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MECHANISM OF PHOSPHATES SORPTION BY ZEOLITES DEPENDING ON DEGREE OF THEIR SUBSTITUTION FOR POTASSIUM IONS

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Abstract. The mechanism of phosphates sorption process on clinoptilolite was determined. The significant increase in zeolite sorption capacity was observed while interaction of zeolite and wastewaters with acid reaction. New active centers of zeolite are formed due to disalumination of its surface.

Keywords: zeolite, adsorption, static capacity, phosphates.

1. Introduction

The amount of water resources is the background of social and environmental well-being and economic development. Currently, water management and hydroecological problems gained national importance and have become one of the main factors of national security. Therefore, despite the worsening of environmental problems and the limited funds that can be spent by companies to implement protection measures, it is important to evaluate the effectiveness of technology and the choice of optimal methods of wastewater treatment.

Municipal wastes, manufacturing water of food industry, fertilizers and detergents production, chemical and food industries are the major sources of the hydrosphere pollution [1].

One of the methods to prevent environment pollution by wastewater containing phosphates is the development and implementation of effective, low-budget water treatment technologies, especially phosphates removal. They may be removed from wastewater by natural sorbents [1, 2].

There sorption processes on solid sorbents are: physical adsorption, chemical adsorption and ion exchange. Phosphates are absorbed by all three mechanisms. Thus it is properly to use the term “sorption”.

The effectiveness of inorganic ions sorption depends on many factors, including the external and internal mass-transfer. It is known that natural zeolites have ability to absorb ions not only *via* physical adsorption, but also *via* ion exchange and present themselves as ion exchangers. The sorption mechanisms, namely the isotherms of absorption of various substances on natural zeolite from Sokyrnytsa deposit, which mainly consists of clinoptilolite, are widely described in the literature [2].

The original unit of zeolite framework is tetrahedron, the center of which is occupied by aluminum or silicon atoms, and the vertexes – by four oxygen atoms. Thus, a set of tetrahedrons forms a continuous frame [3]. Zeolites are aluminum silicates with the skeleton structure containing hollows filled with large ions and water molecules. The water content in clinoptilolite varies from 17 to 24 molecules in the elementary cell. The peculiarity of its structure causes considerable mobility of ions and water and provides zeolite participation in the reactions of ion exchange and dehydration. Every atom of oxygen located at the tetrahedron vertex is common for two tetrahedra. Substituting Si^{4+} for Al^{3+} in tetrahedron the negative charge occurs in the frame, which is compensated by the charges of one-valent or bivalent cations, placed together with water molecules in the channel structure. Water molecules may be easily substituted, so the rate of water molecules substitution is inversely proportional, and the ability to ion exchange is directly proportional to the radius of the exchangeable ion. However, H^+ ion has an advantage over other cations [2]. Zeolites participate in the ion exchange reaction under normal conditions [1]. Mordenite (a type of zeolite) may be decationized and disaluminated due to acids. Acid treatment insignificantly affects the water sorption but

considerably increases sorption capacity of sorbents for other molecules [1]. According to the literature data zeolites are capable to exchange water for alcohol, ammonia and other compounds [3]. Currently only the zeolite framework topology is well studied. But in many cases the sorption mechanism, including sorption of phosphates, is not determined in a proper way [3].

Data on phosphate sorption from model solutions of mono- two- and three-component systems and waste water containing ammonium nitrogen, phosphate and protein at low concentrations have been published. Equilibrium values of zeolite sorption capacity have been determined and corresponding sorption isotherms at 293 K have been plotted. The sorption capacity of clinoptilolite relative to one-component systems is higher and decreases during the simultaneous sorption of two and three components from the solution. However, the total sorption capacity for two- and three-component systems increases. The sorption isotherms equation for one-, two- and three-component systems are presented [5, 6]. Previous studies indicate the effect of pH on the sorption capacity of zeolite due to disalumination of zeolite framework under the influence of H^+ [7-9].

The aim of this work is to study the mechanism of phosphate sorption process on natural sorbent – clinoptilolite – depending on the degree of substitution by potassium ions.

2. Experimental

Researches of phosphate sorption on natural zeolite of clinoptilolite type were conducted under static conditions taking one- bi- and trisubstituted potassium phosphates and phosphoric acid as an example.

Zeolite from Sokyrnytsya deposit was used. Its composition is presented in Table 1.

Zeolite has the following characteristics: porosity 44 %; density 2.37 kg/m³; surface area 50–65 m²/g; cation exchange capacity 1.5 mg-eq/g; resistance to alkali pH 7–13 [6, 10]. The procedure of determining the zeolite sorption capacity allows not only to determine a static activity, but to predict a mechanism of this process as well. To determine the zeolite sorption capacity relative to phosphate ions the solutions of H₃PO₄, KH₂PO₄, K₂HPO₄ and K₃PO₄ with different initial concentrations ($C = 25–750$ mg/dm³) were prepared in distilled water. Then the solutions (200 cm³) were placed in the glass flasks and zeolite (~1 g) was added. The samples were kept at

$T = 293 \pm 0.1$ K, for 48 h under periodical stirring to reach an equilibrium. The concentration of phosphate ions in the samples was determined by hydrolysis of phosphate salts to phosphoric acid, obtaining a colored complex of the acid with ammonium molybdate-vanadate and determining the optical density of the colored solution using photoelectrocolorimeter [11, 12].

To determine pH of the investigated solutions the potentiometric method was used.

3. Results and Discussion

The values of zeolite static activity a^* depending on the phosphate concentration in the solution are presented in Fig. 1 recalculated for phosphorus(V) oxide. The results show that the sorption process considerably depends on the degree of orthophosphates substitution for alkali metals ions. Phosphates are the best absorbed in acidic medium. Moreover, at the initial concentration of 2.5–150 mg/l the sorption isotherms of phosphoric acid (H₃PO₄) and potassium dihydrophosphate (KH₂PO₄) are almost identical, but with the increasing concentration of the initial solution, KH₂PO₄ sorption is weaker. At the concentrations of above 100 mg/l the zeolite activity relative to KH₂PO₄ remains constant. At the mentioned concentrations there is almost the same trend only K₂HPO₄ and K₃PO₄ sorption capacity is much lower. For H₃PO₄ concentrations above 150 mg P₂O₅/dm³ we observe a sharp increase in zeolite sorption capacity due to the fact that the acid highly concentrated solutions are capable to disaluminates zeolite, *i.e.* to destruct the zeolite structure. The increase in zeolite sorption capacity owing to the one-side open pores and increased micropore diameter is a positive moment. These processes are well-studied and confirmed by many authors [1, 2, 6]. Na⁺, K⁺, Ca²⁺, Mg²⁺, and other exchangeable cations (counterions) are present in the zeolite structure. Obviously, during the ion exchange absorption the cations from phosphate solutions are absorbed and exchangeable cations enter the solution.

We associate the sharp increase in zeolite exchangeable activity with the presence of exchangeable cations in Na⁺, Ca²⁺, Mg²⁺ zeolites and proceeding of ion exchange reactions. Therefore, we analyzed the concentration of exchangeable ions, namely Na⁺, Ca²⁺, Mg²⁺ in solution to verify the ionic character of the process. The amount of P₂O₅ absorbed by zeolite depends on the degree of phosphate dissociation (Fig. 1), which is characterized by a dissociation constant K .

Table 1

The chemical composition of the studied zeolite

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	P ₂ O ₅	K ₂ O+Na ₂ O	F	As	Pb	Cu
Amount, %	71.5	13.1	0.9	0.5	3.44	0.68	0.014	3.03	0.025	0.0015	0.002	0.02

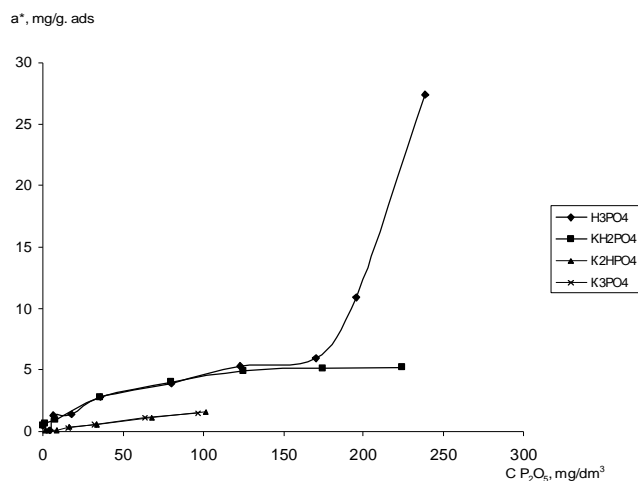
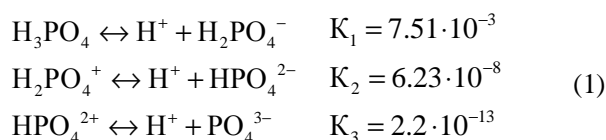


Fig. 1. Isotherms of phosphate sorption on clinoptilolite of Sokyrnytsya deposit

While dissolving phosphoric acid its dissociation occurs according to the following scheme by several stages:



The dissociation according to the first stage is the most possible. The pH value of phosphoric acid varies within 1.57–2.15, potassium dihydrogen – 4.04, potassium hydrogen phosphate – 9.75, potassium phosphate – 12.6. Thus, during the dissociation the solutions of H_3PO_4 and KH_2PO_4 are acid ones; K_2HPO_4 and K_3PO_4 solutions – alkaline ones.

Fig. 2 shows the volume of released Na^+ cation during phosphates sorption depending on concentration and degree of substitution of phosphate. The significant increase in the number of exchangeable Na^+ is observed. Calcium and magnesium ions are not found in the samples, because they form insoluble compounds with phosphate ion.

K^+ and H^+ ions are substituted by Na^+ via ion exchange. As shown in Fig. 2, the main quantity of sodium is exchanged in the phosphoric acid medium due to the reaction of acid with the zeolite framework. In the case of potassium phosphate sorption the potassium ion is substituted by exchangeable cations of zeolite. Since calcium and magnesium phosphates are insoluble, only sodium ions can be found in the solution. In KH_2PO_4 solution the exchangeable cations are K^+ and H^+ ions but in K_2HPO_4 and K_3PO_4 solutions – only K^+ ion. Therefore,

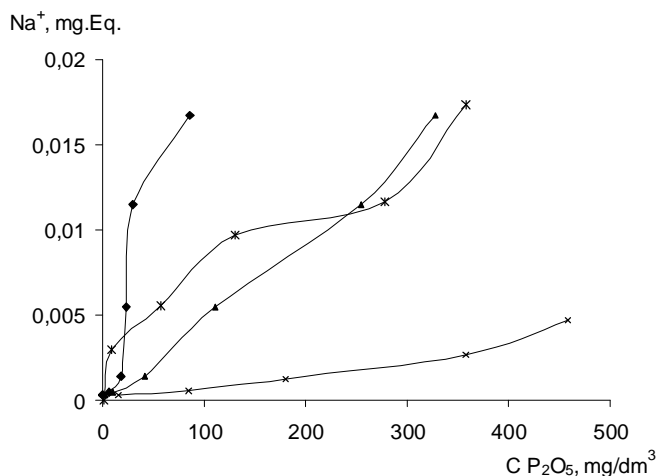
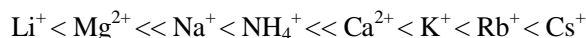


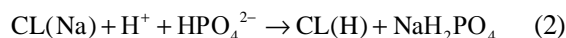
Fig. 2. The amount of released sodium ion m_{Na^+} from the clinoptilolite crystal structure depending on the concentration and degree of substitution of phosphate: \blacklozenge – H_3PO_4 ; \blacktriangle – KH_2PO_4 ; \circ – K_3PO_4 ; \times – K_2HPO_4

the amount of sodium ions in KH_2PO_4 and K_3PO_4 solutions is almost equal, and in K_2HPO_4 solution we observe weaker ion exchange compared with K_3PO_4 owing to the smaller amount of potassium ion and much higher pH value compared with H_3PO_4 and KH_2PO_4 solutions.

According to a series of ions selectivity [1] the potassium is very well absorbed by zeolite as a result of ion exchange process and exchangeable cations, including sodium ion, are released into the solution.

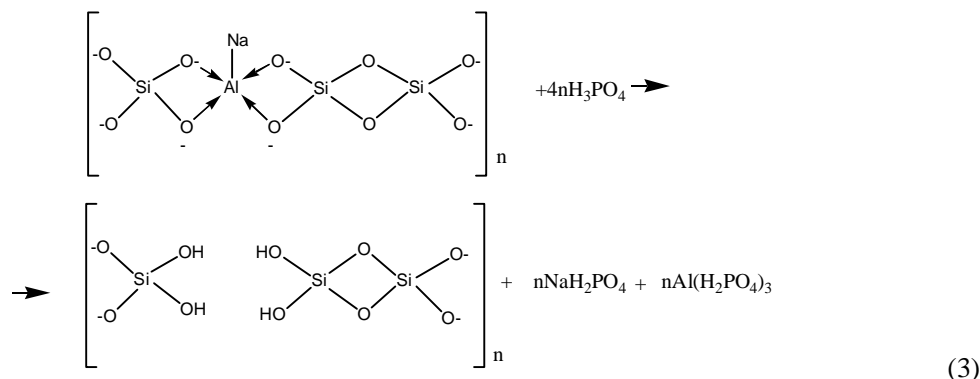


However, zeolites are more selective to the hydrogen ion, which can to some extent substitutes other exchangeable cations. Taking into account that the ionization constants of acids differ in value significantly, the aluminosilicate framework protonation will proceed mainly on the first and second stages of phosphoric acid dissociation (Eq. (1)). At the same time the phosphoric acid solution is neutralized and forms soluble sodium dihydrogen according to Eq. (2):



where CL – zeolite framework.

The atoms of silicon and aluminum do not undergo ion exchange under normal conditions, but under the influence of strong acids the process of zeolite dealumination occurs (Eq. (3)). Moreover, the amount of released aluminum should be equivalent to pH. Proton of the acid reacts with a fragment of the zeolite crystal lattice $[\text{Si}-\text{O}-\text{Al}]$, which is a Brønsted acid center [4], as follows:



Under mentioned conditions, at low pH, there is a chemical interaction of proton with zeolite framework, accompanied by the release of sodium into the solution, the destruction of the zeolite surface layer and the release of zeolite new sorption centers, which are located in zeolite volume. This is demonstrated by the sorption of phosphoric acid (Fig. 1). Probably AlPO_4 , the structure of which is similar to SiO_2 , is formed in the lattice. NaH_2PO_4 , Na_2HPO_4 , $\text{Al}(\text{H}_2\text{PO}_4)_3$ and $\text{Al}_2(\text{HPO}_4)_3$ are formed in zeolite pores at high concentration of the acid [7, 13, 14]. While comparing Figs. 1 and 2 we observe different amounts of absorbed phosphates and released sodium during sorption of phosphoric acid and monosubstituted potassium phosphate. It means that in case of H^+ and K^+ substitution for Ca^{+2} ions the calcium ion of zeolite reacts with dihydrophosphate ion of the solution and thus the insoluble calcium phosphate is formed and remains in the zeolite volume. In case of bi- and trisubstituted potassium phosphate in alkaline medium the potassium is substituted for sodium and calcium. In addition, calcium reacts with hydrophosphate and phosphate ions forming stoichiometric and non-stoichiometric calcium hydroxyapatite.

Experimental study of pH changes during the phosphate sorption by clinoptilolite. The lower pH, the better dealumination of zeolite. With the increase of concentration the pH value of phosphoric acid sharply decreases during sorption in contrast to KH_2PO_4 solution, the initial pH of which is higher than that of H_3PO_4 .

At low H_3PO_4 concentration pH of medium is 3.9 before sorption and 5.8 – after sorption (Fig. 3). The initial value of pH of KH_2PO_4 solution is $1.04 \cdot 10^{-3} \text{ kg/m}^3$. During sorption this value is 4.8 and after the sorption – 6.2 (Fig. 4). Obviously, the increase of pH is caused by substitution of Na^+ in the zeolite framework for H^+ and with the increase in concentrations calcium dihydrophosphate is absorbed less than orthophosphoric acid.

The pH values of di- and trisubstituted phosphates vary very similarly (Figs. 5 and 6). At low concentrations the reaction medium is a weak-acid one ($\text{pH} \approx 6.5$). With the increase in concentration the equilibrium is achieved

and sodium is substituted for potassium and calcium [8, 9]. The decrease in pH value of di- and trisubstituted phosphates is explained by alkaline nature of these salts. As it was mentioned above, the potassium ions are very well absorbed by zeolite and calcium ions are released, forming low-dissociated $\text{Ca}(\text{OH})_2$. To equalize the charge of phosphate ions the equilibrium of water dissociation equation shifts and causes the decrease in pH value. When zeolite absorbs a certain amount of phosphates (with the formation of insoluble phosphates of calcium, magnesium, etc.) the amount of PO_4^{3-} , HPO_4^{2-} ions decreases due to the shift of dissociation reaction equilibrium to the left (to form H_2PO_4^-), that also decreases pH.

Zeolite exhibits amphoteric properties relative to phosphates. Moreover, during the sorption of phosphoric acid we observe a sharp increase of zeolite absorption capacity at $\text{pH} > 2.5$. As it was mentioned above, this indicates release of aluminum from the lattice, destruction of zeolite upper layer and readiness of the sorbent bottom layer to react. In this case, we would expect aluminum presence in the solution after sorption of phosphates. But it is possible only under the formation of colloidal particles of aluminum phosphate. The concentration of aluminum released from zeolite during the phosphate absorption was determined by the standard method. Aluminum was not found in the test solutions.

To determine the amounts of phosphates absorbed according to physical adsorption mechanism, we investigated P_2O_5 desorption. It was found that the amount of desorbed phosphate ion was less than the sensitivity threshold of the method and is close to 0. In rinse water of zeolite only trace amounts of phosphates were determined.

Moreover, the absence of phosphate in the test solution after desorption indicates the phosphate binding by zeolite *via* the mechanism of chemical sorption with insoluble compounds formation. This experiment confirms the conclusions concerning the formation of aluminum phosphate in the zeolite pores [3, 8].

So, natural zeolites are quite effective sorbents relative to phosphates and may be used for the treatment of industrial wastewater with high acidity.

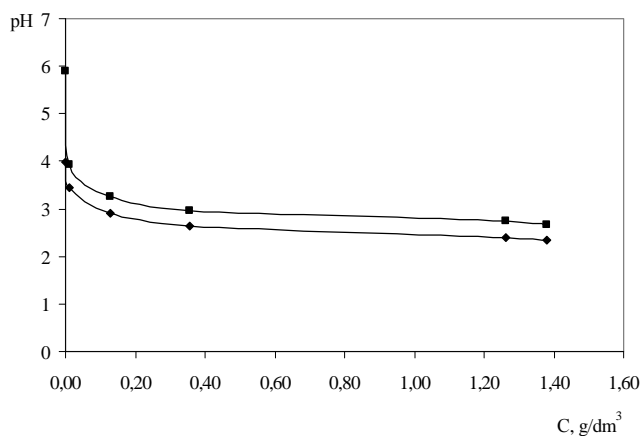


Fig. 3. Change of pH during H_3PO_4 sorption: ◆ - pH before sorption; ■ - pH after sorption

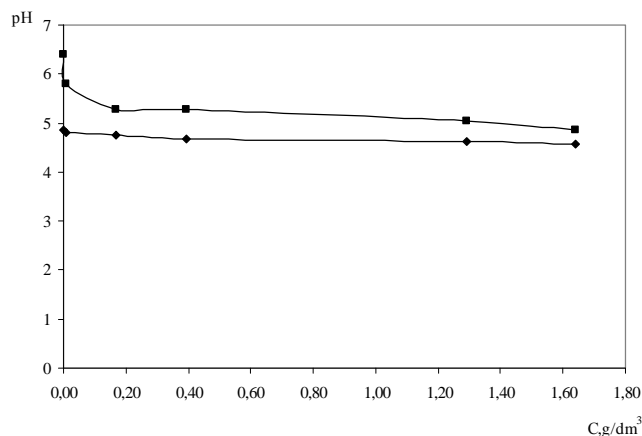


Fig. 4. Change of pH during KH_2PO_4 sorption: ◆ - pH before sorption; ■ - pH after sorption

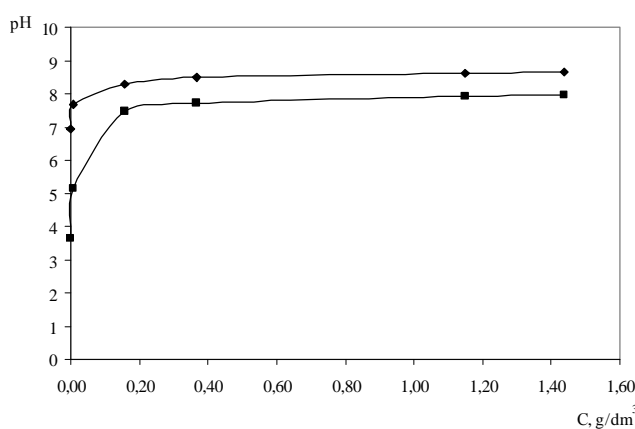


Fig. 5. Change of pH during K_2HPO_4 adsorption: ◆ - pH before sorption; ■ - pH after sorption

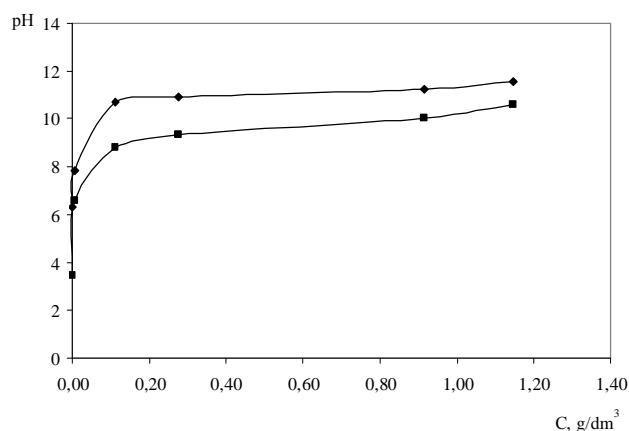


Fig. 6. Change of pH during K_3PO_4 adsorption: ◆ - pH before sorption; ■ - pH after sorption

4. Conclusions

Sorption of phosphates by natural zeolite, the main component of which is clinoptilolite, proceeds *via* different mechanisms: ion exchange, physical sorption, chemisorption, depending on the degree of hydrogen ion substitution for potassium.

Phosphoric acid is absorbed *via* ion exchange mechanism with the release of sodium counterion into the liquid phase, that is confirmed by the chemical analysis.

For acidic phosphate compounds (H_3PO_4 and KH_2PO_4) the pH value increases due to the decrease in the concentration of hydrogen counterion. During sorption di- and trisubstituted phosphates reduce pH due to the chemical absorption of a certain amount of PO_4^{3-} and HPO_4^{2-} phosphate ions that changes the equilibrium in the solution toward the increase in alkali metal ion concentration.

According to the results of pH determination of phosphoric acid solutions after the establishing equilibrium we can assert that the neutralization reaction proceeds at the first stage. Sodium hydrophosphate is formed only after the establishment of the second equivalence point.

During potassium dihydrophosphate sorption by clinoptilolite the sodium atoms in the lattice are substituted for potassium and partially for hydrogen ion at the second stage of ionization. According to pH value we can indicate the presence mainly of sodium dihydrophosphate. The phosphate ion is absorbed depending on its charge due to its location on the singly charged matrix in the point of aluminum atom location. Taking into account the negative charge of zeolite framework we can confirm that ion exchange of sodium for potassium occurs through the chemical interaction. The regularities of phosphates pH changes during P_2O_5

sorption on natural zeolites were examined. The character of phosphate ions bonds with the zeolite matrix was determined. The processes of phosphates desorption from zeolite volume was investigated.

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МЕХАНІЗМ СОРБЦІЇ ФОСФАТІВ ЦЕОЛІТАМИ У ЗАЛЕЖНОСТІ ВІД СТУПЕНЯ ЇХ ЗАМІЩЕННЯ ІОНАМИ КАЛІЮ

Анотація. Встановлено механізм процесу сорбції фосфатів на клиноптилоліті. Досліджено, що в процесі взаємодії цеоліту зі стічними водами, які мають кислу реакцію, спостерігається значне збільшення сорбційної ємності цеоліту. Це пояснюється утворенням нових активних центрів цеоліту внаслідок dealюмування його поверхні.

Ключові слова: цеоліт, сорбція, статична ємність, фосфати.