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Comparative sorption capacity of Pb(II) and Cd(II) by natural zeolite in phosphoric acid medium

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ABSTRACT

Zeolite, a well-known inorganic compound, was used for Pb(II) and Cd(II) sorption. For this purpose, the model system composed with "H_3PO_4–Pb^{2+}–Cd^{2+}" medium was selected and applied with various amounts of both heavy metal salts. The results revealed that sorption capacity of the sorbent was higher for Pb^{2+} cation than in the diluted phosphoric acid (20% H_3PO_4) for all periods. The absorption of toxic metal ions was measured by atomic absorption spectroscopy. Different physical and chemical analysis techniques such as Fourier Transform infrared, scanning electron microscope, DTA, and XRD showed that natural state of zeolite in a diluted phosphoric acid (20% H_3PO_4) system underwent protonation and hydroxylation to produce additional OH^- groups that are active in the sorption process and no destruction was observed in the structure.

Keywords: Adsorption; Phosphoric acid medium; Zeolite; Purification; Lead and cadmium ions

1. Introduction

Human activities have destroyed the biosphere because of the enormous amount of pollutants including heavy metals. Heavy metals are one of the most common and toxic pollutants for the human being [1,2]. Heavy metals in the biosphere lead to accumulation in the soil greater than background reasons in many times and cause the reducing of soil productivity and also negatively affect the flora and fauna and ultimately in humans [3,4]. Impurity of soil also causes economic damage in agricultural products obtained from the contaminated areas and should be banned of sale.

Energy companies, industrial corporations, aviation, road, and rail transportations, fertilizers and chemicals used for fertilizers, pesticides, and irrigation water are the main sources for the heavy metals contamination in the soil. Cadmium content in phosphates in USA (Florida) is 13 mg/kg, while it is about 25–50 mg/kg in those of North Africa and more than 70 mg/kg in those of Senegal. Phosphate fertilizers such as feed stocks contain approximately 10–170 mg

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cadmium in per kg of P_2O_5 and the amount of 0.3–50 g of cadmium may come into the soil from these sources every year. The contamination of heavy metals in soil and their interaction with soil components have been occurred by the migration of heavy metals with different ways [5–7].

To find a usable and durable solution of all aforementioned problems, the preliminary purification of phosphoric acid with sorbents has been identified as a suitable method to reduce the concentration of heavy metals. Sorption is a simple and well-controlled process, allowing us to remove heavy metal cations till any residual concentration. Natural aluminosilicates such as clay minerals are used as adsorbents for this goal. Elements having a radius of 0.052–0.093 nm ions (e.g. Mn, Zn, Cu, Co, Ni, and Cr) may occupy in the octahedral clay minerals or rearranges in aluminosilicates instead of Al, Fe, and Mg. However, not all heavy metals can be absorbed by clay minerals. For example, lead and cadmium ions have larger size so that their absorption with clays could be inefficient [8–10]. In general, clays are able to absorb only cations but crystalline ones (allophane, etc.) may not capture and adsorb cations, anions, and metals.

The most desirable material for purification is the natural ones which have a high silicon crystal structure capable and absorb both cations and anions. Natural zeolite is a relatively new class of raw materials and is used in the sewage treatment. The modified surface area, good adhesion force, and adsorption and ion exchange properties allow to efficiently extract organic and inorganic contaminants, including ammonium ions, heavy metals, and radionuclides from the liquids, colloidals, and dissolved media.

Use of natural adsorbents has attracted considerable economical interest, since their estimated cost of production, milling, and sieving are less than that of synthetic ones [11–16]. Due to the widespread use of highly porous bodies and materials in the industry as sorbents, catalysts, fillers, etc. calls for a comprehensive study of their structure and properties.

Monoethanolamine-modified β-Zeolite has been investigated for Pb^{2+} adsorption against a variety of reaction situations such as metal ion concentration, solution pH, temperature, and contact time. It has been indicated that the maximum adsorption is obtained at pH 4.0 of solution [17].

Modification of zeolites with particular amines can also decrease the sorption capacity of Cd and Pb, since the channels on zeolite are blocked by the amine molecules. On the other hand, the partial dimerization of employed amine tends to increase the overtaking of Pb^{2+} and Cd^{2+} [18].

Reversible sorption of Cd(II) and Pb(II) in different solution concentrations has previously investigated by zeolite and bentonite. Sorption and desorption processes were calculated according to the Freundlich model. Irreversible absorption of Pb(II) was found to be more than Cd(II) in both materials. Bentonite released the cations more than zeolite into water or solution [19,20].

In the present work, Shankanaj, deposits of Kazakhstan, were used as a sorbent which has a high sorption ability and subject of extensive study. Zeolite was modified in situ with phosphoric acid and the metal (Pb^{2+}–Cd^{2+}) cations adsorption was carried out. Various phosphoric acid medium experiments were performed and results were evaluated (Fig. 1).

It was observed that the sorption capacity of natural zeolite increases in the first 30 and 40 min then it starts decreasing due to the desorption. In our previous studies [21–23], we described that the mineral treated with an acid has a good sorption capability for cations such as iron, copper, and lead especially in concentrated phosphoric acid.

2. Experiment

2.1. Materials and methods

We used Shankanaj deposits with the following composition, wt.%: K_2O—1.38; Na_2O—0.95; Fe_2O_3—0.16; Al_2O_3—10.81; CaO—2.32; MgO—0.93; SiO_2—65.28, p.p.p—18.15 [24]. Cadmium nitrate $Cd(NO_3)_2.4H_2O$ and lead nitrate $Pb(NO_3)_2$ were supplied from Sigma Aldrich and Fluka Chemical Corporations. The phosphoric acid with a concentration of 85% H_3PO_4 was used for the acid treatment experiments. pH was checked frequently throughout the experiment by a pH meter or pH paper stick. It was adjusted in case of the any unexpected reaction condition. Concentrations of lead and cadmium were determined by an atomic absorption spectrophotometer (PerkinElmer atomic absorption spectroscopy-400). Fourier Transform infrared (FT-IR) spectra of the samples were analyzed with a Perkin Elmer Spectrum 100 with ATR apparatus. X-ray powder diffraction patterns were carried out by an X-ray powder diffractometer D8 Discovery of Bruker, using Cu Kα radiation at 40 kV and 40 mA. The microstructure and surface morphology of the samples were obtained with a scanning electron microscope (SEM) (model QUANTA 250 FEG). Thermal properties of the structures were investigated by a Shimadzu DTG-60 instrument.

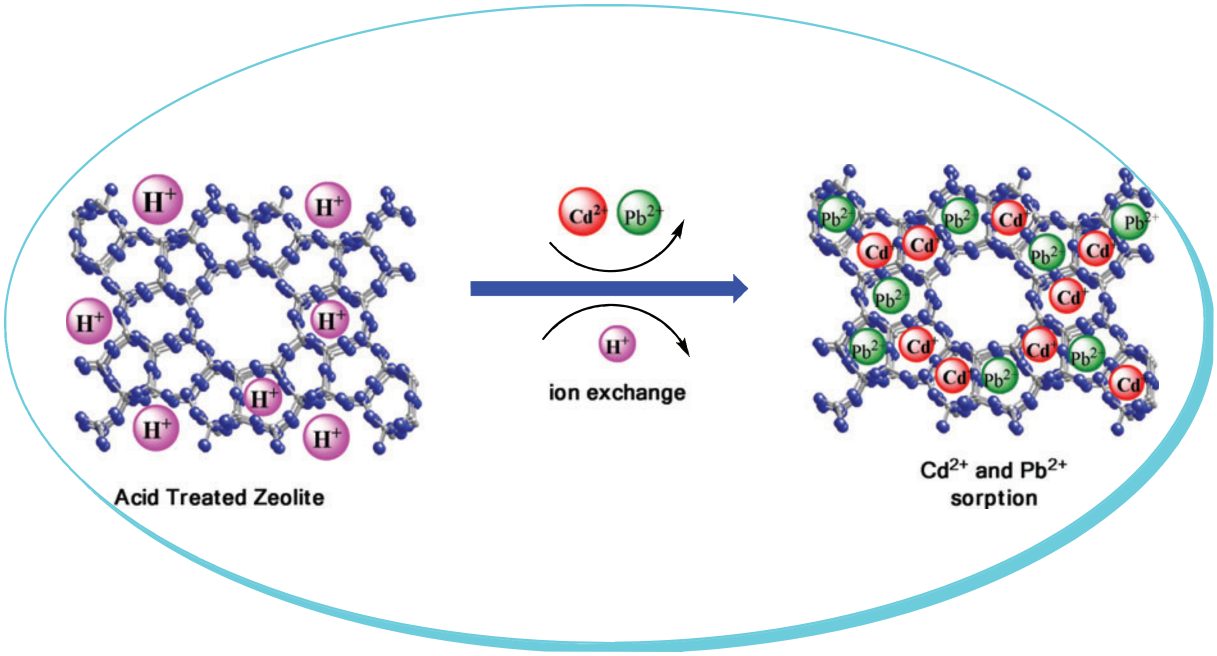

Fig. 1. The illustration of adsorption experiment.

2.2. Procedure of sorption

Sorption capacity of natural zeolite with respect to lead(II) and cadmium(II) cations in the presence of phosphoric acid was studied in a model system called as "H_3PO_4–Cd^{2+}–Pb^{2+}". The sorption was carried out with a stirrer in a constant ratio of H_3PO_4: (Liquid: Solid) (10:100) at about 25˚C. The used phosphoric acid contained about 20% P_2O_5. Phosphoric acid concentration was selected between 18 and 23% to find the optimum conditions for the purification of the phosphoric acid obtained from Karatau (Kazakhstan). The concentrations of cations, Pb^{2+} and Cd^{2+} were predetermined by adding a calculated amount of lead nitrate, $Pb(NO_3)_2$ and cadmium nitrate, $Cd(NO_3)_2$ into the prepared phosphoric acid solution. In order to determine the effect of time on the process of sorption, experiments were carried out in the range of 5–60 min with equal amounts of Pb^{2+} and Cd^{2+} cations. Influence of the concentration ratio of lead and cadmium on the sorption process was investigated in a constant concentration of Pb^{2+} (0.0505 g/L = 50.5 ppm) as a function of the various concentrations of Cd^{2+} (0.001; 0.0209; 0.0505; 0.0802; and 0.1 g/L) for 30 min.

3. Results and discussion

3.1. SEM analysis of natural zeolite

Electron microscopic analysis of natural zeolite and the acid-treated sample was studied and their surface properties were compared. As seen in Fig. 2(a) and (b), their porosity varies considerably under the phosphoric acid conditions. The micrograph indicated that the presence of small bright spots on natural zeolite correspond to the cavities and voids on the surface. The light spots become significantly larger on the zeolite treated with the phosphoric acid (Fig. 2(b)) than those of natural zeolite (Fig. 2(a)). Micrograph of the acid-treated one contains elongated cylinders which are not present in that of natural zeolite. This outcome explains that the size of the voids and channels increases in the phosphoric acid-treated structure which is an indication for the impact of acid treatment. It was found that sorption of zeolite apparently increases by the acid treatment.

Therefore, a physical–chemical study of natural zeolite and the acid-treated one with sorption of lead (II) and cadmium(II) revealed that phosphoric acid in the structure of natural zeolite is really useful for retaining of Pb^{2+} and Cd^{2+} cations. The structure of zeolite did not decompose after treating with phosphoric acid and sorption experiment. In addition to that a higher adsorption was observed using it.

3.2. Thermal studies

Thermal analysis of natural zeolite showed that there is an endothermic peak at 787.84˚C in the DTA curve and the total weight loss of the sample was found to be about 9.25% (Fig. 3). The peak of natural

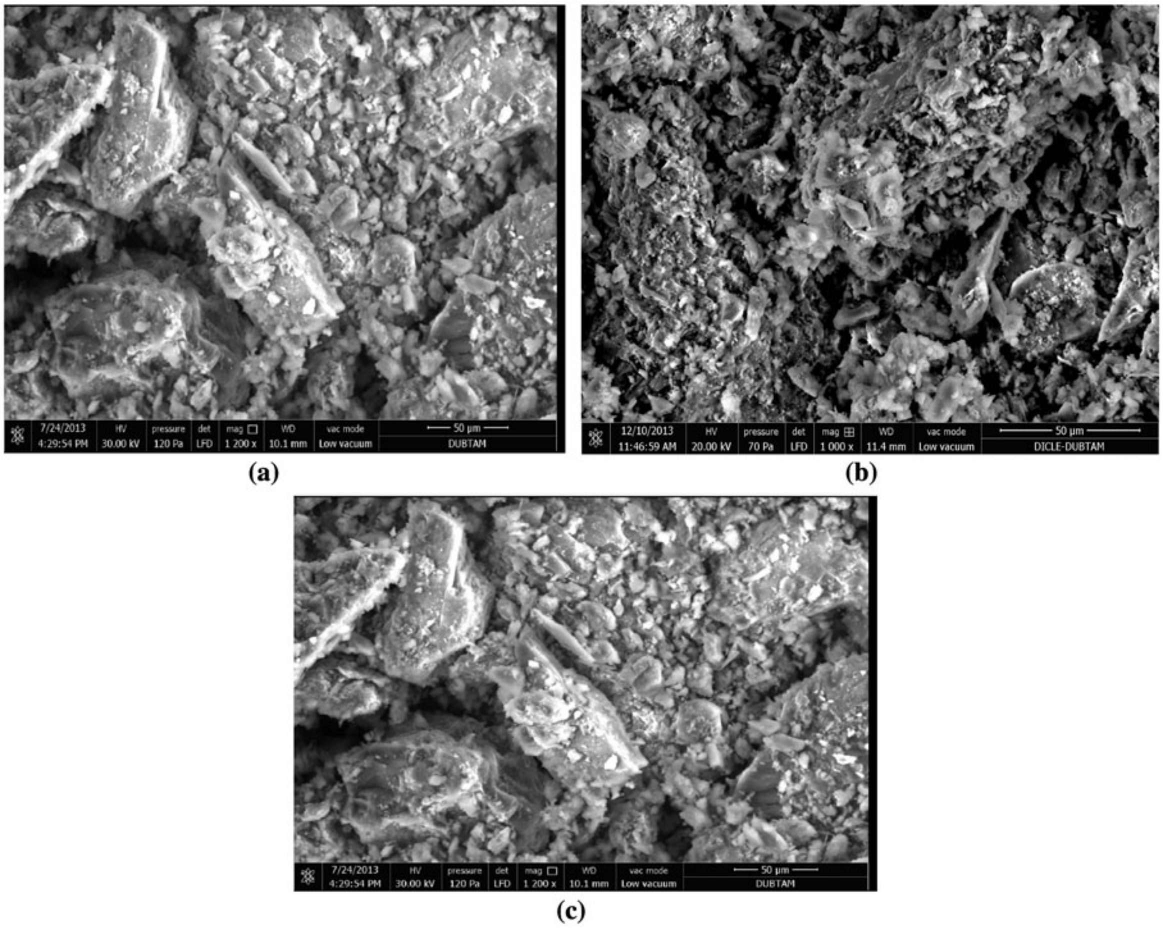
(a) (b) (c)

Fig. 2. Photomicrograph of natural zeolite (a) of the acid-treated natural zeolite (b) and of selected after sorption (c).

zeolite was expanded and shifted to the lower temperature range after acidic workup. The treated zeolite showed 13.19% of weight loss by heating (Fig. 4), which means that the difference between weight losses is 3.93%. This indicates that treatment with phosphoric acid causes for the formation more acidic sites on the natural zeolite due to the nature of calcium, magnesium, and aluminum elements. These elements occupy tetrahedral framework by exchanging with H^+ and OH^- groups. These results were supported by the infrared spectroscopic data implying the formation of additional hydroxyl groups which can interact with hydrogen and oxygen atoms via weak covalent binding (Fig. 4).

The total weight loss of the sample isolated after sorption of lead(II) and cadmium(II) was found to be 9.37% (Fig. 5) which is considerably less than that of the sample interacted with H_3PO_4 (Fig. 4). This indicates a decrease in the exchange of positions with H^+ centers and OH^- groups. Thus, when natural zeolite was contacted with lead and cadmium, the sorption occurred with the cations. Moreover, the mass loss of the samples is very close to that of natural zeolite.

The thermograms also show that the DTA curve of the zeolite sample has similar characteristics after interacting with cadmium and lead salts. Thus, it can be said that the reusability of zeolite is the most significant aspect of our research as it is restored after adsorption of lead and cadmium from phosphoric acid.

3.3. Infrared spectra

A comparative analysis of the infrared spectra for natural zeolite, the phosphoric acid-treated sample, and the situation after sorption was conducted. As seen in Fig. 3, the FT-IR spectrum of the acid-treated one (curve b) varies considerably. Stretching vibrations of water changed and new peaks were obtained as 3,818, 3,733, 2,351, 1,555, and 1,334 cm^{-1}. There is a shift to the lower frequency values in several

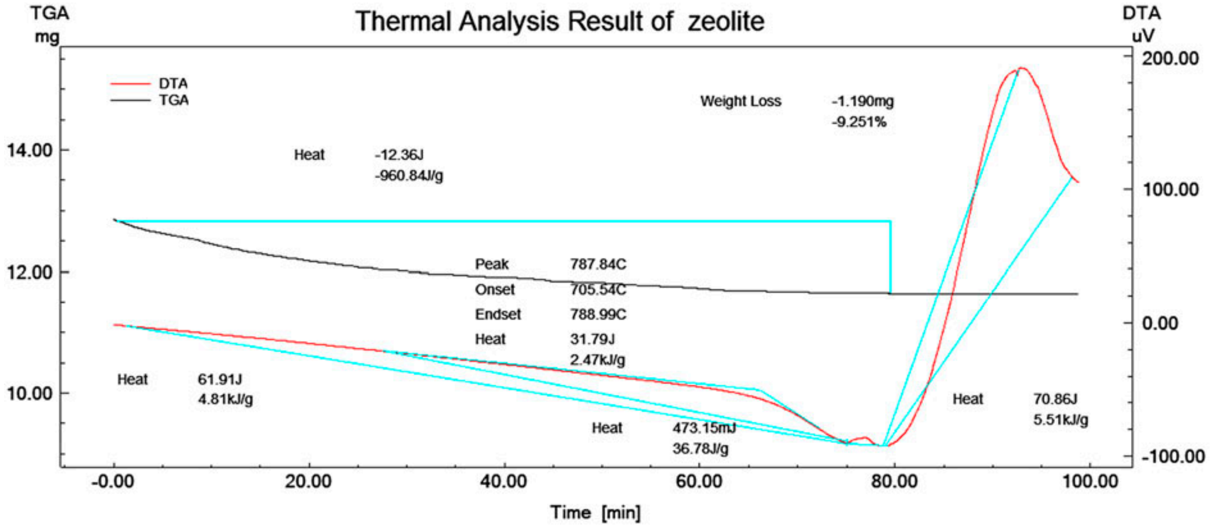

Fig. 3. Thermogram of natural zeolite.

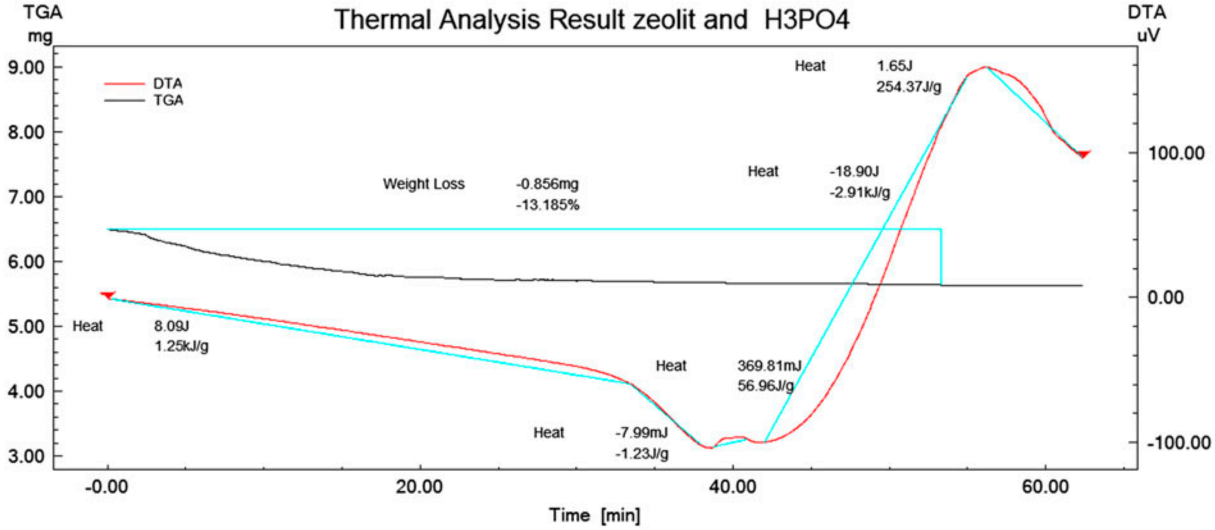

Fig. 4. Thermogram of the acid-treated zeolite.

peaks such as 2,160→2,115 cm^{-1}, 2,050→2,011 cm^{-1}, 1,985→1,974 cm^{-1}, and 1,645→1,635 cm^{-1}. It was thought that this may be due to the formation of the additional O–H bonds resulted with the exchange of calcium cations, aluminum with acid protons [25].

However, the possibility of the proton formation from the $H_{\text{п}+2}O_m$ should not be excluded [26,27]. The number of components for the absorption deformation band coincides with the number of molecules types in the substance. The occurrence of additional component with the characteristic shifting vibrations of water indicates the acid-treated structure in different natures [16,28,29].

The lower frequency region of the spectra directly corresponds to the lattice vibrations. It is also subjected to change the stretching vibrations of Al, (Si)–O communication framework which was defined as 985 cm^{-1} intense frequency to 763 cm^{-1} frequency after acid treatment. The stretching vibration at 527 cm^{-1} related to the deformational fluctuations of its frame is shifted to higher frequencies: 985→990 cm^{-1}, 763→817 cm^{-1}, 527→575 cm^{-1}. A new stretching peak at 625 cm^{-1} corresponds to SiO_2 in a tetrahedral geometry [30]. Aluminum–silicon–oxygen backbone frame was not destroyed in phosphoric acid medium. The changes may be due to aforementioned processes

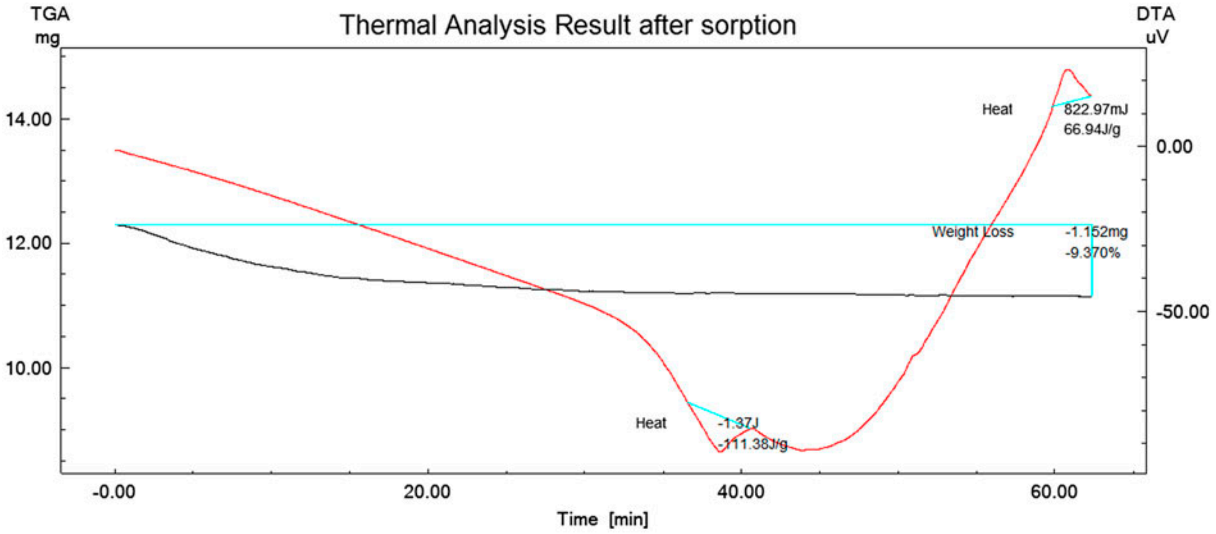

Fig. 5. Thermogram of the substance after sorption.

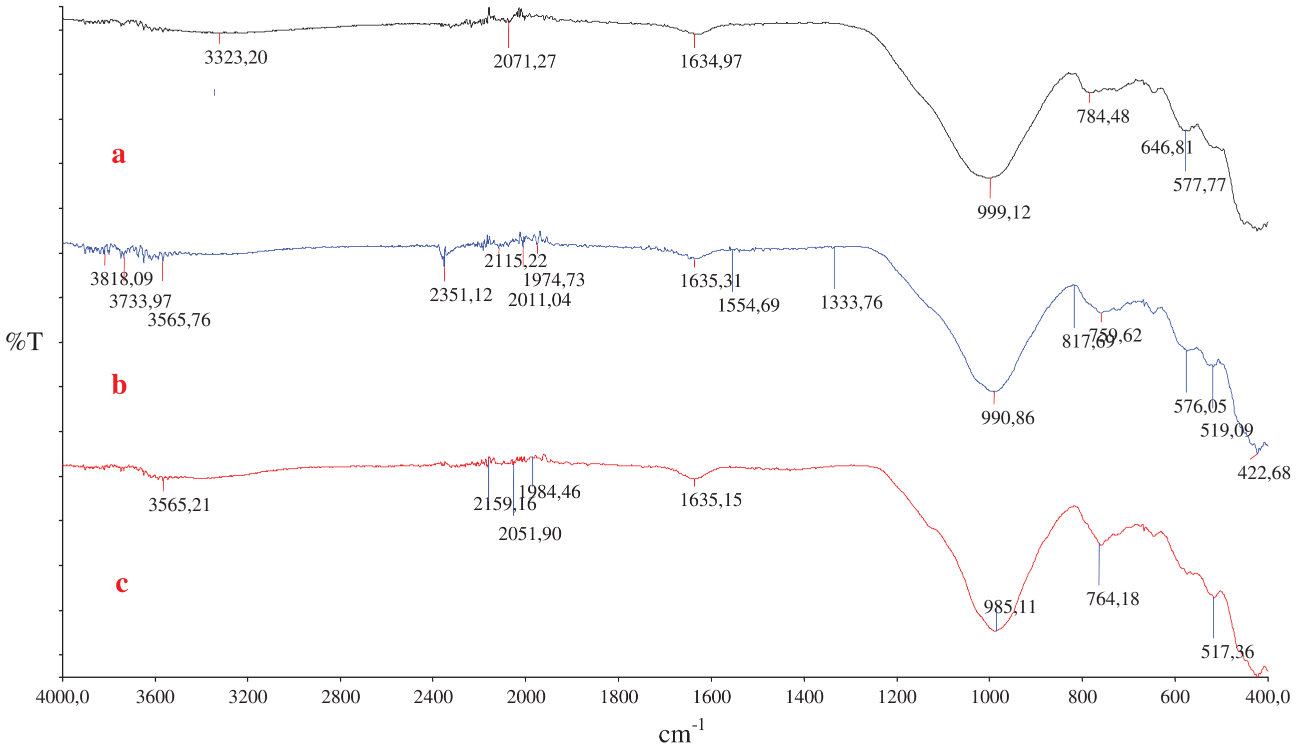

Fig. 6. IR spectra of (a) natural zeolite, (b) the acid-treated one and (c) natural zeolite after sorption of Pb^{2+} and Cd^{2+}.

as well as the sorption of phosphate ions as indicated by the presence of a frequency at 422 cm^{-1}.

The FT-IR spectrum is significantly different (curve a) after the sorption of Pb^{2+} and Cd^{2+} (curve c). The stretching peaks at 3,323, 2,071, 1,634 cm^{-1} can be assigned to the shifting vibration of water and the oscillations of the external relations of the tetrahedral structure. Al, (Si)–O connection can be assigned at 990→999 cm^{-1}, the deformation, broadening, and shifting at 817→784 cm^{-1} can also be expressed as a deformation of skeleton. This indicates that upon contact of natural zeolite's atoms, exchanged with the

Pb^{2+} and Cd^{2+} cations in phosphoric acid, localizes the channels and pores with the free aluminum, proton cations [31–33]. The appearance of a shoulder at 400 and 352 cm^{-1} after sorption may be attributed to the stretching vibrations of $V_{Me–O}$ which corresponds to the development area at about (300–500 cm^{-1}) [34,35] (Fig. 6).

3.4. XRD analysis

XRD analysis of the zeolite (Fig. 7) in phosphoric acid, before and after adsorption of lead(II) and cadmium(II) showed that a number of diffraction maxima with deviations and the intensity of the values and the theta positions can be summarized as follows: 4.65400 Å (30)→4.53694 Å (73), 43.83500 Å (10)→3.75809 Å (43), 3.38300 Å (25)→3.34129 Å (99.9), 3.16500 Å (40) Å→3.24040 Å (97), 3.07400 Å (20)→3.06198 Å (72), 2.97600 Å (65)→2.99379 Å (10.4), and 2.73300 Å (25)→2.57161 Å (73). In the X-ray spectra of the zeolite after sorption, new diffraction maxima were observed as 15.28560 Å (37.8), 3.97100 Å (100), and 3.91000 Å (70) and intense line in (2.51198…..1.37208)Å. Specified changes in X-ray spectrum suggest the presence of new elements binding to the atoms in the zeolite structure [36–39].

3.5. Removability of toxic ions

Analyzed data showed that the degree of sorption of heavy metal cations first increases and then starts to decrease slightly by increasing the process time to 30–40 min in diluted phosphoric acid (20% H_3PO_4). The optimum time was found to be around 30 min for adsorption of cadmium and lead. The maximum sorption of Pb^{2+} was reached at 30 min with 89.24%. Cd^{2+} reached to a maximum at 40 min with 71.25%. The sorption of natural zeolite was calculated using the following equation:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

The sorption curves of lead and cadmium appear as a small maximum due to their desorption process in phosphoric acid and this occurs due to the prolonged contact with the sorbent of the cleaning solution. A comparison of sorption of lead and cadmium showed Pb^{2+} cations were more adsorbed than Cd^{2+} in the test conditions. For example, at 30 min, adsorption of Pb^{2+} was found as 89.24% ($R_{Pb}{}^{2+}$) while the Cd^{2+} was 69.35% ($R_{Cd}{}^{2+}$) (Table 1).

The optimal time for sorption of cadmium and lead together in diluted phosphoric acid is 30 min. Sorption of the cations was further investigated to determine the effect of their concentrations onto the sorption by natural zeolite in phosphoric acid for 30 min simultaneously. Analysis of the results showed that in the diluted phosphoric acid (20%), Pb^{2+} has a better sorption capacity than the Cd^{2+} cations regardless of the concentration of Cd^{2+} (Table 1) (Fig. 8). The ratio of Pb^{2+} of 0.05 g/L (50 ppm) is constant while the variations of Cd^{2+} is changed from 0.001 g/L (1 ppm) to 0.021 g/L (21 ppm). The adsorption of Pb^{2+} has exhibited 89.58 and 97.61% close to the 85.99 and 87.55% sorption percentages of Cd^{2+}.

Concentration of cadmium in the phosphoric acid increased and the removal of lead was also found to be high in each step (Table 2). This would help

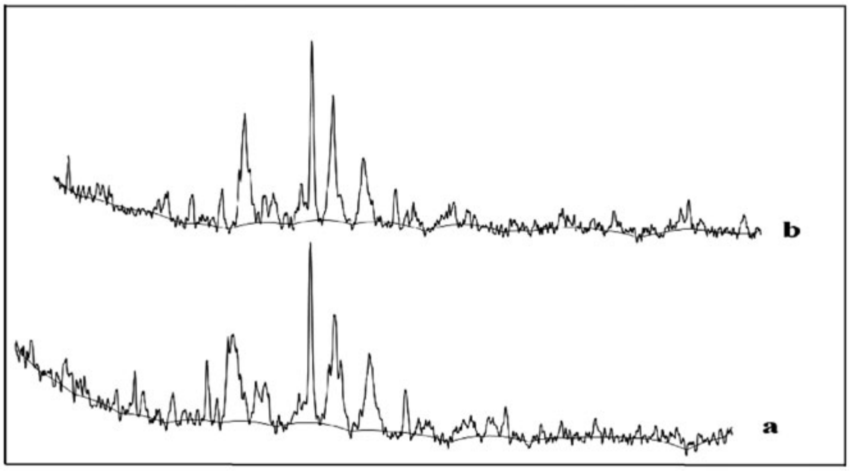

Fig. 7. X-ray powder diffraction patterns of acid-treated zeolite (a) and the zeolite after sorption of Pb^{2+} and Cd^{2+} (b).

Table 1
Effect of time on the sorption of cadmium and lead in the presence of phosphoric acid. $C_{Cd}^{2+} = C_{Pb}^{2+} = 0.0505$ g/L

	Percentages of sorption (%)	
Time/min	Pb^{2+}	Cd^{2+}
$C_{P2O5} = 20.0\%$		
5	79.17	54.34
10	85.16	58.44
20	87.07	63.68
30	89.24	69.35
40	89.24	71.25
60	88.78	65.61

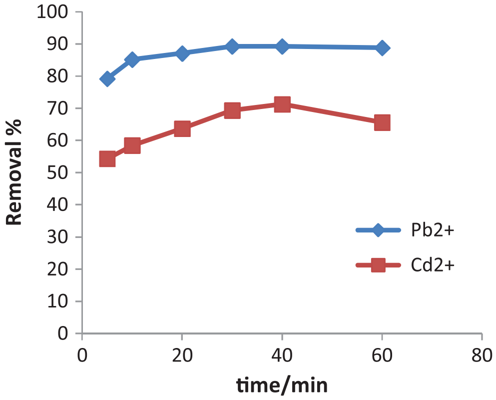

Fig. 8. The percentage removal of adsorptions of Pb(II) and Cd(II) by natural zeolite in 20% of H_3PO_4.

Table 2
Effect of cadmium concentration on the sorption of lead in phosphoric acid

Initial concentration (g/L)		Degree of sorption (%)	
Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
0.0505	0.001	89.58	85.99
0.0505	0.021	97.61	87.55
0.0505	0.0505	89.24	71.25
0.0505	0.08	86.99	16.85
0.0505	0.1	85.71	29.52

us to choose the best concentration ratios of lead and cadmium that let us to purify the phosphoric acid from toxic metals. The pictogram can be seen in Fig. 9.

3.6. Reproducibility and reusability

The reusability of obtained models is also evaluated. The cations (Pb^{2+}, Cd^{2+}) show desorption tendency after 40 min. It was concluded that the zeolite, used as adsorbent, can be employed for further purifications of wastewater contaminations. Reproducibility of adsorbents can also be increased at higher temperatures because of the low adsorption inclination of "H_3PO_4–Cd^{2+}–Pb^{2+}" model systems. Pb^{2+} and Cd^{2+} adsorptions are more than 90% in "H_3PO_4—Cd^{2+}–Pb^{2+}" and "20% H_3PO_4–Cd^{2+}–Pb^{2+}" model system in the first 45 min. This provides us to use zeolite repeatedly after removal of cations [40].

In order to evaluate the application potential of diatomite in the removal of Co(II) from wastewater in real work, the sorption reversibility and repeated availability of diatomite for Co(II) sorption were tested through many cycles of sorption/desorption processes. From Fig. 5, it is clear that the recycle was valid for at least six times based on the satisfied removal percentage even in the sixth round. This result suggests that the diatomite can be employed repeatedly in Co(II) sorption. It can also be found that Co(II) sorption on diatomite was highly reversible.

3.7. Adsorption kinetics

Pseudo-first-order, pseudo-second-order, and Weber–Morris intra-particle diffusion kinetic models are usually used to investigate the amount of adsorption. We applied two of them to enlighten the adsorption kinetics for the adsorbed heavy metals by the phosphoric acid-treated zeolite.

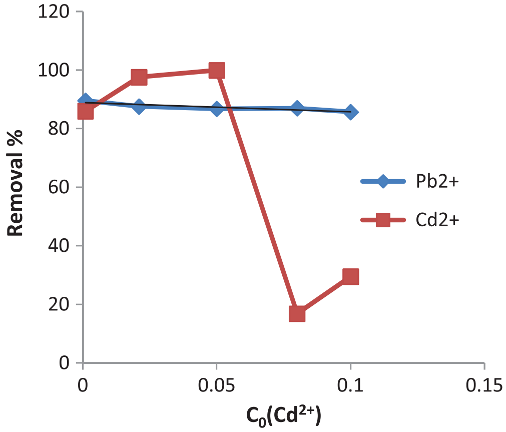

Fig. 9. Influence of the nature of a cation on sorption ability in phosphoric acid.

Table 3
Kinetic parameters for adsorption for Pb^{2+} and Cd^{2+} ions

		First-order kinetic model			Second-order kinetic model		
Adsorbent system	T (K)	q_e, cal (mg g^{-1})	k_{ads}, (1 min^{-1})	R^2	q_e, cal (mg g^{-1})	k_{ads}, g (mg min)$^{-1}$	R^2
In 20% H_3PO_4 for Pb^{2+}	298	1.14	0.095	0.9076	7.37	0.798	0.9999
In 20% H_3PO_4 for Cd^{2+}	298	2.08	0.085	0.9406	5.15	0.22	0.9968

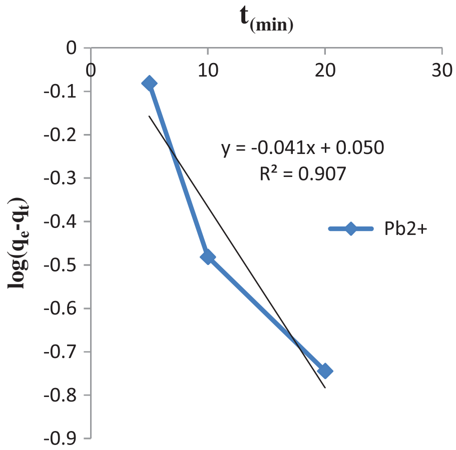

Fig. 10. Pseudo-first-order kinetic model for Pb^{2+} within 20% H_3PO_4.

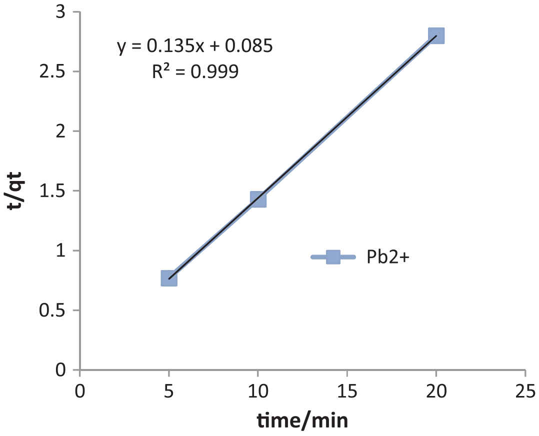

Fig. 12. Second-order kinetic model for Pb^{2+} within 20% H_3PO_4.

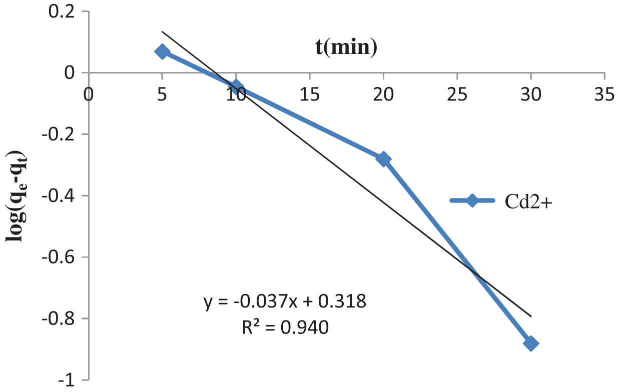

Fig. 11. Pseudo-first-order kinetic model for Cd^{2+} within 20% H_3PO_4.

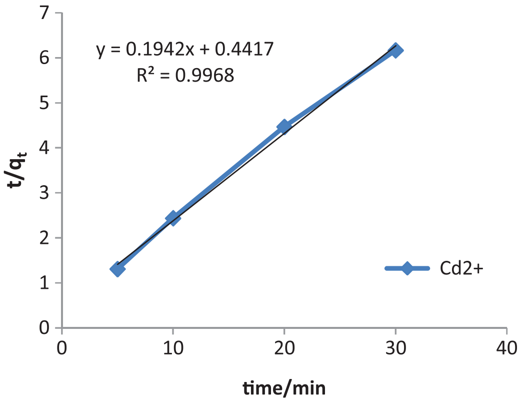

Fig. 13. Second-order kinetic model for Cd^{2+} within 20% H_3PO_4.

Firstly, the kinetic data were fitted using pseudo-first-order model. The linear equation of pseudo-first-order model is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads}}{2.303}t \tag{2}$$

where q_e (mg g^{-1}) is the amount of adsorbed heavy metals by the adsorbent at equilibrium, q_t (mg g^{-1}) is the time t and $k_{ads,1}$ (min^{-1}) is the rate constant of pseudo-first-order adsorption.

The pseudo-second-order rate model was also used in the experiment given as:

$$\frac{t}{q_t} = \frac{1}{k_{\text{ads},2}q_e^2} + \frac{1}{q_e} \quad (3)$$

where $k_{\text{ads},2}$ (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption.

A considerable evaluation was made and it was concluded that kinetic parameter of pseudo-second-order kinetic model is finely suited for the Pb^{2+} and Cd^{2+} sorption in 20% H_3PO_4 [41]. The correlation coefficients, k_{ads1} and k_{ads2} are shown in Table 3. The changes in sorption of heavy metals were evaluated with the both kinetic models can be seen with meaningful correlation coefficient from the curves plotted in Figs. 10–13.

4. Conclusion

A comparative study on the sorption capacity of natural zeolite for Pb(II) and Cd(II) cations in a model system "H_3PO_4–Pb^{2+}–Cd^{2+}–zeolite" revealed preferred sorption of sorbent for lead. The first sorption capacity of natural zeolite increases and then decreases by increasing time to 30–40 min due to desorption from the zeolite in acid. The increase in the Cd^{2+} cations concentration reduces the sorption capacity of the zeolite for Pb^{2+} cations. Thus, phosphoric acid $C_{Cd} = 0.021$ mg/L lead sorbed 97.6%, while $C_{Cd} = 0.1$ mg/L—85.7%.

Physical and chemical techniques (FT-IR, electron microscopy, DTA) show that the natural zeolite in diluted phosphoric acid (20% P_2O_5) undergoes protonation and hydroxylation to produce additional OH groups, which are active in the sorption. Moreover, there was no destruction in the structure of the zeolite.

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