**Technology for the Preparation of Ion-Selective Ion Exchangers Based on Phosphates**

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**Abstract:** This study focuses on the synthesis and characterization of a novel organo-inorganic ion-exchange polymer, poly(divinylfurfuryl sodium tripolyphosphate) (Polifos-1), derived from furan derivatives. The synthesis pathway involved the reaction of a synthesized intermediate, 1-(tetrahydrofuran-2-yl)pent-4-en-2-1-ol (obtained from furfuryl alcohol and vinyl acetate), with thiourea, sodium tripolyphosphate, and polysilicic acid in the presence of an initiator. The structure of a key intermediate, 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)thiourea, was confirmed by chromatographic-mass spectrometry (m/z - 210) and its fragmentation pattern. The resulting granular cation exchanger exhibited high mechanical strength, retaining over 75% of its mass after 5 hours of vigorous attrition testing. Sorption studies under dynamic conditions revealed a selectivity sequence of Ca2+ > Mg2+ > Cu2+ > Mn2+ > Pb2+, with dynamic exchange capacities of 3.81 g-eq/m3 for Ca2+ and 4.83 g-eq/m3 for Mg2+. Static sorption tests demonstrated high removal efficiencies for key ions: Ca2+ (98.65%), Mg2+ (99.75%), and Cu2+ (98.62%). The application of Polifos-1 in treating real water samples (industrial wastewater, boiler feed water, artesian water) effectively reduced water hardness, confirming its potential as an effective ion-exchange material for water softening and selective cation removal.

**Keywords:** Organo-inorganic hybrid polymer; Cation exchanger; Furan derivatives; Poly(divinylfurfuryl sodium tripolyphosphate); Polifos-1; Ion-exchange capacity; Mechanical strength; Sorption selectivity; Water softening; Dynamic exchange.

**INTRODUCTION**

Currently, the scale of industrial organic synthesis is such that the issue of the limited natural reserves of oil and gas necessary to satisfy its requirements has become a pressing concern. At the present stage of scientific and technological development, polymer composite materials formed on the basis of combinations of components with different chemical natures represent a new class of materials which, in terms of their properties, significantly surpass those of the individual constituent components taken separately. Due to the combination of their composite properties, they exhibit unique physical–mechanical, magnetic, and optoelectronic characteristics, possess high chemical and thermal stability, and demonstrate increased resistance to various types of radiation. In recent years, the development of materials and composites containing phosphate groups with desirable properties has become increasingly important. Phosphate-containing natural compounds are integral components of numerous widely used pharmaceutical preparations. Compounds with phosphate functional groups constitute the foundation not only of inorganic chemistry but also of the fundamental processes of life. The ability of phosphate groups to undergo facile modification with organic compounds is of significant practical and theoretical importance and remains a subject of intense scientific interest[1].

Ion-exchangers based on Group IV elements of the periodic table represent a promising direction in the study of ion-exchange materials with high selectivity [2].

Based on their physicochemical properties, including the degree of crystallinity, ion-exchange materials are classified into amorphous, semi-crystalline, crystalline, and crystalline fibrous types [3].

Amorphous phosphates of these metals are obtained by direct contact of a soluble metal(IV) salt with phosphoric acid or its salt. These compounds possess non-stoichiometric compositions, and even minor variations in the synthesis conditions can result in the formation of a material with a different composition. Amorphous sorbents are characterized by a highly developed porous structure and favorable kinetic properties. When phosphoric acid itself or its salts are used as the precipitating agent, amorphous phosphates with varying phosphorus-to-metal ratios can be obtained [4].

By employing the precipitation method, it is possible to synthesize samples ranging from amorphous to crystalline states by varying the phosphorus-to-metal molar ratio in the initial mixture, the synthesis temperature, and the duration of gel aging in the initial solution. For example, the authors of [5] obtained a series of cerium phosphates: at 20°C, the product precipitated in an amorphous form; at 60°C and 80°C, semi-crystalline ion-exchangers were formed; and at 90°C, a crystalline fibrous material with a phosphorus-to-cerium molar ratio of two was obtained. It was concluded that the crystallinity of the material and the P:Ce molar ratio in the solid phase increase with longer aging of the precipitate and higher phosphoric acid concentration.

The precipitation method at the boiling temperature of the initial mixture is one of the approaches for obtaining crystalline forms of metal(IV) phosphates, characterized by the direct formation of the crystalline product in the initial solution [6].

**Sorbents with varying degrees of crystallinity can be obtained by altering the synthesis conditions, in particular: the P:Me molar ratio, the duration of sorbent structure formation, the pH of the medium, and the temperature. For example, products are formed as a result of the interaction of soluble titanium sulfate or chloride with orthophosphoric acid and its salts, where the TiO2-to-P2O5 ratio depends on the experimental conditions. The variable composition of titanium phosphates is a consequence of their instability with respect to hydrolytic decomposition [7].**

The introduction of hydrofluoric acid into the initial mixture leads to the formation of crystalline phosphates in the form of large crystals. It is well known that hydrofluoric acid acts as an effective complexing agent, with the fluoride ion forming a complex with the metal cation, which, upon the addition of phosphoric acid, gradually decomposes to yield the metal phosphate. Such crystal enlargement is characteristic of zirconium phosphate. Titanium phosphate also precipitates from solutions in the presence of hydrofluoric acid, although the particle size differs slightly from that obtained under boiling conditions. The formation of larger crystalline phosphates can be achieved by adding hydrofluoric acid to the initial mixture. It is well known that hydrofluoric acid acts as an effective complexing agent: the fluoride ion forms a complex with the metal cation, which then gradually dissociates upon the addition of phosphoric acid to yield the metal phosphate. Such crystal growth (enlargement) is characteristic of zirconium phosphate. Titanium phosphate also precipitates in solutions in the presence of hydrofluoric acid; however, the particle size does not differ significantly from that obtained by the conventional boiling method[8].

In addition to the methods for obtaining crystalline samples discussed above, there are also specific alternative approaches. One such method is the sol–gel process, which involves the synthesis of gel spheres of titanium hydroxide followed by treatment (conversion) with water-soluble phosphates. Tetravalent metal phosphates with a crystalline fibrous structure have been the least studied in terms of their synthesis and ion-exchange properties. In, a fibrous phosphate was obtained. However, since the structure of metal fibrous phosphates remains unknown, providing a systematic classification based on their ion-exchange properties is challenging. From a technological perspective, these products are highly interesting. They can be transformed into flexible films for use as membrane materials, while the ground products can function as conventional inorganic exchangers. The formation of fibrous crystalline phosphate materials is influenced by the concentrations of reactants, the temperature of precipitation, and the duration of the process. It is well known that, in addition to the +4 oxidation state, Group IV elements also exhibit lower oxidation states; for example, titanium and tin can exist in the +3 and +2 states, respectively. Although these lower oxidation states are less stable than the +4 state, they allow for the formation of various compounds, including phosphates.

**METHODS**

One of the pressing challenges today is the development of a new class of polymer composite materials with diverse chemical properties mechanical, magnetic, optical, and electronic arising from the combination of components, as well as the synthesis and technological development of organic–inorganic hybrid ion exchangers that exhibit high chemical and thermal stability, along with thermal, radiation, and mechanical resistance. Another rapidly advancing area involves the synthesis of highly reactive compounds by introducing unsaturated groups into organic molecules. The incorporation of a vinyl group provides nearly unlimited opportunities for the directed organic synthesis of multifunctional furan compounds, particularly in the preparation of divinylfurfuryl ethers. However, the active application of divinylfurfuryl ethers is limited by the lack of simple and scalable synthetic methods. Compared to alkyl vinyl ethers, these compounds are significantly less studied; their chemical behavior is unique due to the presence of additional functional groups, making them prone to both electrophilic and radical reactions. Accordingly, the synthesis of silsesquioxanes and (oligo)polymers that enhance the mechanical strength and thermal stability of composites, the study of their properties, and the development of technology for producing ion exchangers based on them are of significant importance. In this study, the synthesis process based on furan derivatives was carried out as follows: a reaction flask was charged with 50 mg of vinylfurfuryl ether, 0.1 mol of thiourea, 50 mg of sodium tripolyphosphate, 50 mg of polysilicic acid, and 1 wt% of dinitrilazobisisimic acid (DAA) as the initiator relative to the monomer mass. The flask was equipped with a thermometer, placed on a magnetic stirrer, and heated at 85–120 °C for 2 hours. Upon completion of the reaction, the sticky, yellowish, solidifying polymer—poly(divinylfurfuryl sodium tripolyphosphate) (Polifos-1)—was washed three times and dried to a constant mass.



Data on the direct vinylation of furfuryl alcohols with vinyl acetate are very limited. Considering the tendency of furfural to undergo the Cannizzaro reaction in alkaline media, furfuryl alcohol was selected as the starting compound. The synthesis of divinylfurfuryl ether from furfuryl alcohol and vinyl acetate was carried out in a strongly basic system at room temperature and atmospheric pressure, yielding 1-(tetrahydrofuran-2-yl)pent-4-en-2-1-ol. The resulting intermediate offers a wide range of possibilities for modification with various compounds. In particular, it allows for the synthesis of reactive derivatives by introducing molecules containing free electron pairs. Therefore, the potential for obtaining an organo–inorganic ion exchanger was investigated by modifying the intermediate with thiourea, sodium tripolyphosphate, and polysilicic acid. The reaction was performed in the following sequence:

Initially, thiourea was dissolved in a small amount of hot ethanol to ensure good mixing with the reaction medium and the formation of a homogeneous system. Using a separatory funnel, 1-(tetrahydrofuran-2-yl)pent-4-en-2-1-ol was then added dropwise onto the solution. After reaching an equimolar ratio, a few drops of acid (e.g., 0.1 M HCl or H2SO4) were added, and the mixture was heated at 50–60 °C for 1–2 hours. As a result, a condensation reaction occurred, forming a C–N bond with the release of water, which was visually monitored. Through these reaction processes, 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)thiourea was obtained.

Initially, thiourea reacts with the hydroxyl group of the intermediate form according to the following scheme.



The resulting intermediate undergoes polymerization. The reaction proceeds in a specific sequence within a single system.



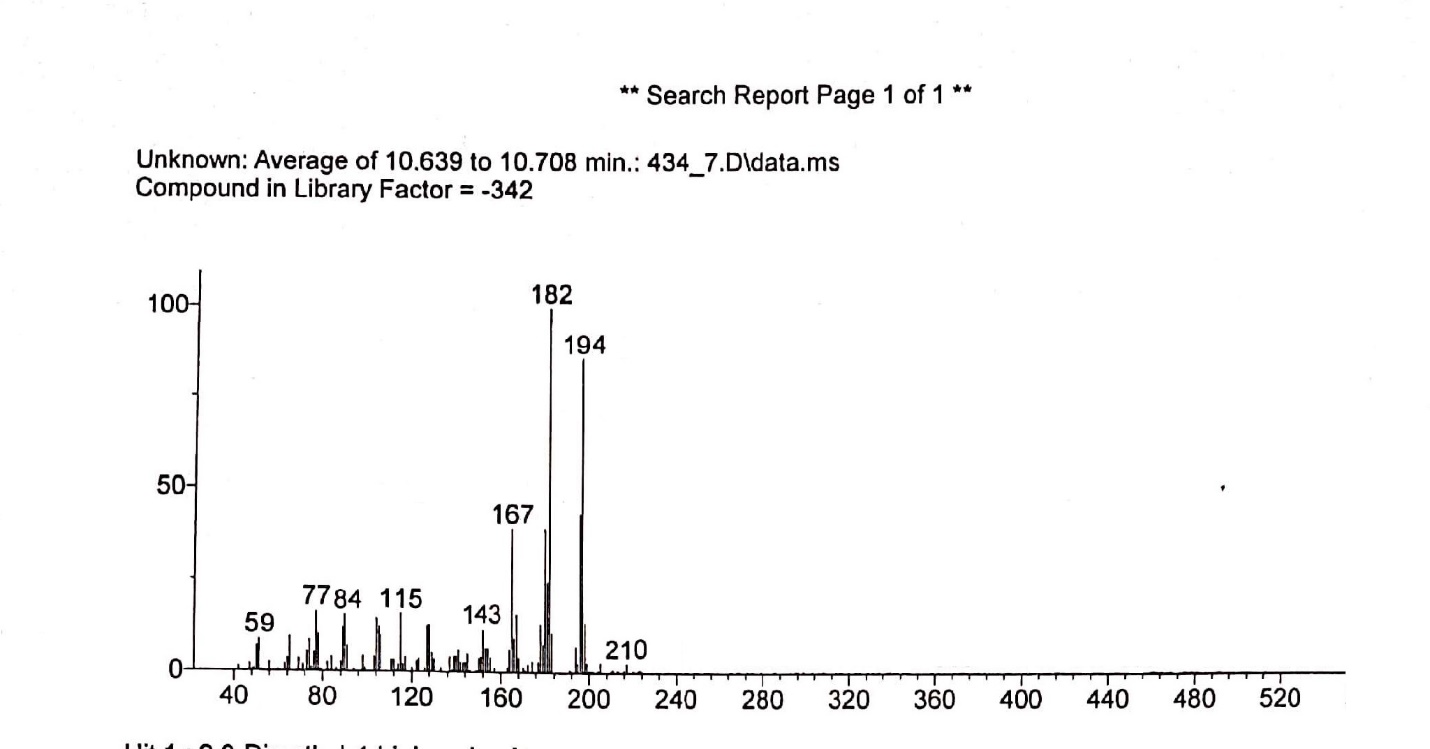
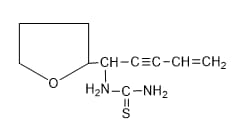
Sodium tripolyphosphate was used to increase the number of active sites and electron pairs in the resulting polymer, as well as to enhance its mechanical strength. The overall process can be described as follows:.







The resulting ion exchanger was purified using an extraction method with various solvents. The separation of the initial, intermediate, and final products based on their solubility in different solvents ensures a high degree of purity. Accordingly, a solvent was selected that does not dissolve the final product but is capable of dissolving the initial and intermediate compounds. Furthermore, the structure of the new compound can be inferred from the fragmentation pattern observed in its chromatographic-mass spectrum. After introducing 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl) thiourea into the chromatographic-mass spectrometer under the selected conditions, the molecular ion of 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)thiourea with m/z 210 was observed at a retention time range of 10.639 to 10.708 minutes.





Additionally, the spectrum revealed the formation of fragment ions with m/z values of 210, 194, 167, 143, 84, and 59. At 10.639 minutes, the ion of 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)thiourea underwent loss of a hydroxyl (-OH) radical, resulting in the formation of the m/z 194 ion. This peak corresponds to the N-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)ethanethioamide ion, which is consistent with the expected bond dissociation energies.



From the tertiary N-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)ethanethioamide ion, the loss of a methylene radical results in the formation of the m/z 167 ion. This peak corresponds to N-(1-(tetrahydrofuran-2-yl)but-2-yn-1-yl)ethanethioamide.



In turn, from the N-(1-(tetrahydrofuran-2-yl)but-2-yn-1-yl)ethanethioamide ion, the loss of radicals at 10.708 minutes resulted in the formation of the m/z 59 ion.



Finally, the kinetic behavior of the resulting N-(1-(tetrahydrofuran-2-yl)ethyl)ethanethioamide ions occurs in accordance with the complexity of the ring-opening process. In the initial stage, the cleavage of ions from the side chain, followed by ring fragmentation, confirms the correctness of the compound’s structure and its accurate identification, consistent with the observed fragmentation patterns.

One of the important parameters for the application of ion-exchange polymers is their mechanical strength. To determine the mechanical strength of the synthesized cation-exchanger, 100 g of cation-exchanger (particle size 0.5 cm) and 100 ml of water were placed in a flask and subjected to a vibrator for 10 hours. During the sieving process, the gel-like fraction corresponding to cation-exchanger particles smaller than 0.5 cm was evaluated. Table-1 presents the results of the study on the mechanical attrition resistance of the cation-exchanger, including comparative data on the mechanical strength of two different cation-exchangers. The ion-exchangers obtained in the study were tested at the Central Scientific Research Laboratory of the “Navoi Mining and Metallurgy Combine” state enterprise, and the results obtained are reflected accordingly.One of the main characteristics of the ion-exchanger, brought to a granular form after the addition of polysilicic acid, is its dispersibility and mechanical strength. Its mechanical strength was tested using a vibrator, and the results are presented in Table 1.

**TABLE 1. Mechanical strength of the ion-exchanger**

|  |  |  |
| --- | --- | --- |
| **Sample** | **Processing time, hours** | **Mechanical strength, %** |
| **Ion** | 0,25 | 99,4 |
| 0,5 | 99,3 |
| 0,75 | 99,0 |
| 1,0 | 97,5 |
| 1,25 | 96,8 |
| 1,5 | 96,2 |
| 1,75 | 95,8 |
| 2,0 | 93,5 |
| 2,25 | 92,1 |
| 2,5 | 90,1 |
| 2,75 | 88,3 |
| 3,0 | 86,2 |
| 3,25 | 83,6 |
| 3,5 | 82,5 |
| 3,75 | 80,2 |
| 4,0 | 79,1 |
| 5,0 | 75,3 |

To determine the mechanical strength, 100 g of ion-exchanger was weighed and subjected to a rotational motion on a sieve, and its tendency to fragment into smaller pieces was studied. The percentage of the sample retained on the sieve was calculated by measuring its mass.

Furthermore, 1000 g of ion-exchanger was subjected to rotational motion on a sieve for 10–15 minutes. The granulometric composition of the resulting ion-exchanger was determined by passing it through sieves of different mesh sizes and measuring the masses. Its degree of fragmentation and dispersibility were assessed (Table 2.), and recommendations were developed for its use during subsequent operational periods.

**TABLE 2.** Distribution of the ion-exchanger by dispersibility

|  |  |  |
| --- | --- | --- |
| **№** | **Size, mm** | **Amount, %** |
|  | 0,3-0,4 | 15,5 |
|  | 0,4-0,5 | 14,9 |
|  | 0,5-0,6 | 14,1 |
|  | 0,6-0,7 | 12,8 |
|  | 0,7 -0,8 | 11,4 |
|  | 0,8-0,9 | 9,7 |
|  | 0,9-1,0 | 6,3 |
|  | 1,0-1,1 | 5,1 |
|  | 1,1-1,2 | 4 |
|  | 1,2-1,3 | 2,7 |
|  | 1,3-1,4 | 2,1 |
|  | 1,4-1,5 | 1,3 |

The dispersibility of the ion-exchanger depends on particle sizes related to the exchange capacity, as these determine the available surface area. A larger surface area results in a higher exchange capacity, which is a key factor. Excessive dispersibility, however, can lead to clogging in equipment such as filters, causing an increase in pressure. Therefore, the optimal particle size ranges from 0.3 mm to 1.25 mm. Particles larger than this range have a smaller surface area, which reduces the degree of ion exchange and sorption. Conversely, particles smaller than the specified range hinder the passage of the solution through the ion-exchanger, also decreasing exchange and sorption efficiency and limiting the feasibility of their production. The static and dynamic exchange capacities of ion-exchangers with particle sizes outside the recommended range differ significantly. This indicates that particle sizes other than the recommended range directly affect the effective surface area available for interaction.

Due to the furan ring-crosslinked ion-exchanger having a complex three-dimensional structure, high strength, and granular form, its structure was studied using physicochemical analytical methods in parallel with chemical analysis techniques.

In the production process, taking into account the operation of the ion-exchanger under dynamic conditions, its dynamic exchange capacity was first determined according to the standard methodology (Table 3.).

**TABLE 3.** Dynamic exchange capacity of the ion-exchanger over 5 hours at a flow rate of 1 L/h

|  |  |  |  |
| --- | --- | --- | --- |
| **Type of metals** | **Concentration of the working solution, mol/dm³ (n)** | **Volume of the ion-exchanger, cm³** | **Dynamic exchange capacity, (g-eq/m³)** |
| Ca2+ | 0,1 | 50 | 3,81 |
| Mg2+ | 0,1 | 50 | 4,83 |
| Cu2+ | 0,1 | 50 | 0,95 |
| Mn2+ | 0,1 | 50 | 0,75 |
| Pb2+ | 0,1 | 50 | 0,47 |

To determine the selectivity of the ion-exchanger during dynamic exchange, the amount of each ion adsorbed at a given time was monitored using the titrimetric method (Table 4.).

**TABLE 4.** Results of determining the selectivity of the ion-exchanger

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Time, min** | **Ca2+** | **Mg2+** | **Cu2+** | **Mn2+** | **Pb2+** |
| 30 | 0,9 | 1,4 | 0,05 | 0,02 | 0,01 |
| 60 | 1,3 | 1,64 | 0,07 | 0,06 | 0,019 |
| 90 | 1,5 | 1,78 | 0,09 | 0,09 | 0,24 |
| 120 | 1,9 | 2,4 | 0,14 | 0,14 | 0,27 |
| 150 | 2,1 | 3,1 | 0,2 | 0,18 | 0,33 |
| 180 | 2,8 | 3,84 | 0,4 | 0,3 | 0,38 |
| 210 | 3,4 | 4,3 | 0,7 | 0,5 | 0,41 |
| 240 | 3,7 | 4,8 | 0,9 | 0,7 | 0,46 |
| 270 | 3,81 | 4,83 | 0,95 | 0,75 | 0,47 |

Based on the analysis of the results obtained from Table 4.2, the selectivity sequence can be established as follows: Ca2+ > Mg2+ > Cu2+ > Mn2+ > Pb2+.

Among the chemical and operational properties of ion-exchangers, the most important is their ion-exchange capacity, which characterizes the performance of the ion-exchanger. Its value primarily depends on the number of ionogenic groups in the cation-exchanger, their degree of dissociation, the pH value, as well as the nature and concentration of the exchanging ions. The cation-exchange capacity, obtained by conventional methodology and theoretically, was calculated using the following formula :, mg-ekv/g

Here Etheor. – **Theoretical exchange capacity**, mg-ekv/g;

– Molecular weight of the monomer of the obtained cation-exchanger

When the amount of ion-exchanger is 100 g and the solution volume is 500 ml, the degree of sorption serves as the main parameter for evaluating the ion-exchanger. The results of the sorption degree under static conditions are presented in Table 5.

**TABLE 5. Values of the ion-exchanger sorption degree under static conditions**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **№** | **Type of metals.** | **Concentration of the solution before sorption mg/dm3** | **Concentration of the solution after sorption mg/dm3** | **Concentration of the solution after sorption,**  **mg/g** | **Degree of sorption,** |
| 1 | Ca2+ | 901,8 | 12,16 | 4,4482 | 98,65 % |
| 2 | Mg2+ | 401,3 | 1,0 | 2,0015 | 99,75 % |
| 3 |  | 1035,3 | 194,97 | 4,20165 | 81,16 % |
| 4 | SO42- | 2578,9 | 2344,1 | 1,174 | 9,10 % |
| 5 | Mn | 0,17 | 0,03 | 0,0007 | 82,35 % |
| 6 | Pb | 0,04 | 0,03 | 0,00005 | 25 % |
| 7 | Cu | 2,9 | 0,04 | 0,0143 | 98,62 % |
| 8 | Cr | 0,05 | 0,05 | 0 | 0 |

Based on the results presented in Table 5., the values obtained under static conditions are close to those obtained under dynamic conditions, with approximately 99% of calcium and magnesium ions retained from the solution.

**TABLE 6.** Use of cation-exchange resin in certain water softening processes

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **№** | **Synthesized cation-exchanger** | **Industrial wastewater of Navoi Mining & Metallurgy Combine JSC** | | **Boiler house water of the Gazli Gas Processing Plant, Gazli city, Bukhara region** | | **Bukhara City, Bukhara State Technical University** | |
| **Artesian water** | |
| **Hardness mEq/L** | | | | | |
| **before** | **after** | **before** | **after** | **before** | **after** |
| 1. | Polifos-1 cation H-form | 7,8 | 7,2 | 9,5 | 5 | 18,3 | 8,5 |
| 2. | Polifos-1 cation Na-form | 7,8 | 6 | 9,5 | 2 | 18,3 | 6,2 |

**CONCLUSION**

The dynamic and static ion-exchange capacities of Polifos-1 were studied to evaluate its sorption performance. The dynamic exchange capacity followed the order: Ca2+ > Mg2+ > Cu2+ > Mn2+ > Pb2+, indicating a clear selectivity of the ion-exchanger during the dynamic process. The uptake of calcium, magnesium, copper, manganese, and lead ions per unit time was quantified, demonstrating the efficiency of Polifos-1 in removing these cations from solution. The static exchange capacity was determined based on the degree of sorption. The results revealed that Ca2+ – 98.65%, Mg2+ – 99.75%, Cl- – 81.16%, SO₄2- – 9.10%, Mn2+– 82.35%, Pb2+ – 25%, and Cu2+ – 98.62% of ions were exchanged. Cr ions were not exchanged under the same conditions. Notably, Polifos-1 was able to retain nearly 99% of calcium and magnesium ions from the solution, highlighting its potential for selective ion removal.

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