contained Cd^{2+} solution at a concentration of 20 ppm. Certain amount of zeolite was added to result in final sorbent concentration of 5 mg/ml. The results for copper uptake at equilibrium at different pH are shown in Table 3. A slight increase in the Cd^{2+} ion uptake is noted with increase in the initial pH of the solution. Effect of pH on the sorption of metals ions is normally attributed to the negative charges prevailing at the surface of the sorbent at high pH values, which give rise to the attraction forces between the clay and the copper ions. At considerably low pH, the surface is surrounded by hydronium ions (H^+), which prevented the metal ions (Cd^{2+}) from approaching the binding sites on the sorbent [15].

3.4. *Effect of temperature*

To study the effect of temperature on the adsorption of Cd^{2+} ions, experiments were carried out at 25°C, 35°C

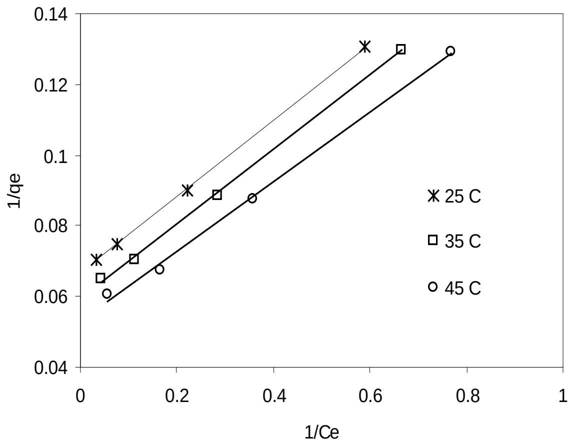

Fig. 5. Relationship between equilibrium concentration and Cd^{2+} uptake at different temperatures. Symbols: experimental data; line: Langmuir model.

and 45°C using different initial Cd^{2+} concentrations in the range of 20–50 ppm. That way, equilibrium isotherms at different temperatures can be obtained and the energy of adsorption can be calculated. The equilibrium isotherm data were presented in the form of linearized Langmuir isotherm as shown in Fig. 5. It is noticed that metal ion adsorption is increased when increasing the temperature suggesting exothermic nature of the process. The Langmuir constants were calculated at different temperatures from the slopes and intercepts of the plots of Fig. 5. The Langmuir constant A at different temperatures is plotted as ln A vs. $1/T$ in Fig. 6, in order to estimate the enthalpy of adsorption (ΔH) for this process. According to the slope of this plot a value of $\Delta H = -58.39$ kJ/mol was determined. The negative sign confirms the exothermic nature of the adsorption process. According to Fogler [16], physical adsorption is assumed for a sorption process with $\Delta H < -62.7$ (as absolute value); the sorption process by this newly developed adsorbent is considered to be physical adsorption.

3.5. *Effect of salt addition*

Soft and hard ions are among agents that interfere with the adsorption of heavy metal onto adsorbents. In this study, various concentrations of Na^+ ions in the form of NaCI were added to the adsorbent — Cd^{2+} ions suspension in order to investigate such parameters. Fig. 7 shows that the presence of Na+ ions in the solution decreases the uptake of Cd^{2+} ions by natural zeolite. In fact, the diffusion coefficient of Na+ ions in water (1.33×10^{-9} m^2/s) is greater than that of Cd^{2+} ions in water (0.72×10^{-9} m^2/s) [17]; thus, Na^+ ions will reach the surface of the zeolite before Cd^{2+} ions and there will be more competition between the ions in the solution for the negatively available charged binding sites on the surface of zeolite. Consequently there will be less vacant sites available for Cd^{2+} ions and the uptake will decrease.

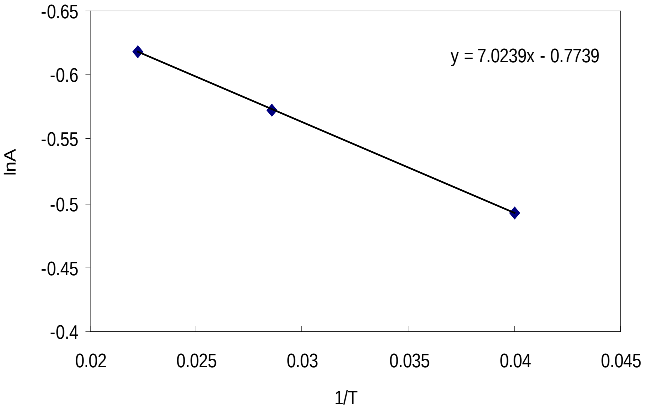

Fig. 6. Relationship between ln$A$ and $1/T$ for adsorption of Cd^{2+} by zeolite.

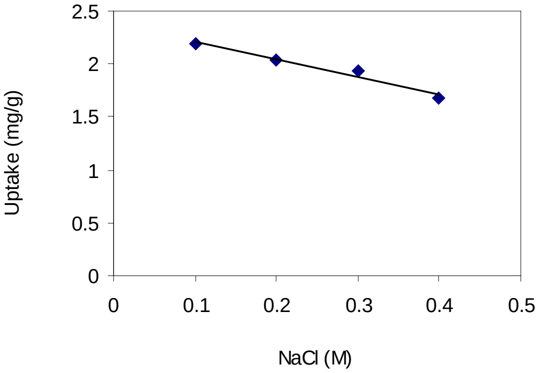

Fig. 7. Effect of NaCl concentration on the adsorption of Cd^{2+} ions by zeolite.

4. Conclusions

This work demonstrated the ability of natural Jordanian zeolite, namely mixed phillipsite, to remove pollutant divalent cations such as cadmium ions from water. Natural zeolite appeared to be more effective when the solution pH was raised from 2.1 to 6.4. The uptake of Cd^{2+} ions increased with an increase in solution temperature. The process is exothermic and the sorption is physical in nature. The residual concentration of Cd^{2+} ions decreased with an increase in sorbent concentration. Cadmium uptake was shown to increase with the metal/sorbent ratio.

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