IRSTI 87.53.13.; 31.15.35 https://doi.org/10.26577/ijbch-2019-i2-17

[1*]A.B. Rakhym, [1]U.Zh. Bekturganova, [1,2]G.A. Seilkhanova, [3]A. Csavdari

[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan
[2]Center for Physical and Chemical Research and Analysis Methods, Almaty, Kazakhstan
[3]Babes-Bolyai University, Cluj-Napoca, Romania
e-mail: akmaral.rahym@gmail.com

Chamotte clay sorbent for the extraction of lead and cadmium ions from aqueous solutions

Abstract: Nowadays the problem of wastewater pollution by heavy metal (HM) ions is extremely urgent. HM are harmful for health and environment, they are not biodegradable and can accumulate in plants and body. Clay minerals are known for their high adsorption capacity towards heavy metal ions. There are many research studies on appliance of different types of clays for wastewater treatment. Chamotte clay is a white heat-treated kaolin clay with stone properties, resistant to aggressive media, which contains highly dispersed hydroaluminosilicates. The clay does not require additional purification after secondary use. It is used in industry in large quantities, though wastes of clay are needed to be utilized. In current work chamotte clay wastes are offered to be used as a sorbent for lead (II) and cadmium (II) ions extraction. The choice of the ions is based on the high toxicity and abundance of these metals in wastewaters. Polivynylpyrrolidone (PVP) was used as a modifier to increase adsorption capacity of the clay. The extraction degree of ions by initial chamotte clay reaches (97 ± 7.2) % and (67 ± 6.0) % for Pb^{2+} and Cd^{2+} respectively. The modification with PVP increases the extraction degree of Cd^{2+} to (86.0 ± 6.4) %. The initial and modified clay was characterized by scanning electron microscopy, energy dispersive spectroscopy and Fourier transform infrared spectroscopy methods. The adsorption process was carried out under static conditions at pH = 6 and T = 298 K, initial concentration of the metal ions was 10 mg/l. The optimal mass for the sorption of lead and cadmium ions was also determined during the study and is equal to1 g per 100 cm^3 of solution. The use of chamotte clay as the basis for the development of sorbents helps reducing the cost of cleaning water bodies, and also allows solving the problem of wastes disposal.
Key words: adsorption, chamotte clay, polyvinylpyrrolidone, heavy metal ions, wastewater treatment

Introduction

Large industrial production is characterized by the formation of effluents containing heavy metal ions (HM). Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed [1-3]. However, due to large emissions as a result of industrialization and urbanization, HMs pose a great threat. Unlike organic pollutants that are capable of biodegradation, heavy metals do not decompose into harmless end products and have global consequences for both the human body and the environment [4]. According to studies [5, 6], some TM ions are nutrients for the physiological functions of humans in small doses, but in large quantities they have a negative effect on health.

Many methods are known to reduce the concentration of pollutants or to completely purify water from heavy metal ions (HM), but many of them are expensive. One of the most effective and low-cost methods for the neutralization of HM ions is sorption [7]. The sorption method makes it possible to purify water from HM ions with high efficiency, approximating the concentration of contaminants to maximum acceptable concentration (MAC) and general sanitary standards.

There is a shortage of clean drinking water existing in some regions of Kazakhstan [8]. One of these regions is the village of Alatau Batyr. The local population is forced to drink low-quality water containing TM ions. During the experiment, a number of water samples were taken and their composition was studied. As it turned out, the water in the region needs to be treated as TM ions in high concentrations, which do not meet sanitary standards, were found in the samples.

In recent years, the use of industrial waste as secondary products has been of great interest [9].

The use of industrial waste as an adsorbent solves 2 problems: 1) purification of water from pollution; 2) wastes disposal. For the first time, secondary commodities of refractory material chamotte clay (ChC) were used for water purification. ChC is a white heat-treated kaolin clay with a stone properties, resistant to aggressive media, which contains highly dispersed hydroaluminosilicates. The clay does not require additional purification after secondary use. It can be used in industry in large quantities [10, 11].

Polyvinylpyrrolidone (PVP) was chosen as a modifier. The choice of modifier is based on the availability and safety of this compound. The presence of the lactome cycle in PVP macromolecule ensures its good solubility in water [12]. The high molecular weight PVP compound is chemically stable and capable of complexation due to the presence of potential nitrogen monoxide donors in its structure. The binding of PVP increases pores on the clay surface, thereby improving its sorption properties [13, 14]. The adsorbing properties of polyvinylpyrrolidone allow it to be used as part of detoxifying agents. It is used in medicine as a stabilizer of emulsions and suspensions [14].

Experimental part

Materials and methods.

In this work, chamotte clay (the Ukrainian deposit Teplosvet Inzhiniring, LLC, Kiev) was selected as an object of the study and polyvinylpyrrolidone 10000 (AppliChem GmbH) – as a modifier. To prepare model solutions for studying the adsorption properties of the obtained sorbents, chemically pure grade salts of $Pb(NO_3)_2$ and $CdCl_2$ (Laborfarm) were used. The residual concentrations of Pb^{2+} and Cd^{2+} ions were determined by atomic absorption spectroscopy on a 'Shimadzu 6200' (Japan) instrument.

The obtained samples were studied by physicochemical methods of analysis, which included FTIR – spectroscopy (Spectrum 65, Perkin Elmer, USA), scanning electron microscopy (SEM) (Zeiss Supra 40VP instrument) to determine particle size and topography, elemental analysis by EDAX (energy dispersive spectroscopy) method to study chemical composition (Quanta FEG 250 scanning electron microscope, FEI, USA)

Composite sorbents obtainment.

The process of obtaining composite material consisted of the following steps:

1) A weighed portion of ChC (20 g) was poured into 100 ml of a 1% PVP solution (these objects did not need preliminary treatment). The resulting mixture was stirred using a dynamic stirrer for 1 hour, then left for 24 hours.

2) the drying process was carried out at T368–373K for 3-4 hours. The resulting sorbent was subjected to grinding to obtain a homogeneous powder mass.

Adsorption experiments.

A portion of the obtained sorbent was added to a 10 mg/l aqueous solution containing lead or cadmium ions at a temperature of (296 ± 2) K. At certain time intervals, samples were taken, filtered, and the content of heavy metal ions was determined. The degree of extraction of the studied ions was calculated by the Formula 1:

$$E = (C_0 – C_e) / C_0 * 100\%, \quad (1)$$

where E is the degree of extraction of metal ions,%;

C_0 and C_e – initial and equilibrium concentrations of metal ions, respectively, mg/l.

Results and discussion

The technical characteristics of the chamotte clay used in the current work are presented in Table 1 [15].

Table 1 – Technical characteristics of the ChC [15]

Specifications	Values
Average grain size	2 mm
Moisture absorption	from 2% to 20%
Humidity	not more than 5%
Refractoriness	from 1550^{0}C to 1850^{0}C

The technical characteristics of ChC are especially important, since with prolonged storage or upon expiration (3 years) it loses its unique properties [16].

The structure of the modifier for creating the sorbent (PVP) is shown in Figure 1. The presence of the lactome cycle in the polymer macromolecule ensures solubility in water. PVP molecules in aqueous solutions are static tangles that bind molecules that results ability to complexation with ChC [17].

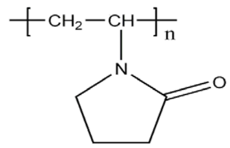
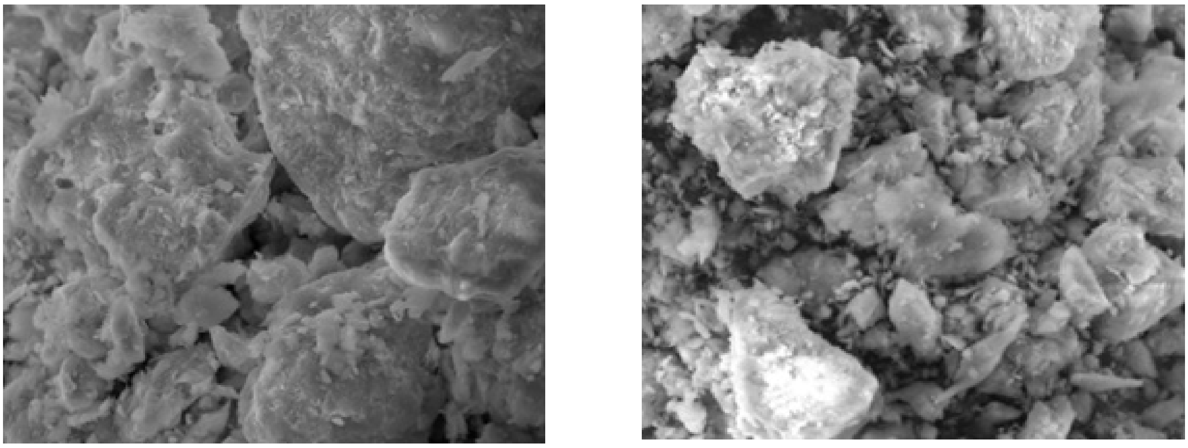


Figure 1 – Molecular structure of PVP



a) The original ChC b) The modified ChC

Figure 2 – Fragments of SEM images of Chamotte clay and its modified form (at zoom 20000x)

Figure 2 shows microphotographs of the initial and modified with polyvinylpyrrolidone ChC obtained by scanning electron microscopy (SEM). As it is known, SEM is widely used to study the microstructure of various objects [18]. From figure 2a it follows that the sample of secondary raw materials has a dense structure, represented by hydroaluminosilicates of various shapes and sizes. As a result of the modification of ChC by the PVP polymer, the surface structure of clay changes (2b). As it can be seen from Figure 2b, the ChC sample becomes more uniform after modification, the sizes of hydroaluminosilicates are enlarged, which leads to an increase in its porosity and hence, sorption activity increases. It can be observed that the addition of the PVP polymer affects the porosity of the hydroaluminosilicates in ChC structure.

Table 2 presents the results of elemental analysis of chamotte clay obtained by energy dispersive spectroscopy (EDS). The qualitative and quantitative composition of ChC was established. As can be seen from Table 2, the main components of ChC are oxygen, aluminum and silicon, since the clay is an aluminosilicate material. Also it contains significant doses of carbon, (which is part of the clay in the form of magnesium and calcium carbonates) and such metals as potassium, sodium and magnesium. The lasts contribute to the formation of fusibility and are found in the form of soluble salts.

Table 2 – Data of elemental analysis of chamotte clay

Raw materials	The content of the element, wt.%						
	O	Si	Al	C	K	Mg	Na
Chamotte clay	43.22	26.62	22.40	6.71	0.86	0.50	0.44

To confirm the presence of a modifier in the sample, the initial and modified chamotte clay was studied by FTIR spectroscopy. The results of the analysis are presented in figures 3-4. Narrow absorption bands of weak intensity are observed in ChC spectra. The IR spectrum of the sample shows a weak band at 1027 cm^{-1}, corresponding to stretching vibrations of Si – O – Si tetrahedra of the silicon-oxygen skeleton, which are clearly manifested in the spectrum of chamotte clay [19]. The observed intense absorption bands at 468.40 cm^{-1}, 540.20 cm^{-1} and 519 cm^{-1} can be attributed to deformation vibrations of Me-O type groups related to alkaline-earth metals. Absorption bands in the region of 695 cm^{-1} and 1448 cm^{-1} indicate that calcite impurities are present in the composition. The band 797.15 cm^{-1} is due to the Si – O – Mg bond in the octahedral positions of kaolinite. The intense absorption band of the deformation vibrations of water molecules bound by OH groups is in the range of 1832–3697 cm^{-1} [20].

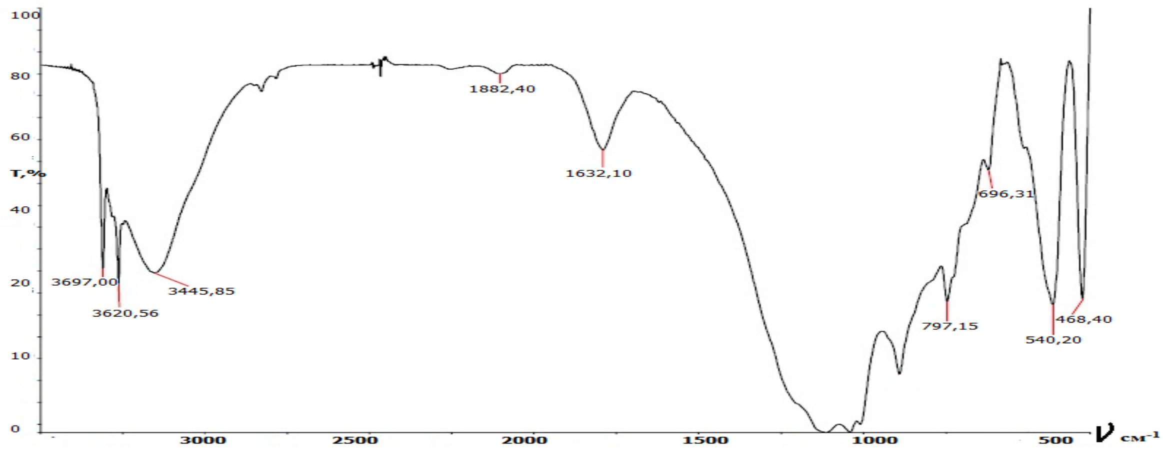


Figure 3 – IR spectrum of ChC

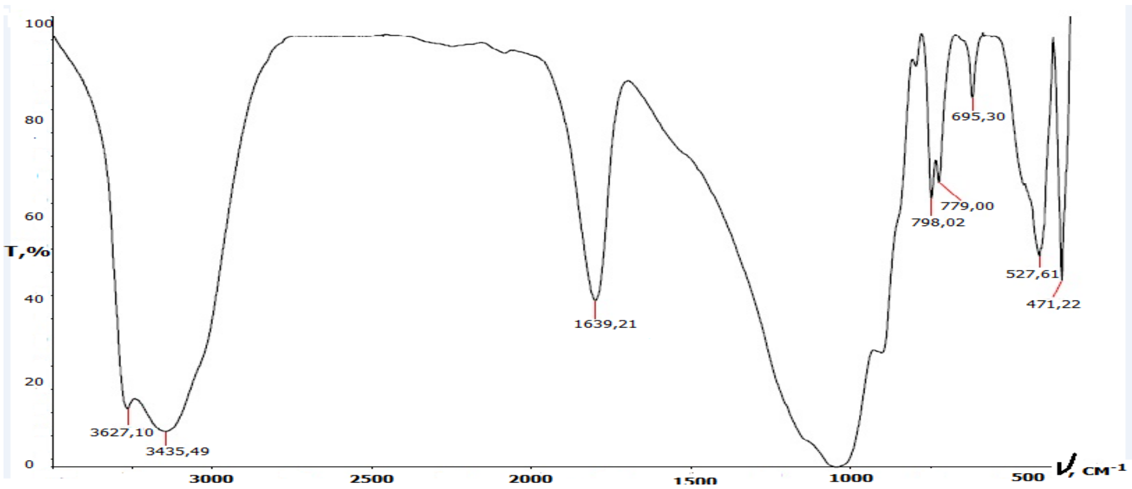


Figure 4 – IR spectrum of ChC + PVP

The IR spectrum of modified clay has absorption bands with wave numbers corresponding to stretching vibrations of $–CH_2–$ and C-N bonds due to the possible formation of a complex compound of PVP and clay. The stretching vibrations of the $–CH_2–$ group are located in the range of 1480–1440 cm^{-1}, and the C-N bonds are between the absorption bands of 2260–2240 cm^{-1}, which characterize PVP [21]. This indicates the presence of PVP or its complex compounds in the sorbent. It was found that the band at 1027 cm^{-1}, which is responsible for the stretching vibrations of Si – O bonds, remains unchanged; therefore, the modification does not affect the silicon content in the samples [22].

The research results presented in Figure 5 show that the extraction of lead ions by the initial clay reaches (97 ± 7.2) %, and the degree of extraction of cadmium from the aqueous solution reaches only (67 ± 6.0) %. Therefore, the activation of ChC by PVP is effective, since the degree of extraction of cadmium ions by modified sorbent reaches (86 ± 6.4) %. Also it was found during the experiment that the degree of extraction of lead and cadmium ions at the beginning sharply increases and then reaches equilibrium within 30 minutes. The adsorption ability of sorbents towards identically charged metal ions depends on the radius of the ion and charge density [23]. Between two ions of the same charge, ions with a large radius exhibit higher sorption ability, because they are less prone to the formation of a hydration shell, which reduces the forces of electrostatic attraction. Since lead has a larger ionic radius (0.112 nm) compared to cadmium ions (0.099 nm), it should be sorbed better, which corresponds the results of the study. The highest degree of recovery is (97 ± 7.2) % for lead ions and (86 ± 6.4) % for cadmium ions.

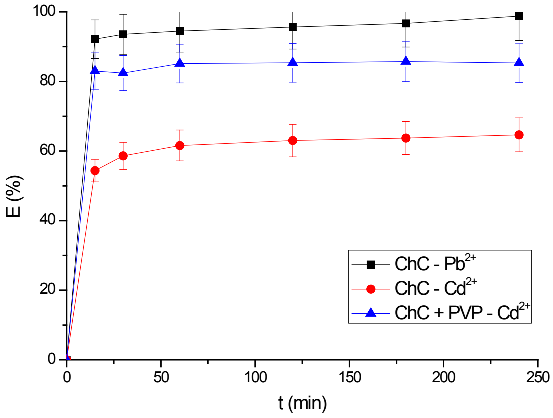
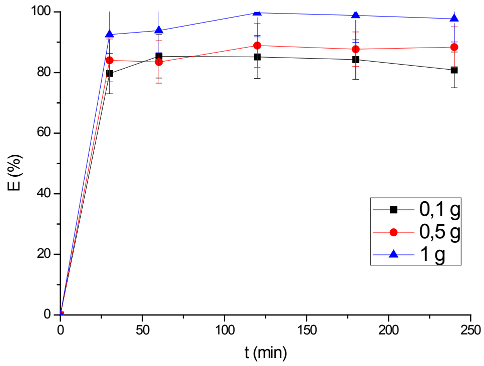
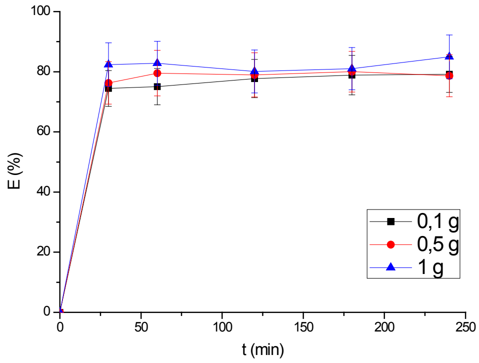


Figure 5 – Dependence of the degree of extraction of Cd^{2+}, Pb^{2+} ions (T = 298K, pH = 6, C = 10 mg /l) on time



a) ChC – Pb^{2+}



b) ChC + PVP – Cd^{2+}

Figure 6 – Dependence of the degree of extraction of Pb^{2+} (a) and Cd^{2+} (b) ions with different masses of ChC(a) and ChC+PVP (b) on time (T = 298 K, pH = 6, C = 10 mg/l)

As the results presented in Fig. 6 show, the efficiency of extracting HM ions from solution increases with a raise in sorbent mass. It was found that the optimal sorbent mass required for the most complete extraction of metal ions was 1 g per 100 cm^3 of a metal salt solution for both cadmium and lead.

Conclusion

It was found that the degree of extraction of Pb^{2+} ions by ChC reaches (97.0 ± 7.2)%, while for Cd^{2+} ions it shows a lower efficiency – (86.0 ± 6.4)%. This is probably due to the fact that lead ions have a larger ionic radius (0.112 nm) compared to cadmium ions (0.099 nm). Based on the analysis of the physicochemical characteristics of ChC, it was found that the imposition of polyvinylpyrrolidone significantly increases the sorption ability towards Cd^{2+} ions. The optimal mass for the sorption of lead and cadmium ions – 1 g per 100 cm^3 of solution was also determined during the study at T = 298 K and pH = 6. The use of chamotte clay as the basis for the development of sorbents helps reducing the cost of cleaning water bodies, and also allows solving the problem of wastes disposal.

References

1 Fu F., Wang Q. (2011) Removal of heavy metal ions from wastewaters: A review. *J Env Man*., Vol. 92, pp. 407-418. doi:10.1016/j.jenvman.2010.11.011

2 Khan F., Khan M., Samad A., Noor Y., Rashid M., Jan B. (2015) In-situ stabilization of heavy metals in agriculture soils irrigated with untreated wastewater. *J. Geochemical Explor*., Vol. 159, pp. 1-7. doi:10.1016/j.gexplo.2015.07.002

3 Klimenko T.V. (2013) Ochistka stochnyih vod ot ionov tyazhelyih metallov (Wastewater treatment from heavy metal ions). *Sovremennyie nauchnyie issledovaniya i innovatsii (Modern scientific research and innovation),* No.11 [Electronic resource]. URL: http://web.snauka.ru/issues/2013/11/28484 (accessed: 03.03.2016). (in Russian)

4 Boskabady M., Marefati N., Farkhondeh T., Shakeri F., Farshbaf A., Boskabady M.H. (2018) The effect of environmental lead exposure on human health and the contribution of inflammatory mechanisms, a review. *Env. Int.,* Vol.120, pp, 404-420. doi: 10.1016/j.envint.2018.08.013

5 Vodyanitsky Yu.N. (2012) Standards for the contents of heavy metals and metalloids in soils. *Eurasian Siol Science.* Vol.45, Is. 3, pp. 321-328.

6 Jan A. T., Azam, M.,Siddiqui K., Ali A., Choi I., Mohd Q, Haq R. (2015) Heavy Metals and Human Health: Mechanistic Insight into Toxicity and Counter Defense System of Antioxidants. *Int J Mol Sci.* , Vol.16, Is.12, pp. 29592–29630.doi: 10.3390/ijms161226183

7 Kostin A.V., Mostalygina L.V., Bukhtoyarov O.I. (2012) Izuchenie mehanizma sorbtsii ionov medi i svintsa na bentonitovoy gline (Studying the mechanism of sorption of copper and lead ions on bentonite clay). *Sorbtsionnyie i hromatograficheskie protsessyi (Sorption and chromatographic processes)*, Vol.12, Is. 6, pp.949-957. (in Russian)

8 Balykbaeva A. S. (2017) Zagryaznenie vodnyih resursov Kazahstana i metodyi ochistki vodyi (Water pollution of Kazakhstan and methods of water treatment). Oku-Zaman.

9 Shishakina O.A., Palamarchuk A.A. (2019) Obzor napravleniy utilizatsii tehnogennyih othodov v proizvodstve stroitelnyih materialov (Overview of directions for the utilization of industrial wastes in the production of building materials). *Mezhdunarodnyiy zhurnal prikladnyih i fundamentalnyih issledovaniy (International Journal of Applied and Basic Research).* No. 4, pp.-198-203. (in Russian)

10 Omotoyinbo, Ajibade J., Leke O. (2008). Working Properties of Some Selected Refractory Clay Deposits in South Western Nigeria. *J Min and Mat Char and Eng*., Vol.7, Is. 3. doi: 10.4236/jmmce.2008.73018.

11 Sharshenbekkyzy A., Kochkorova Z.B., Murzubraimov B.M. (2017) Issledovanie vozmozhnosti polucheniya prirodnoy kaolinovoy glinyi Choko-Bulakskogo mestorozhdeniya (Study of the possibility of obtaining natural kaolin clay of the Choko-Bulakskoye deposit). *Izvestiya Vuzov Kyirgyizstana (University news of Kyrgyzstan)*. Vol.7, pp.74-77. (in Russian)

12 Masimov E.A., Shirinov N.Z., Bagirov T.O. (2016) The effect of the molecular weight of polyvinylpyrrolidone on the phase diagram of a water-two-phase system of dextran-polyvinylpyrroidone. *Int J App and B Res.* No. 12 (part 1), pp. 95-98.

13 Evtyukhov, S.A., Berezgon V.G. (2003) Study of the sorption properties of natural aluminosilicates (clay, loam, sandy loam, zeolite). *Rus J Appl Chem*., Vol. 76, Is. 9. – S. 1454-1457.

14 Nikiforova, T.E., Kozlov, V.A., Gagina, A.N. (2010) Sorption of copper ions by cellulose sorbents modified with a dichlorotriazine compound and polyvinylpyrrolidone. *Russ J Appl Chem.,* Vol. 83, Is.10, pp. 1774-1780. doi: 10.1134/S1070427210100083

15 Santos, Flavia D., Leyvison Rafael V. Da Conceição, Annie Ceron, and Heizir F. De Castro (2017) Chamotte clay as potential low cost adsorbent to be used in the palm kernel biodiesel purification. *Applied Clay Science*, Vol.149 (9), pp. 41-50. doi:10.1016/j.clay.2017.09.009

16 Vladimirov V.S., Galagan A.P., Ilyukhin M.A., Karpukhin I.A., Moisis S.E., Moisis E.S. (2002) Novyie ogneupornyie i teploizolyatsionnyie materialyi i tehnologii ih proizvodstva(New refractory and heat-insulating materials and technologies for their production). *Nauchno-tehnicheskiy i proizvodstvennyiy zhurnal "Novyie ogneuporyi" (Scientific -technical and production journal "New refractories").* No. 1, pp. 87-88. (in Russian)

17 Vartepyan R. Sh., Khozina E.V., Chalykh A.E. et.al. (2003) Issledovanie molkulyarnoy podvizhnosti smesi polietielenglikol/polivinilpirrolidon metodami impulsnogo YaMR (Study of the molecular mobility of a mixture of polyethylene glycol / polyvinylpyrrolidone by pulsed NMR). *Coll J.,* Vol. 65, Is. 6, pp. 748-755. (in Russian)

18 Goldstein, J., Newbury Dale, Michael Joseph, Ritchie Nicholas, Scott John, Joy David (2018) Scanning Electron Microscopy and X-Ray Microanalysis. doi:10.1007/978-1-4939-6676-9.

19 M.V. Volkenstein, L. A. Gribov, M. A. Elyashevich, B. I. Stepanov (1972) Molecular Vibrations. Moscow, Nauka.

20 G.S. Koptev, Yu.A. Pentin, (1977) Calculation of molecular vibrations. Ed. Moscow State University.

21 Prech E., Bulmann F., Affolter K. (2006) Opredelenie stroeniya organicheskih veschestv. (Determination of the structure of organic substances). Moscow, Mir. (in Russian)

22 Nakamoto K. (1991) Infrakrasnyie spektryi neorganicheskih i koordinatsionnyih soedineniy (Infrared spectra of inorganic and coordination sequences). Moscow, Mir. (in Russian)

23 Telkhozhayeva Madina, Seilkhanova Gulziya, Rakhym, A., Imangaliyeva Ainur, Akbayeva Dina. (2018). Sorption of lead and cadmium ions from aqueous solutions using modified zeolite. *Chem Bull KazNU*, Is.1, pp. 16-22. doi:10.15328/cb980.