SORPTION REMOVAL OF Pb^{2+}, Cd^{2+}, Cu^{2+} FROM DILUTED ACID SOLUTION BY CHITOSAN MODIFIED ZEOLITE

Marzhan Zh. Kussainova[1], Raisa M. Chernyakova[2], Umirzak Zh. Jussipbekov[2], Hamdi Temel[3], Salih Pasa[4], Raushan A. Kaiybayeva[2], Aktolkyn A. Agatayeva[2]

[1]*Satbayev University, Almaty, Kazakhstan*
E-mail: marzhan.zhan.84@mail.ru
[2]*JSC «Chemical Sciences Institution after A.B. Bekturov»*
106 Ualikhanov str., 050010, Almaty, Kazakhstan
[3]*Dicle University, Science and Technology Research and Application Center, 21280, Diyarbakir, Turkey*
[4]*Afyon Kocatepe University, Education Faculty Department of Science, 03200, Afyonkarahisar, Turkey*

Received 17 May 2017
Accepted 20 October 2017

ABSTRACT

The results of investigations on sorption activity of chitosan modified natural zeolite in regard to the simultaneous presence of Pb^{2+}, Cd^{2+} and Cu^{2+} are presented. The influence of the process duration and the cations concentration on the degree of their adsorption in diluted (20 % H_3PO_4) phosphoric acid is determined. The sorption curves show peaks at the 5-th and the 10-th minute most probably because of desorption from the sorbent. Under identical concentrations of all heavy metal cations studied ($C_{Pb}^{2+} = C_{Cd}^{2+} = C_{Cu}^{2+}$), the sorption degree in respect to lead cations is within the range of 78.02 % - 90.65 %, that in respect to cadmium cations varies from 71.22 % to 92.39 %, while that in respect to copper - from 42.00 % to 95.26 %. The character of the sorption curves recorded at identical concentrations of Pb^{2+} and Cd^{2+} but at a greater content of Cu^{2+} is the same. The degree of cadmium cations sorption varies from 92.39 % to 70.22 %. Cu and Pb cations are sorbed in a less amount. The degree of their sorption within 10 min refers to 88.42 % and 90.65 %, respectively, in case $C_{Pb}^{2+} = C_{Cd}^{2+} < C_{Cu}^{2+}$.

Keywords: lead, cadmium, copper ions, phosphoric acid, sorption, chitosan, modified zeolite.

INTRODUCTION

Economic activity of man results in the uptake of a great quantity of contaminants including heavy metals in the biosphere.

Heavy metals refer to the most distributed and toxic contaminants. Their main sources refer to industrial power plants, aviation, automobile and railway transport, mineral fertilizers and substances used as fertilizers. Most often a high content of heavy metal impurities is observed in phosphoric fertilizers as well as fertilizers obtained using phosphoric acid extraction [1].

The phosphoric industry based on raw materials of the phosphorus-bearing field of Karatau makes a significant contribution to the economy of the southern region of the Republic of Kazakhstan. So, for about 40 years the Karatau deposit [2] has been the ore base of home phosphoric industry. The content of the main component P_2O_5 there ranges from 19 % to 26 %.

In this regard, a preliminary purification from phosphoric acids is required. Sorption methods have been widely used in this aspect because they provide an easy and guided operation removing heavy metals up to any residual concentrations. For instance, $Pb^{2+}$and Cd^{2+} are large ions, and which is why their sorption by clays is not effective [3]. Sorption of heavy metals by clays decreases with soil acidity increase [4]. Unlike clays which sorb only cations non-crystalline zeolites can fix and adsorb both metal containing cations and anions as they have a high silicic crystalline structure.

Clinoptilolites are promising sorbents in regard to heavy metal cations. They have a crystalline structure which provides removal of cations not only in wastewater but in H_3PO_4 as well. It is known that clinoptilolite has a larger adsorption capacity in regard to Pb^{2+}, while a less one to Cd^{2+} and Cu^{2+} [5, 6].

Great deposits of zeolites have been explored in the Republic of Kazakhstan. Their mining is carried out by the open method. Among the explored deposits, Shankanay deposit in Taldykorgan region is worthy of note.

Shankanay zeolite refers to the acid-resistant group and is characterized both by high cation-exchange and anion-exchange properties [7]. This determines the possibility of using it for diluted phosphoric acid removal.

The presence of pollutants including mineral acids in the aqueous media and sewage requires the elaboration of new, more effective sorbents possessing not only selective properties for definite types of substances but also high sorption properties in regard to heavy metals [8].

Chitosan derivatives attract attention as cheap materials of a high adsorption potential due to the high content of functional hydroxylic and amino groups $(C_6H_{11}O_4N)_n$. Chitosan is characterized by chemical stability, high reactivity and selectivity to toxic cations [10, 11].

This work reports a study of the adsorption ability of clinoptilolite activated by chitosan in regard to Pb^{2+}, Cd^{2+} and Cu^{2+} in their joint presence in 20 % diluted H_3PO_4.

EXPERIMENTAL

Materials and methods

Acid-resistant zeolite of Shankanai deposit [7, 8, 12] was used. $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, and $Cu(NO_3)_2$ were of an analytical grade. They were purchased from Sigma Aldrich and Fluca. 85 % thermal phosphoric acid was also used in this work.

The determination of lead, cadmium and copper was carried out using an atomic-absorption spectrophometer of the type AAS-400 of Perkin Elme, USA. The infrared spectra were recorded on Perkin Elmer Spectrum 100 FT-IR spectrometer, USA. The microstructure of the samples was studied using stereomicroscope (SEM) (model QUANTA 250 FEG).

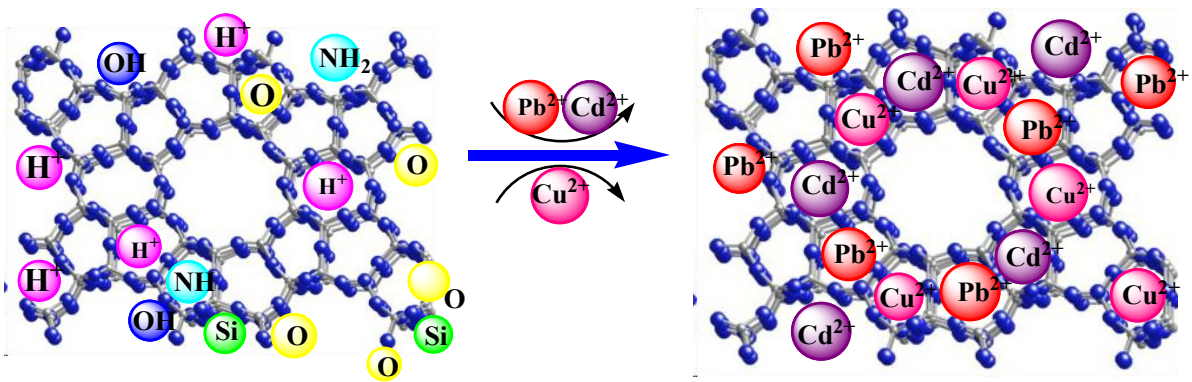
RESULTS AND DISCUSSION

The experiments referring to the degree of phosphoric acid removal with sorbents are carried out on a laboratory scale. The obtained data allow the calculation of the metal ion removal efficiency (R, %). It is defined by the difference of the initial and residual concentrations according to Eq. 1:

$$\%R = \frac{C_t - C_e}{C_t}.100 \qquad (1)$$

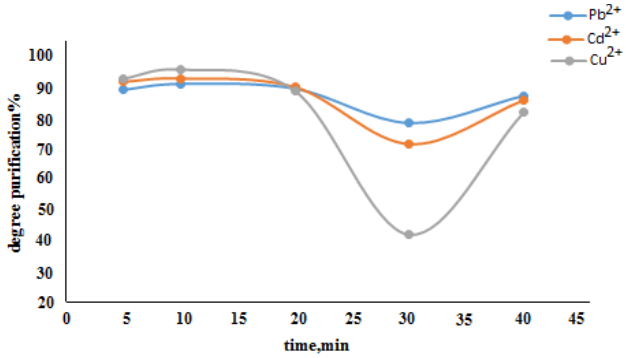
The sorption ability of activated clinoptilolite in regard to bivalent cations of lead, cadmium and copper in their joint presence in diluted H_3PO_4 is studied on a model system. The process of sorption in this system is carried out under the conditions of stirring at constant ratio of H_3PO_4:modified zeolite (L:S) = 10:100 at 25ºC. A pre-determined concentration of Pb^{2+}, Cd^{2+} and Cu^{2+} cations is prepared by introduction of an estimated amount of the corresponding nitrates of lead, cadmium and copper into the acid (Fig. 1).

The investigation of the sorption process of Pb, Cd and Cu ions shows that for all experiments chitosan



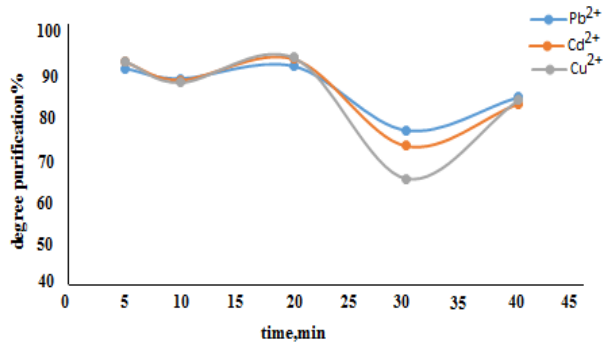
Chitosan modified zeolite — Pb^{2+}, Cd^{2+} and Cu^{2+} sorption

Fig. 1. Schematic illustration of cations adsorption by activated clinoptilolite.



(C_{Pb}^{2+}=C_{Cd}^{2+}=C_{Cu}^{2+})

Fig. 2. Sorption curves of Pb^{2+}, Cd^{2+} and Cu^{2+} depending on the time of the process.



$C_{Pb}^{2+} = C_{Cd}^{2+} < C_{Cu}^{2+}$

Fig. 3. Sorption curves of Pb^{2+}, Cd^{2+} and Cu^{2+} depending on the time of the process.

modified natural zeolite manifests high sorption ability towards Pb^{2+}, Cd^{2+} and Cu^{2+} (Fig. 2). The effect of time on the sorption ability is followed as well. The time interval studied refers to 40 min. The results obtained are presented in Figs. 2 - 4. The analysis of the data obtained shows that in case of equal contents of Pb, Cd and Cu cations at the 5-th and the 10-th minute of the process H_3PO_4 is characterized by the cations least content irrespectively of their nature. The minimum content of ions in H_3PO_4 is recorded at the 10-th minute of the process.

The peaks outlined in the figures considered are due probably to desorption of heavy metals from the sorbent. Judging by the obtained results, the modified zeolite shows the least sorption degree in respect to Pb cations within the time interval studied. The values obtained in case of lead are within 78.02 %- 90.65 %, those of cadmium and copper are in the ranges of 71.22 % - 92.39 % and 42.00 %- 95.26 %, correspondingly.

Up to the 40-th minute most of all copper cations are sorbed (95.26 %). On further time increase the degree of sorption of copper, lead and cadmium decreases from 95.26 to 88.42 %, from 90.65 to 89.16 %, and from 92.39 to 89.65 %, respectively.

The sorption curves recorded in presence of identical Pb^{2+} and Cd^{2+} concentrations but greater content of Cu^{2+} are similar (Figs. 3, 4). The utmost sorption is recorded during the first 5 - 10 minutes of the process. Activated clinoptilolite manifests better adsorption ability towards Cd^{2+} which remains the same up to 40 minute of the operation. The purification degree in this case varies from 92.39 % to 70.22 %.

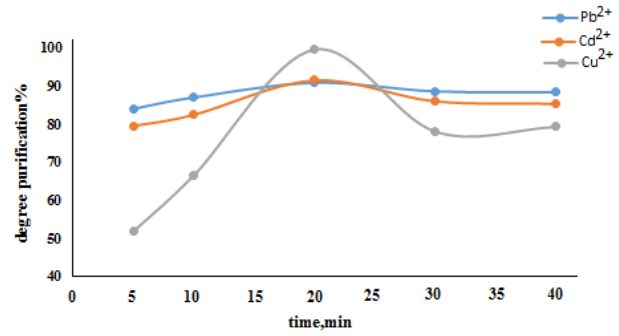
Cu and Pb cations are sorbed in a less amount, the degree of their sorption within 10 min reaches a value of 88.42 and 90.65 %, respectively.

Under the conditions of identical lead and cadmium cations concentrations but a higher content of copper within the initial 5 min the concentration of lead ions is less than that of cadmium, i.e. cadmium follows copper in respect to the amount adsorbed. The greatest sorption of ions from H_3PO_4 is observed at the 5-th minute. The activated clinoptilolite manifests the highest sorption ability towards Cu^{2+} cations. The degree of copper adsorption varies from 94.85 % to 65.63 % during the initial 20 min of the process.

Lead and cadmium are sorbed in a somewhat less amount. The degree of their sorption makes up 92.82 % and 94.52 %, respectively.

In case of identical concentrations of Pb and Cu cations in H_3PO_4 but greater Cd cations content, the residual cations content decreases with time until the 10-th minute. It increases on further time increase.

The sorption curves referring to all heavy metal



$CPb^{2+} = CCu^{2+} < CCd^{2+}$

Fig. 4. Sorption curves of Pb^{2+}, Cd^{2+} and Cu^{2+} depending on the time of the process.

cations studied have a similar form as in the previous case. But in a higher Cd cations presence the sorption degree increases within the initial 20 min. In the 20 min - 40 min range the sorption curves show a tendency of sorption degree decrease – from 2.25 % to 21.59 %. The sorption degree of copper is in the range of 99.61 % - 78.02 %, that of cadmium cations varies between 91.48 % - 85.35 %), while that of lead cations - between 90.67 % and 88.41 %.

SEM-study

The electron micrographs of natural and activated clinoptilolite are shown in Fig. 5. The images specify that the zeolite surface is coated by chitosan. The area of the activated clinoptilolite is covered by disposed particles (Fig. 5b). There is no intercalation of chitosan into the inside pores of clinoptilolite, i.e. its pores are not blocked, which is in agreement with the findings reported in ref. [10]. The electron micrographs of chitosan modified clinoptilolite prior to (Fig. 5b) and after adsorption (Fig. 5c) differ.

The activated clinoptilolite surface after sorption shows swelling particles, formation of greater aggregates being in a chaotic arrangement.

FT-IR study

The IR spectroscopic analysis of chitosan modified zeolite in the range of 987.45 $cm^{-1} \rightarrow$ 995.42 cm^{-1} shows an increase in intensity, shifting of the frequency and less pronounced peak in comparison with the spectrum of natural zeolite. This indicates strengthening of C-O bond (Fig. 6 a,b).

A weak peak at 691.8 cm^{1} appears in the spectrum of the modified zeolite (Fig. 6c). It is conditioned by the appearances of frequencies at 1145.85 cm^{-1} and 1202.7 cm^{-1}. It is attributed to the presence of primary amine. The peak at 3405.17 cm^{-1} is due to the presence of secondary amine. The appearance of weak frequencies at 2092 cm^{-1}, 2169.92 cm^{-1} and 2289.22 cm^{-1} indicates the presence of a compound with a double carbon bond in the modified zeolite, while widening of frequency at 1634.94 cm^{-1} indicates the presence of tertiary amines

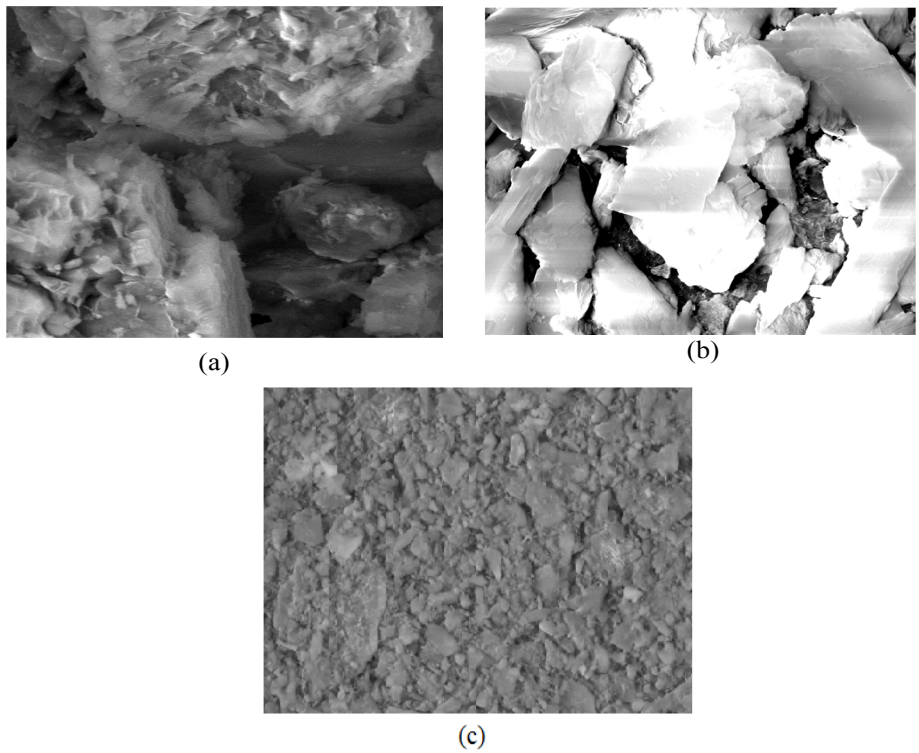


Fig. 5. SEM images of (a) - natural clinoptillolite, (b) - chitosan modified clinoptilolite, (c) - modified clinoptilolite after sorption of Pb^{2+}, Cd^{2+}, Cu^{2+}.

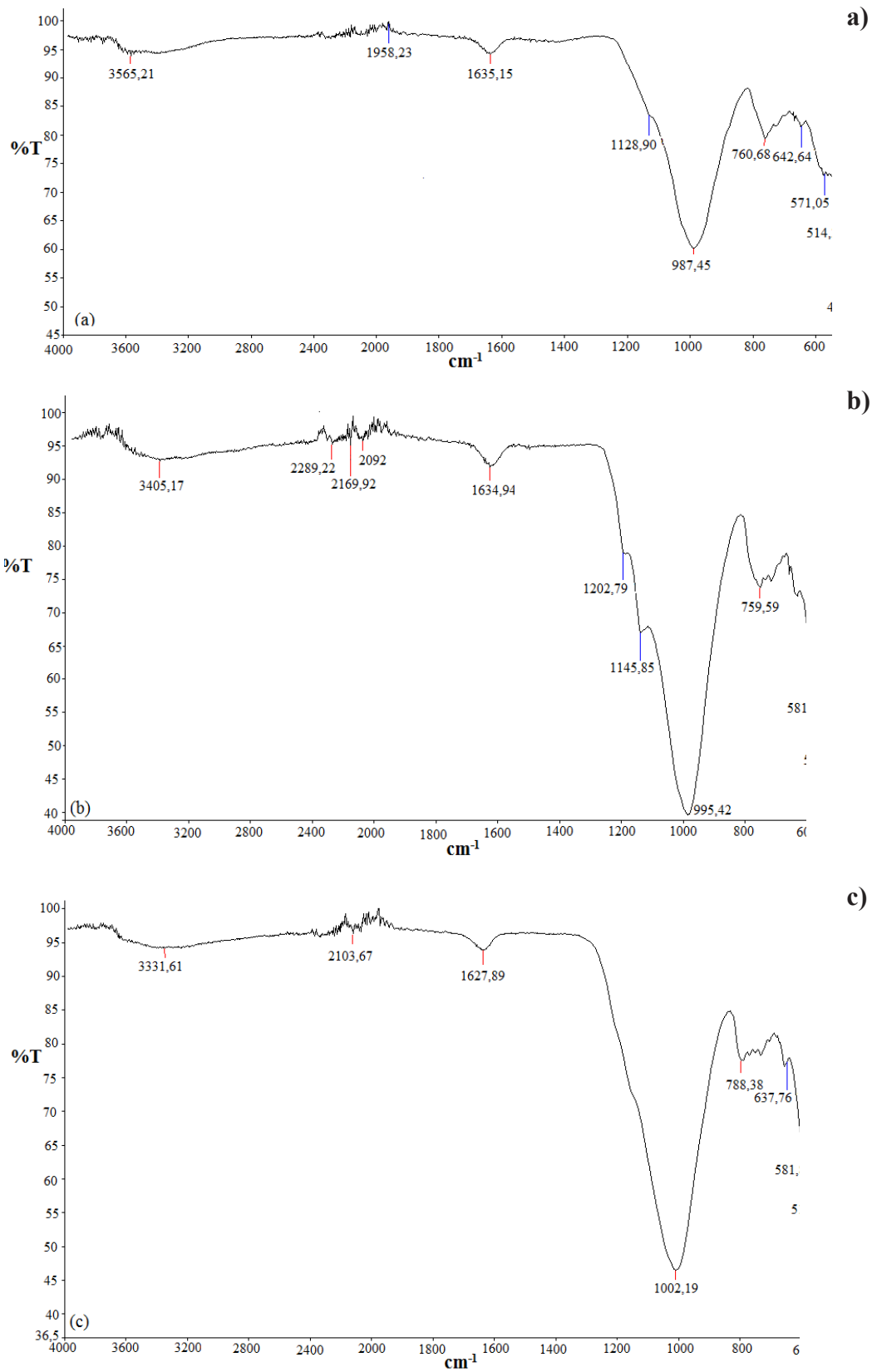


Fig. 6. IR-spectra of the samples: (a) - clinoptilolite, (b) - clinoptilolite after acid sorption, (c) - activated clinoptilolite, (d) - activated clinoptilolite after sorption of Pb^{2+}, Cd^{2+}, Cu^{2+}.

C=N. The changes of the spectral pattern of the modified zeolite verifies the cross-linking of chitosan with the surface of zeolite [14].

The FTIR analysis of clinoptilolite activated by chitosan after adsorption of heavy metals cations (Fig. 6c) is characterized by intensity decrease and maxima shift (3405.17 cm^{-1}→3332.61 cm^{-1} and 1634.94 cm^{-1}→1627.89 cm^{-1}) characteristic [15] of vibrations of secondary and tertiary amines.

The peaks at 2092.0 cm^{-1} and 2289.22 cm^{-1} in the spectra of compounds containing a double bond vanish and another one appears at 2103.67 cm^{-1}. This is observed in the spectrum of the modified zeolite but the latter is shifted to 2169.92 cm^{-1}. The spectrum of the adsorbent recorded after adsorption shows peaks at 1146.85 $cm^{-1}$and 1202.7 cm^{-1} indicative of primary amine absence. The peak at 416.23 cm^{-1} is attributed to strengthening of Me-O bond [16].

CONCLUSIONS

The process of purification of a concentrated acid solution from Pb^{2+}, Cd^{2+} and Cu^{2+} through sorption on natural zeolite modified by chitosan is studied for the first time. The effect of the sorption process duration, the concentration and the nature of the cations sorbed on the sorption ability of the sorbent prepared is shown. It is stated that the modified zeolite manifests high sorption ability in regard to all cations studied within the initial 5 min - 20 min of the process. The greatest degree of acid purification under the conditions of identical cations concentrations but at a high content of cadmium cations is achieved for 20 min, while that in presence of a higher concentration of copper cations requires 10 min. The degree of phosphoric acid purification from Pb cations is in the range of 92.26 % - 92.82 %, in case of Cd cations it varies from 93.79 % to 94.52 %, while in case of Cu cations - from 93.97 % to 94.85 %.

REFERENCES

1. N.N. Bushuyev, Interaction of metals with various components of soil, Abstracts of the international scientific - practical conference, 2007, 137-144, (in Russian).
2. B.K.Yussupbekov, A.I.Timchenko, A.I. Shein, Open development of Karatau phosphoritic deposits, Academy of Sciences of the Kazakh SSR, 1970, 188, (in Russian).
3. Y.V. Alekseev, Heavy metals in soils and plants, Agropromizdat, 1987, 142, (in Russian).
4. N.M. Alykov, E.Y. Shachneff, Study of sorption on the sorbent flocculants CV-1-A, Life Safety 8, 2010, 39-42, (in Russian).
5. N.N.Kozhabekova, G.B. Dzhunusbekova, R.M. Chernyakova, U.Zh. Jussipbekov. Sorption of copper and iron from sulfuric acid by natural zeolite, Industry of Kazakhstan, 53, 2009, 97-99, (in Russian).
6. G.S. Sultanbaeva, U.Zh. Jussipbekov, R.M. Chernyakova, M.T. Oshakbayev, Physico-chemical studies of Shankanay field zeolite and study of the sorption of phosphate ions, Proceedings of the National Academy of Sciences of RK, 5, 2003, 30-33, (in Russian).
7. G.S. Sultanbaeva, R.M. Chernyakova, G.S. Cochin, Sorption of iron and phosphate ions from phosphoric acid sludge of Shankanay zeolite deposit, Herald of the Kyrgyz National Balasagyn University named, 3, 2004, 260-264, (in Russian).
8. N.N. Kozhabekova, G.B. Dzhunusbekova, R.M. Chernyakova, U.Zh. Jussipbekov. Studies of the sorption of copper cations in the model system H_2SO_4 - Cu^{2+}- zeolite, Proceedings of National Academy of Sciences of Kazakhstan, 2, 2009, 35-37, (in Russian).
9. U. Wingenfelder, B. Nowack, G. Furrer, R. Schulin, Adsorption of Pb and Cd by amine-modified zeolite, Water Research, 39, 2005, 3287-3297.
10. J. Xie, Ch. Li, L. Chi, D.Wu, Chitosan modified zeolite as a versatile adsorbent for the removal of different pollutants from water, Fuel, 103, 2013, 480-485.
11. Y.L. Liu, C.Y. Hsu, Y. H. Su, J.Y. Lai, Biomacromolecules, 6, 2005, 368.
12. G.Sh. Sultanbayeva, R. Holze, R.M. Chernyakova, U.Zh. Jussipbekov, Removal of Fe^{2+}, Cu^{2+}-, Al^{3+}- and Pb^{2+}- ions from phosphoric acid by sorption on carbone – modified zeolite and its mixture with bentonite, Microporous and mesoporous materials, 170, 2013, 173-180.
13. A. Meenakshi, A.M. Kathryn, B. Yoshinari, M.P. Jilska, W.S. Geoff, Surface modification of natural zeolite by chitosan and its use for nitrate in cold regions, Cold Regions Science and Technology, 62, 2010, 92-97.
14. V.S. Aleksandrov, A.P. Zykov, E.Y. Markeev, Ion-exchange properties and IR spectra of natural clinoptilolite modified hydroxy phosphate, Journal of Applied Chemistry, 77, 2004, 32-36.

15. J. Sárkány, Effects of water and Ion-Exchanged Counterion on the FTIR Spectra of ZSM-5.II. (Cu+-CO)–ZSM-5: Coordination of Cu+CO Complex by H_2O and Changes in Skeletal T–O–T Vibrations, Applied Catalysis, 229, 2002, 291-312.
16. W. Mozgawa, The influence of some heavy metals cations on the FTIR spectra of zeolite, Journal of Molecular Structure, 555, 2000, 299-304.
17. E. Zanin, J. Scapinello, M. Oliveira, C.L. Rambo, F. Franscescon, Adsorption of heavy metals from wastewater graphic industry using clinoptilolite zeolite as adsorbent, Process Safety and Environmental Protection, 105, 2017, 194-200.
18. H. Choi, S. http://www.sciencedirect.com/science/article/pii/S1876107016001280 - !Yu, K.H. Kim, Efficient use of Mg-modified zeolite in the treatment of aqueous solution contaminated with heavy metal toxic ions, Journal of the Taiwan Institute of Chemical Engineers, 63, 2016, 482-489.
19. A.R. Abdul Syukor, S. Sulaiman, Md. Nurul Islam Siddique, Integration of phytogreen for heavy metal removal from wastewater, Journal of Cleaner Production, 112, 2016, 3124-3131.
20. D. Angelova, S. Uzunova, I. Uzunov, B. Anchev, Dependence between oil sorption capacity of pyrolyzed rice husks and the composition and amount of fluids dispersed on their surface, J. Univ. Chem. Technol. Metall., 47, 2, 2012, 147-154.