



## REMOVAL OF TOXIC IONS Pb (II) AND Cd (II) USING SHANKANAY NATURAL ZEOLITE IN PHOSPHORIC ACID

M. Zh. KUSSAINOVA<sup>\*</sup>, R. M. CHERNYAKOVA<sup>a</sup> and U. Zh. JUSSIPBEKOV<sup>a</sup>

Kazakh-British Technical University Almaty, ALMATY, KAZAKHSTAN

<sup>a</sup>Institute of Chemical Substances Named After A. B. Bekturov, ALMATY, KAZAKHSTAN

### ABSTRACT

In concentrated phosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>) sorption capacity of the zeolite with respect to cadmium is in direct proportion to the process duration and increases throughout the studied time interval. After 60 mins, degree of cadmium sorption reaches 90.76%. With respect to lead, zeolite exhibits the highest sorption capacity at 40 mins, and over that time, lead sorption is reduced. However, most of the concentrated phosphoric acid, as in the previous experiment, the lead is absorbed in cations. So, even if the optimal time for adsorbed cation sorption, cadmium is 90.8%, and lead-91.84%.

Physico-chemical methods of analysis (IR, electron-microscopic, X-ray) have shown that in lead-containing phosphoric acid natural zeolite is activated without destroying the structure and absorbs lead, as well as in conjunction with the cadmium cations.

**Key words:** Sorption, Zeolite, Purification, Lead and cadmium ions.

### INTRODUCTION

Natural zeolites are a relatively new class of mineral raw materials used in the purification process and tertiary sewage treatment. The developed surface area, good adhesion, adsorption and ion exchange properties of zeolites allow them to be efficiently extracted from the liquid to be purified using the suspended, colloidal and dissolved organic contaminants and inorganic origin, including ammonium ions, heavy metals and radionuclides. Application of natural zeolites as adsorbents is economically beneficial, as their estimated cost of production, milling and sieving is several times less than the cost of synthetic zeolites. Mineral natural aluminosilicates characterized by numerous physical and chemical properties are described in <sup>1-5</sup>.

---

<sup>\*</sup>Author for correspondence; E-mail: marzhan.zhan.84@mail.ru, ics\_rk@mail.ru

In this paper, zeolite from the Shankanay deposits of Kazakhstan is used as a sorbent, due to its high sorption characteristics, and its acid in recent years is the subject of extensive study. In our previously conducted research, this zeolite is described as a highly siliceous mineral having good sorption properties for cations iron, copper, lead in concentrated phosphoric acid<sup>6-8</sup>.

## **EXPERIMENTAL**

### **Materials and methods**

We used acid-resistant zeolite Shankanay field. This refers to the zeolite minerals to highly (Si/Al = 5.75), belongs to the heulandite-klinoptilolitovoy group has sorption properties (E-3.67 mEq/g, CDE cation-0.997 mEq/g) and good sorption capacity to a number of individual cations in mineral acids<sup>9,10</sup>.

Cadmium nitrate  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , lead nitrate  $\text{Pb}(\text{NO}_3)_2$ , copper nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were supplied from Sigma Aldrich and Fluka Chemical Corporations. The phosphoric acid with a concentration on 85%  $\text{H}_3\text{PO}_4$  was also used for the acid treatment experiments.

Determination of concentrations of lead and cadmium, copper was performed by atomic absorption spectrophotometer AAS-400 (Model: Perkin-Elmer). FTIR spectra of the samples were analyzed with Perkin-Elmer Spectrum 100 with ATR apparatus. The microstructure and surface morphology of the samples were obtained with a scanning electron microscope (SEM) (Model QUANTA 250 FEG).

### **Procedure of sorption**

Study of the sorption capacity of natural zeolite with respect to cations of lead (II) and cadmium (II) in the presence of their phosphoric acid medium was performed in a model system " $\text{H}_3\text{PO}_4\text{-Pb}^{2+}\text{-Cd}^{2+}\text{-zeolite}$ ".

Sorption process in this system was carried out with stirring at a constant ratio  $\text{H}_3\text{PO}_4$ : zeolite (L:S) and  $25^\circ\text{C} = 10:100$ . We used 85% phosphoric acid. Selection of the acid concentration was made due to the fact that in the production of phosphorite Karatau thermal method was used, the thermal of phosphoric acid with a concentration of 55-63%. Predetermined concentration of the cations  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was created by the introduction of the calculated amount of lead nitrate  $\text{Pb}(\text{NO}_3)_2$  and cadmium nitrate  $\text{Cd}(\text{NO}_3)_2$ . In order to determine the effect of time on the process of sorption of 85%  $\text{H}_3\text{PO}_4$ , experiments were performed under conditions equal cations  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in the range of 5-60 mins.

**Table 1: Effect of time on the sorption of lead and cadmium in the presence of 85% phosphoric acid.  $C_{Pb^{2+}} = C_{Cd^{2+}} = 0.0505 \text{ g/L}$** 

Time (min)	Percentages of sorption %	
	Pb <sup>2+</sup>	Cd <sup>2+</sup>
	$C_{H_3PO_4} = 85\%$	
5	85.59	71.50
10	89.83	77.52
20	90.24	76.97
30	90.68	74.36
40	91.84	78.06
60	85.59	90.76

In concentrated phosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>), sorption capacity of the zeolite with respect to cadmium is in direct proportion to the duration of the process and increases throughout the studied time interval. After 60 mins, the degree of sorption of cadmium reaches 90.76%. With respect to lead, zeolite exhibits the highest sorption capacity at 40 mins, and over that time, the sorption of lead is reduced. However, most of the concentrated phosphoric acid, as in the previous experiment, the lead is absorbed in cations. So, even if the time for sorption of adsorbed cations is optimal, cadmium is 90.8%, and lead - 91.84%.

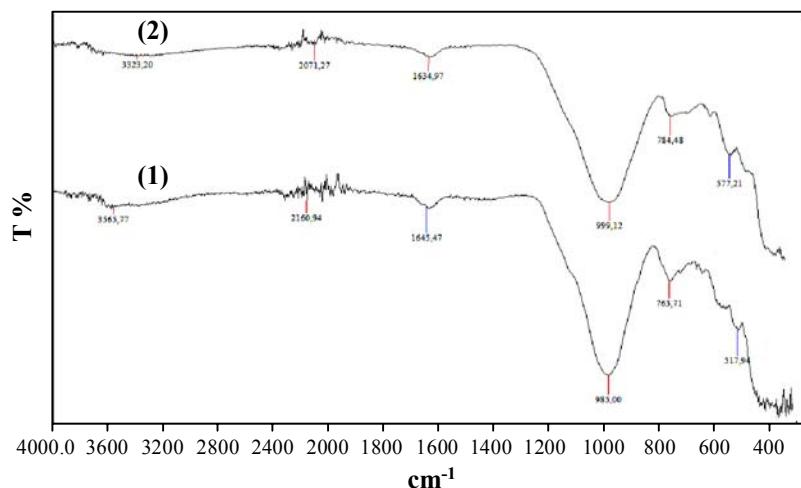
**Table 2: Effect of cadmium concentration on the sorption of lead from phosphoric acid**

Initial concentration (g/L)	Percentages of Sorption %	
	Pb <sup>2+</sup>	Cd <sup>2+</sup>
	$C_{H_3PO_4} = 85\%$	
	$C_{Pb} > C_{Cd}$	
<b>0.05:0.001</b>	70.05	80.42
<b>0.05:0.021</b>	51.06	49.18
	$C_{Pb} = C_{Cd}$	
<b>0.05:0.05</b>	90.68	74.36
	$C_{Pb} < C_{Cd}$	
<b>0.05:0.08</b>	80.06	70.99
<b>0.05:0.1</b>	79.17	71.09

## RESULTS AND DISCUSSION

### Infrared spectra

A comparative analysis of the IR spectra of natural zeolite and isolated from the acid after sorption  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was conducted. As it can be seen from Fig. 1, the IR spectrum of zeolite (Curve 1), intense frequency  $985 \text{ cm}^{-1}$  characterizing stretching vibrations Al, (Si)-O communication framework zeolite, and  $763.71 \text{ cm}^{-1}$  frequency-,  $527.9 \text{ cm}^{-1}$  relating to the deformational fluctuations of its frame is shifted to higher frequencies:  $985 \text{ cm}^{-1} \rightarrow 999.12 \text{ cm}^{-1}$ ,  $763.71 \text{ cm}^{-1}$ ,  $784.48 \text{ cm}^{-1}$ ,  $517.94 \text{ cm}^{-1} \rightarrow 577.21 \text{ cm}^{-1}$ . Aluminum-silicon-oxygen backbone frame and zeolite in phosphoric acid are not just disturbed, and changes probably occur due to the above mentioned processes, as well as the sorption of phosphate ions, as indicated by the presence of a frequency at  $422.68 \text{ cm}^{-1}$ <sup>11,12</sup>.

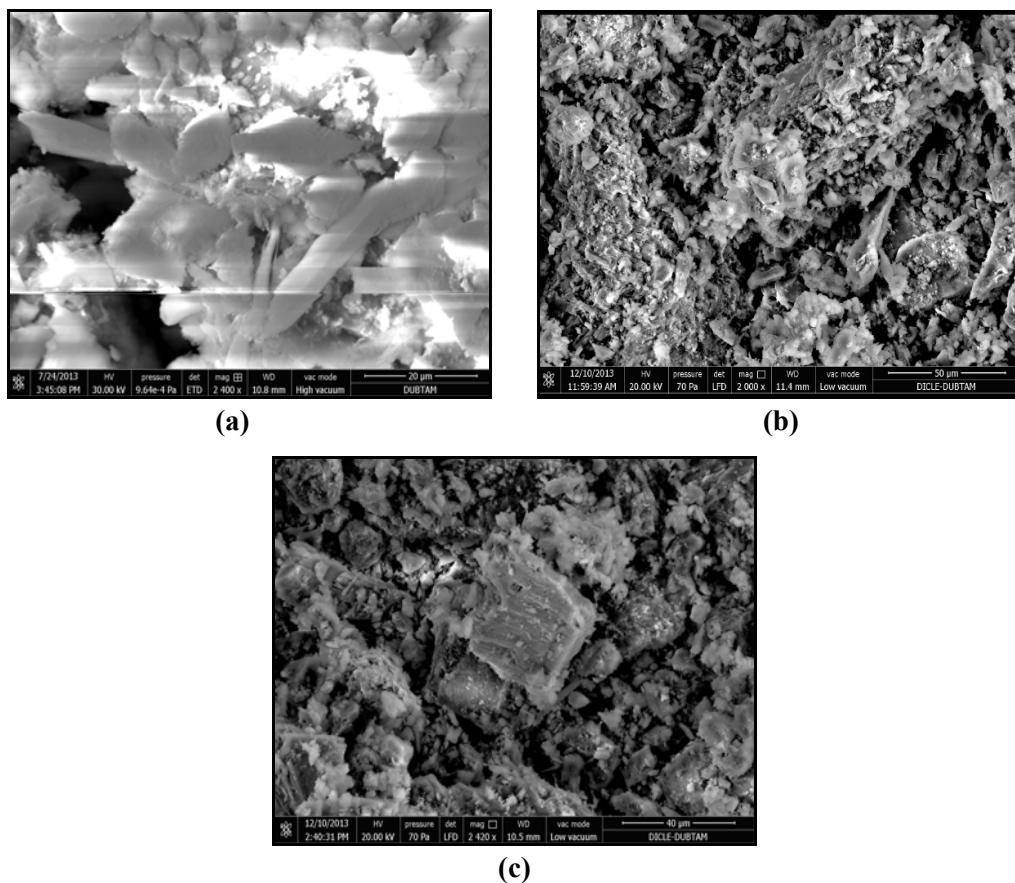


**Fig. 1:** IR spectra of (1) Natural zeolite, (2) Natural zeolite after sorption  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$

IR zeolite selected from the acid sorption after  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  (Curve 2) differs from the spectrum of natural zeolite (Curve 1). Simplified region stretching, deformation vibrations of water and the region of oscillations for External Relations of the tetrahedra, which are prescribed in a single frequency  $3323.20$ ,  $2071.27$ ,  $1634.97 \text{ cm}^{-1}$ . The frequency of the most intense stretching vibrations Al, (Si)-O connection  $985 \text{ cm}^{-1} \rightarrow 999.12 \text{ cm}^{-1}$  are broadened and shifted, and deformation vibrations of zeolite framework are  $763.71 \text{ cm}^{-1} \rightarrow 784.48 \text{ cm}^{-1}$ . This indicates that the natural zeolite, when in contact with the phosphoric acid is present in  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , are exchanged by cations of the proton and the filling of the free regions of localization of the aluminum, as well as filling channels and pores in the zeolite structure with metal cations impurities<sup>13</sup>.

### SEM analysis of natural zeolite

Electron microscopic analysis of natural zeolite and acid treated natural zeolite was analyzed and their surface properties were compared. As it can be seen from Fig. 1(a) and (b), the porosity varies considerably under the influence of phosphoric acid. The micrograph indicated that the presence of natural zeolite has small bright spots corresponding to the cavities and in the voids. The light spots become significantly larger in phosphoric acid treated natural zeolite [Fig. 1(b)] in comparison with a photomicrograph of natural zeolite [Fig. 1(a)].



**Fig. 2: (a) Natural zeolite photomicrograph (b) acid treated of natural zeolite and (c) selected after sorption natural zeolite**

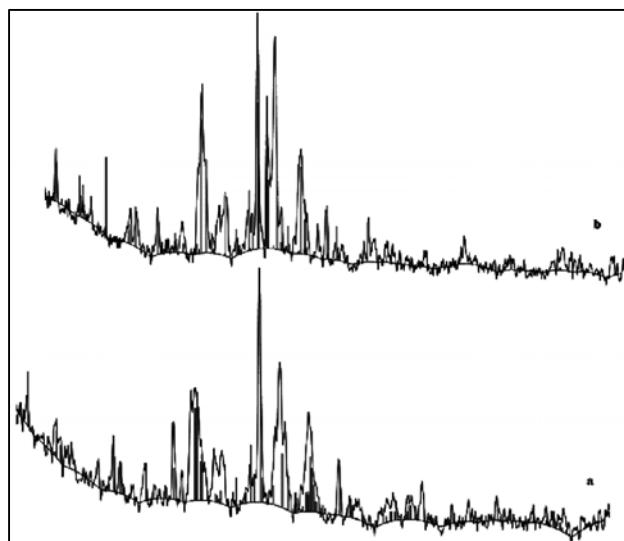
The micrograph shows acid treated natural zeolite of present elongated cylinders that are not in the picture of natural zeolite. That is, under the action of phosphoric acid in the

structure, size of the voids and channels also increases, which indicates the process of activation. Whereby, apparently its sorptive capacity increases with respect to sorbed cations.

Thus, the study of the sorption properties of the natural zeolite and the physical-chemical study of natural zeolites and acid treated zeolite isolated after sorption of lead (II) and cadmium (II), revealed that the phosphoric acid is retained in the structure of the natural zeolite and sorption properties of the zeolite exhibit their combined presence with respect to cations  $Pb^{2+}$  and  $Cd^{2+}$ .

### XRD Analysis

XRD analysis of the zeolite (Fig. 3) selected from phosphoric acid before and after adsorption of lead(II) and cadmium(II) showed that number of diffraction maximums with deviations occurred and the values of intensities and the theta positions can be summarized such:  $4.65400 \text{ \AA}$  (30)  $\rightarrow 4.53694 \text{ \AA}$  (73),  $43.83500 \text{ \AA}$  (10)  $\rightarrow 3.75809 \text{ \AA}$  (43),  $3.38300 \text{ \AA}$  (25)  $\rightarrow 3.34129 \text{ \AA}$  (99.9),  $3.16500 \text{ \AA}$  (40)  $\rightarrow 3.24040 \text{ \AA}$  (97),  $3.07400 \text{ \AA}$  (20)  $\rightarrow 3.06198 \text{ \AA}$  (72),  $2.97600 \text{ \AA}$  (65)  $\rightarrow 2.99379 \text{ \AA}$  (10.4),  $2.73300 \text{ \AA}$  (25)  $\rightarrow 2.57161 \text{ \AA}$  (73). In the X-ray spectra of the zeolite after sorption are new diffraction maxima  $15.28560 \text{ \AA}$  (37.8),  $3.97100 \text{ \AA}$  (100),  $3.91000 \text{ \AA}$  (70) and intense line in  $(2.51198.....1.37208) \text{ \AA}$ . Specified changes in X-ray spectrum claim the presence new elements binding to the atoms in the zeolite structure.



**Fig. 3: X-ray powder diffraction patterns of (a) acid treated zeolite and (b) the zeolite after sorption  $Pb^{2+}$  and  $Cd^{2+}$**

## CONCLUSION

Comparative analysis of the sorption capacity of natural zeolite cations Pb (II) and Cd (II) in a model system "H<sub>3</sub>PO<sub>4</sub>-Pb<sup>2+</sup>-Cd<sup>2+</sup>-zeolite" revealed preferred sorption capacity of the sorbent to lead. With increasing time of 30-40 mins sorption the sorption capacity of natural zeolite cations increases and then decreases due to desorption from the zeolite in acid.

Physico-chemical analyzes (IR, electron microscopy, DTA) shows that the natural zeolite in a concentrated phosphoric acid undergoes protonation and hydroxylation process without destroying the structure of the zeolite to produce additional OH groups, active in the processes of sorption.

## REFERENCES

1. E. Álvarez-Ayuso, A. García-Sánchez and X. Querol, Purification of Metal Electroplating Waste Waters using Zeolites, *Water Research*, **37(20)**, 4855-4862 (2003).
2. R. Apiratikul and P. Pavasant, Sorption of Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> using Modified Zeolite from Coal Fly Ash, *Chem. Engg. J.*, **144(2)**, 245-258 (2008).
3. K. K. H. Choy and G. McKay, Sorption of Cadmium, Copper, and Zinc Ions onto Bone Char using Crank Diffusion Model, *Chemosphere*, **60(8)**, 1141-1150 (2005).
4. A. Chlopecka and D. C. Adriano, Influence of Zeolite, Apatite and Fe-oxide on Cd and Pb Uptake by Crops, *Science of The Total Environment*, **207(2-3)**, 195-206 (1997).
5. F. Ji, C. Li, B. Tang, J. Xu, G. Lu and P. Liu, Preparation of Cellulose Acetate/Zeolite Composite Fiber and its Adsorption Behavior for Heavy Metal Ions in Aqueous Solution, *Chem. Engg. J.*, **209(0)**, 325-333 (2012).
6. E. S. N. M. Alykov, Investigation of the Sorption Process Flocculants Sorbent CB-1-A Chemistry and Chemical Technology, T. **53(8)**, 50-54 (2010).
7. E. S. N. M. Alykov, Sorbent for Water Purification from Flocculants Ecology and Industry of Russia, **8**, 20-21 (2010).
8. E. S. N. M. Alykov, Using Sorbent CB-1-A to Purify Water from Flocculants, J. Basic Appl. Res., **4(29)**, 158-167 (2009).
9. G. Sh. Sultanbaeva, U. Zh. Jussipbekov, R. M. Chernyakova and M. T. Oshakbayev, Physico-chemical Studies of Zeolite Shankanaj Field and Study of the Sorption of Phosphate Ions, Proceedings of the National Academy of Sciences MES RK. Ser.him., No. 5 (2003).

10. N. N. Kozhabekova, G. B. Dzhunusbekova, R. M. Chernyakova and Jussipbekov U. Zh., Studies of the Sorption of Copper Cations in the Model System,  $\text{H}_2\text{SO}_4\text{-Cu}^{2+}$ -Zeolite, Proceedings of the National Academy of Sciences of Kazakhstan, ser.him., No. 2, 35- 37 (2009).
11. V. S. Aleksandrov, A. P. Zykovad and E. Y. A. Markeev, Ion-Exchange Properties and IR Spectra of Natural Clinoptilolite Modified Hydroxy Phosphate, *J. Appl. Chem.*, **77**, 32-36 (2004).
12. J. Sárkány, Effects of Water and Ion-Exchanged Counterion on the FT-IR Spectra of ZSM-5: Part III,  $\text{Cu}^+(\text{CO})_2$ -ZSM-5: Interaction of  $\text{Cu}^+(\text{CO})_2$  Complex with  $\text{H}_2\text{O}$  and Changes in Skeletal T-O-T Vibrations, *Applied Catalysis A: General*, **229**, 291-312 (2002).
13. W. Mozgawa, The Influence of Some Heavy Metals Cations on the FTIR Spectra of zeolites, *J. Molecular Structure*, **555**, 299-304 (2000).

*Revised : 07.06.2014*

*Accepted : 10.06.2014*