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 $\text{Si}^{4+}$ for $\text{Al}^{3+}$ 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, $\text{H}^+$ 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 process. The amount of P ions the solutions of HPO$_4^{2-}$ and K$_2$PO$_4$ are almost identical, but with the increasing concentration of the initial solution, KH$_2$PO$_4$ sorption is weaker. At the concentrations of above 100 mg/l the zeolite activity relative to KH$_2$PO$_4$ remains constant. At the mentioned concentrations there is almost the same trend only K$_2$HPO$_4$ and K$_3$PO$_4$ sorption capacity is much lower. For H$_3$PO$_4$ concentrations above 150 mg P/dm$^3$ we observe a sharp increase in zeolite sorption capacity due to the fact that the acid highly concentrated solutions are capable to disaluminate 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$^+$, Ca$^{2+}$, Mg$^{2+}$, 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$^+$, Ca$^{2+}$, Mg$^{2+}$ zeolites and proceeding of ion exchange reactions. Therefore, we analyzed the concentration of exchangeable ions, namely Na$^+$, Ca$^{2+}$, Mg$^{2+}$ in solution to verify the ionic character of the process. The amount of P$_2$O$_5$ absorbed by zeolite depends on the degree of phosphate dissociation (Fig. 1), which is characterized by a dissociation constant $K$.

### 3. Results and Discussion

The values of zeolite static activity $a_0$ 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 (H$_3$PO$_4$) and potassium dihydrophosphate (KH$_2$PO$_4$) are almost identical, but with the increasing concentration of the initial solution, KH$_2$PO$_4$ sorption is weaker. At the concentrations of above 100 mg/l the zeolite activity relative to KH$_2$PO$_4$ remains constant. At the mentioned concentrations there is almost the same trend only K$_2$HPO$_4$ and K$_3$PO$_4$ sorption capacity is much lower. For H$_3$PO$_4$ concentrations above 150 mg P/dm$^3$ we observe a sharp increase in zeolite sorption capacity due to the fact that the acid highly concentrated solutions are capable to disaluminate 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$^+$, Ca$^{2+}$, Mg$^{2+}$, 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.

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### Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O+Na$_2$O</th>
<th>F</th>
<th>As</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, %</td>
<td>71.5</td>
<td>13.1</td>
<td>0.9</td>
<td>0.5</td>
<td>3.44</td>
<td>0.68</td>
<td>0.014</td>
<td>3.03</td>
<td>0.025</td>
<td>0.0015</td>
<td>0.002</td>
<td>0.02</td>
</tr>
</tbody>
</table>
While dissolving phosphoric acid its dissociation occurs according to the following scheme by several stages:

\[
\begin{align*}
H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- & \quad K_1 = 7.51 \cdot 10^{-3} \\
H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} & \quad K_2 = 6.23 \cdot 10^{-8} \\
HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-} & \quad K_3 = 2.2 \cdot 10^{-13}
\end{align*}
\]

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, 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.

\[Li^+ < Mg^{2+} << Na^+ < NH_4^+ << Ca^{2+} < K^+ < Rb^+ < Cs^+\]

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):

\[
CL(Na) + H^+ + HPO_4^{2-} \rightarrow CL(H) + NaH_2PO_4
\]

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 disalumination 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 [Si–O–Al], which is a Bronsted 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 AlPO₄, the structure of which is similar to SiO₂, is formed in the lattice. NaH₂PO₄, Na₃HPO₄, Al(H₂PO₄)₃ and Al₃(HPO₄)₂ 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 Ca²⁺ 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 disalumination of zeolite. With the increase of concentration the pH value of phosphoric acid sharply decreases during sorption in contrast to KH₂PO₄ solution, the initial pH of which is higher than that of H₃PO₄.

At low H₃PO₄ concentration pH of medium is 3.9 before sorption and 5.8 – after sorption (Fig. 3). The initial value of pH of KH₂PO₄ solution is 1.04·10⁻³ kg/m³. 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 (pH ≈ 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 Ca(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 PO₄³⁻, HPO₄²⁻ ions decreases due to the shift of dissociation reaction equilibrium to the left (to form H₃PO₄), 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 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 P₂O₅ 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.
Mechanism of Phosphates Sorption by Zeolites Depending on Degree of their Substitution

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$_3$PO$_4$ and KH$_2$PO$_4$) 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$_2$O$_5$...
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.

References