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**THE INFLUENCE OF SORBENT NORM AND TIME  
ON THE PROCESS OF PURIFICATION OF PHOSPHORIC ACID  
FROM CATION OF LEAD (II) BY ACIDOMODIFICATED ZEOLITE  
FROM SHANKANAY DEPOSIT**

**Abstract.** The effect of the norm of the acid-modified zeolite of the Shankanay deposit and the time on its sorption capacity with respect to the Pb (II) cations in 26 and 83% H<sub>3</sub>PO<sub>4</sub> was studied. It was found that in 26 and 83% phosphoric acid, the modified zeolite exhibits a high sorption ability with respect to the Pb<sup>2+</sup> cations, with the optimal ratio "acid-modified zeolite: H<sub>3</sub>PO<sub>4</sub>" equal to 10: 100. 26% and 83% of H<sub>3</sub>PO<sub>4</sub> acid, respectively, are cleared at 98.94 and 99.60%. It has been established, that the curves of the residual content of Pb<sup>2+</sup> cations after purification with 83% H<sub>3</sub>PO<sub>4</sub> in time for all investigated temperatures and C<sub>Pb</sub> are rectilinear and decrease with increasing duration of the process. The highest degree of sorption of Pb (II) by sorbent is achieved in 60 minutes of the process.

**Key words:** heavy metals, lead cations, acid-modified zeolite, sorption, phosphoric acid.

**Introduction.** At present, pollution of the environment with heavy metals is one of the problems of ecology and public health. The flow of heavy metals (HM) into the biosphere occurs for various reasons. The natural source of their entry into the aquatic environment is the dissolution and leaching of rocks. However, in recent years, the main contribution has been made by liquid discharges of ore-dressing factories, chemical and metallurgical enterprises, galvanic industries, as well as the production of mineral paints, fertilizers, man-made fibers, the booming oil-producing and oil-refining industry. Another cause of pollution of the HM environment is the involvement of low-grade and off-balance raw materials, in particular low quality phosphorites and phosphorus waste (phosphorus slags and sludges). The phosphoric acid obtained from such raw materials is contaminated with dissolved impurities in the form of various compounds and salts that have passed from the composition of phosphate raw materials, including HM salts [1]. Heavy metals pass into phosphorus fertilizers and then migrate to the soil, ponds, atmosphere. In phosphoric acid, the content of HM of the hydrogen sulfide group, namely Pb, is strictly regulated by the corresponding GOST: mass for Pb in Thermic phosphoric acid (TPhA) of grade A is no more than 0.0005%, grade B: grade 1 is 0.002%, grade 2 is 0.005% [2]. These requirements are due to the fact that, soluble lead salts are not biodegradable and accumulate in living organisms [3], causing various diseases and disorders such as anemia with repro-

ductive, genotoxic, carcinogenic, and neurological consequences, especially for children [4].

The purity of the final product and the absence of certain impurities in it are some of the basic requirements for phosphoric acid, so there is a need for its purification. The problem of cleaning various media, including phosphoric acid, from HM and recycling spent sorbents can be solved by developing new technologies, obtaining promising sorption materials that can effectively extract them. Very promising new sorption materials are sorbents that combine ion-exchange, sorption and filtering properties. At the same time, they must possess a stable chemical nature, the presence of a large number of surface functional groups, good physicochemical characteristics, the possibility of regeneration without a significant loss of sorption capacity and utilization of the spent sorbent, and also a relatively low cost [5]. To date, such materials can include natural zeolites, kaolinites, activated carbons, bentonites and many others. First, zeolites, which are widely used as ion exchangers, deserve attention. This is facilitated by factors such as the granular structure of the zeolite, which makes it possible to carry out the ion exchange process under dynamic conditions, as well as a significant increase in the exchange capacity of the zeolite as a result of various pretreatment methods. Therefore, the work uses an acid-modified zeolite with a sufficiently high sorption activity to cations, in which the statistical exchange capacity (SEC) cation exchanger (0.984 meq/g) is 3.83 times higher than that of the SEC anion exchanger (0.2568 meq/g) [6].

### **Experiment**

The purpose of this work was to study the influence of the sorbent rate and time on the sorption capacity of the zeolite of the Shankanay deposit, modified with hydrochloric acid (0.1n), with respect to  $Pb^{2+}$  ions in phosphoric acid. To eliminate the effect of impurities, a study of the sorption of lead (II) cations with a modified zeolite was carried out on the model system " $Pb^{2+}$ - $H_3PO_4$ -acid-modified zeolite" The specified concentration of lead (II) cations was created by introducing into the phosphoric acid a calculated amount of lead salt  $Pb(CH_3COO)_2 \cdot 3H_2O$ .

The sorption capacity of the sorbent was studied under agitation conditions. A sample of  $H_3PO_4$  was placed in a thermostated, heated to a specific temperature and a lead salt was injected. Then, a modified zeolite was added to the lead-containing phosphoric acid solution at a predetermined ratio "the modified zeolite (Solid-S):  $H_3PO_4$  (Liquid-L)" and mixed for a predetermined time. Sampling of the phosphoric acid to be purified from the reactor was carried out regularly at regular intervals. An aliquot was weighed on an analytical scale to the fourth digit, then the mixture was quantitatively transferred to a 250 ml volumetric flask and filtered through a paper filter. The resulting filtrate was analyzed for the content of lead ions, the determination of which was carried out on an absorption spectrometer (AAC).

The degree of sorption ( $R, \%$ ) was found from the difference between the initial and residual concentrations of metals in solution by the formula:

$$R = \frac{C_0 - C_p}{C_0} \cdot 100\%,$$

where  $C_0$  is the initial concentration of metal ions in solution, mg/l;  $C_p$  is the concentration of metal ions in the solution after purification by sorbent, mg/l.

The effect of the sorbent's rate on its sorption capacity was investigated in dilute (26%) and concentrated (83%) phosphoric acids with a content of 48.4 mg/l  $Pb^{2+}$ . The sorbent consumption was from 5 to 30 g per 100 g of purified phosphoric acid.

The degree of purification of various media depends significantly on the duration of contact of the sorbent with the acid to be purified. The effect of the process time on the sorption of  $Pb^{2+}$  cations by an acid-modified zeolite was studied in 83% of  $H_3PO_4$  with a concentration of cations of  $Pb^{2+}$  equal to (10-100) mg/l in the range (20-70)°C at a constant ratio of S:L = 10:100.

## Results and discussion

The obtained results on the effect of the rate of acid-modified zeolite on its sorption capacity in dilute and strongly concentrated phosphoric acid are presented in the table. From the data obtained, it follows that in dilute  $H_3PO_4$  (26%) with an increase in the rate of acid-modified zeolite from 5 g to 30 g per 100 g of the purified solution, the purification rate increases by 1.28%. When purification of concentrated  $H_3PO_4$  (83%) with an increase in sorbent consumption from 5 g to 10 g per 100 g of purified acid purification rate  $R$  is increased by 0.15%, with a further increase in the sorbent load, a tendency to a slight decrease in the sorbent appears. Perhaps the acid-modified zeolite undergoes greater structural changes in concentrated  $H_3PO_4$  than in dilute  $H_3PO_4$  [7], which affects its sorption ability. This explains why, at a low sorbent rate (S:L = 5: 100), the degree of sorption in concentrated  $H_3PO_4$  is 1.43% higher than that of dilute phosphoric acid.

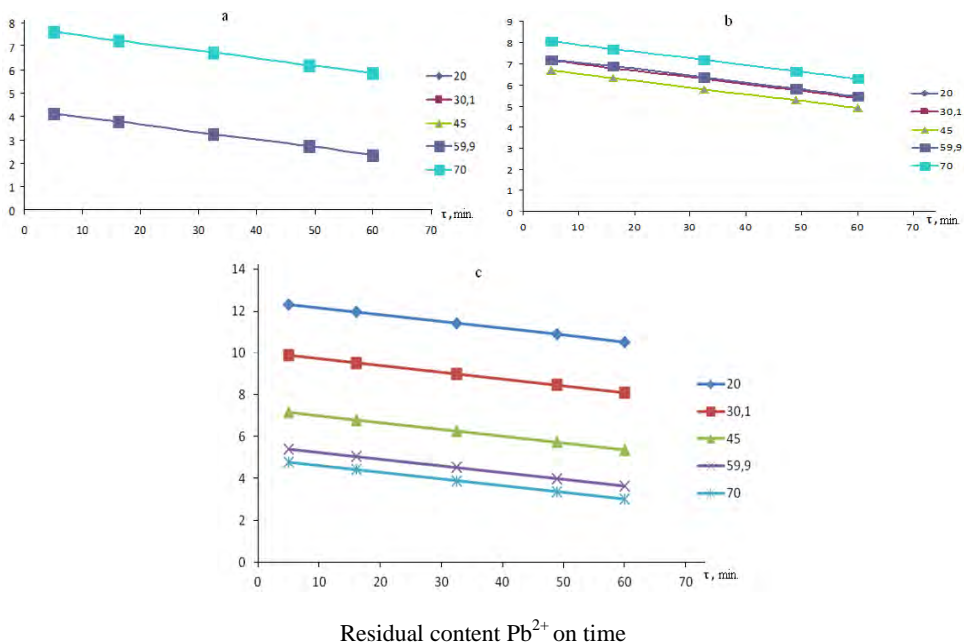
Based on the results obtained, it follows that the acid-modified zeolite in the acids under study shows a high sorption ability with respect to the  $Pb^{2+}$  cations.

The effect of the modified zeolite norm on the sorption of lead (II) ions from phosphoric acids

$C_{H_3PO_4}, \%$	26		83	
S:L	Residual content $Pb^{2+}$ , mg/l	R, %	Residual content $Pb^{2+}$ , mg/l	R, %
5:100	0,99	98,02	0,27	99,45
10:100	0,53	98,94	0,19	99,60
20:100	0,37	99,25	0,23	99,53
30:100	0,35	99,30	0,23	99,52

The degree of sorption reaches 98.0-99.6%. Regardless of the concentration of phosphoric acid for all temperatures, the optimal ratio of "acid-modified zeolite: H<sub>3</sub>PO<sub>4</sub>" is 10:100. Under these conditions, the concentration of phosphoric acid does not have a significant effect on the degree of purification. Thus, 26% and 83% phosphoric acid with acid-modified zeolite is purified at 98.94 and 99.60%.

Analysis of the obtained data on the sorption ability of the acid-modified shankanese zeolite revealed that in the investigated temperature range and concentrations of lead (II) cations, the sorption curves have the same type of character (figure).



a – 10 mg/l Pb<sup>2+</sup>; b – 55 mg/l of Pb<sup>2+</sup>; c – 81.8 mg/l Pb<sup>2+</sup>

The influence of duration time on the residual content of Pb (II) cations in the system "Pb<sup>2+</sup> – H<sub>3</sub>PO<sub>4</sub> – acid-modified zeolite"

The curves of the residual content of Pb<sup>2+</sup> ions are of a rectilinear nature and decrease with increasing duration of the process. That is, as the time increases, the degree of lead sorption increases. For example, in an acidic medium with a concentration of Pb<sup>2+</sup> ions equal to 55 mg/l at 20°C, 85.45% is sorbed for 5 minutes, 86.0% for 85 minutes, 87.0% for 30 minutes, 60 minutes - 88.7%.

Under the investigated conditions, an increase the duration time of the process has a positive effect on the purification of phosphoric acid. The highest degree of sorption of Pb (II) cations with an acid-modified zeolite is achieved in 60 minutes of the process.

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## Резюме

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### ШАҢҚАНАЙ КЕН ОРНЫНЫҢ ҚЫШҚЫЛМЕН МОДИФИКАЦИЯЛАНҒАН ЦЕОЛИТІ АРҚЫЛЫ ФОСФОР ҚЫШҚЫЛЫН ҚОРҒАСЫН (II) КАТИОНДАРЫНАН ТАЗАРТУ ПРОЦЕСІНЕ СОРБЕНТ МӨЛШЕРІ МЕН УАҚЫТТЫҢ ӘСЕРІ

Шаңқанай кен орнының қышқылмен модификацияланған цеолиті мөлшерінің және уақыттың 26 және 83 %  $H_3PO_4$  қышқылындағы Pb (II) катиондарына қатысты сорбциялық қабілетіне әсері зерттелді. 26 және 83 %-ды фосфор қышқылында модификацияланған цеолит  $Pb^{2+}$  катиондарына қатысты жоғары сорбциялық қасиет көрсететіні анықталды. «Қышқылмен модификацияланған цеолит:  $H_3PO_4$ » қатынасы оңтайлы, яғни 10:100 тең болғанда 26 және 83 %  $H_3PO_4$  қышқылы сәйкесінше 98,94 және 99,60 %-ға тазарады.

83 %  $H_3PO_4$  қышқылы тазарғаннан кейін  $Pb^{2+}$  катиондарының қалған мөлшерін көрсететін уақытқа тәуелді қысық зерттеліп отырған барлық температура және  $C_{Pb}$  үшін тік сызықпен сипатталады және процесс уақытын арттырған сайын төмендейді. Сорбент арқылы Pb (II) катионы ең жоғары сорбциялану дәрежесіне 60 минутта жетеді.

**Түйін сөздер:** ауыр металдар, қорғасын катиондары, қышқылмодифицирленген цеолит, сорбция, фосфор қышқылы.

Резюме

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ВЛИЯНИЕ НОРМЫ СОРБЕНТА И ВРЕМЕНИ НА ПРОЦЕСС  
ОЧИСТКИ ФОСФОРНОЙ КИСЛОТЫ ОТ КАТИОНОВ СВИНЦА (II)  
КИСЛОТОМОДИФИЦИРОВАННЫМ ЦЕОЛИТОМ  
МЕСТОРОЖДЕНИЯ ШАНКАНАЙ

Исследовано влияние нормы кислотомодифицированного цеолита месторождения Шанканай и времени на его сорбционную способность по отношению к катионам Pb (II) в 26 и 83 %  $H_3PO_4$ . Выявлено, что в 26 и 83 % фосфорной кислоте модифицированный цеолит проявляет высокую сорбционную способность по отношению к катионам  $Pb^{2+}$ . При оптимальном соотношении «кислотомодифицированный цеолит:  $H_3PO_4$ » равном 10:100. 26 и 83 %  $H_3PO_4$  кислота очищается соответственно на 98,94 и 99,60 %. Установлено, что кривые остаточного содержания катионов  $Pb^{2+}$  после очистки 83 %  $H_3PO_4$  во времени для всех исследуемых температур и  $C_{Pb}$  носят прямолинейный характер и с увеличением продолжительности процесса снижаются. Наибольшая степень сорбции Pb (II) сорбентом достигается за 60 мин процесса.

**Ключевые слова:** тяжелые металлы, катионы свинца, кислотомодифицированный цеолит, сорбция, фосфорная кислота.