

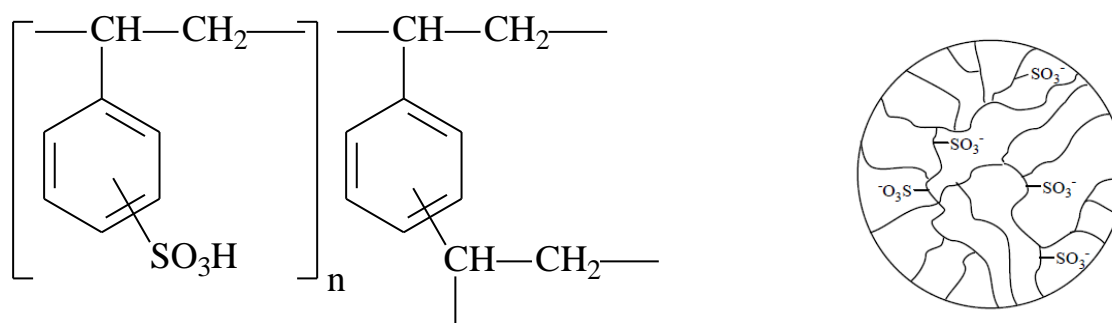
Methods for Obtaining Modified Structured Ion Exchange Polymers

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Abstract: This article describes methods for desalinating and softening wastewater using standard KU-2-8 cation based on sorption technologies. Compared to existing separation methods, modern sorption technologies have several advantages: the high saturation degree of the sorbent's solid phase with target components, the ability to extract the smallest concentrations of target components, high selectivity, and the possibility of continuous and automated processes.

Keywords: Sorbent, ion exchange, cation exchange ionit, modification, equivalent, component.

In this study, the gel-structured cation exchange polymer KU-2-8, obtained through copolymerization of divinylbenzene (DVB) and styrene with subsequent introduction of sulfo groups, was selected. Its chemical and structural composition can be described as follows:



The pores of the KU-2-8 ion exchange polymer have a diameter of 200 nm. Due to its cross-linked structure, it possesses a high relative volume. The brand of the polymer indicates that the cross-linking agent, divinylbenzene, constitutes 8% of the total mass. Standard KU-2-8 ion exchange polymer is a simple spherical granule, measuring 0.325-1.25 mm, with a relative volume of 2.8 cm³/g in H-form, yellowish or almost white in color, and a moisture content of around 48-58%. Due to its chemical resistance to acids, alkalis, and oxidizing agents, it is one of the ion exchange polymers meeting chemical and sanitary-toxicological requirements.

Furthermore, this method ensures a high degree of purity of the filtrate obtained in the sorption process, which greatly simplifies the reprocessing of the sorbent with chemical reagent solutions [1].

Sorption technology is typically carried out under dynamic conditions, allowing for continuous operation with simple or complex automated schemes. Such schemes are crucial in practical applications, ensuring the retention of undesirable particles in the filtrate to minimal concentrations and the extraction of required components in maximum quantities by volume within the column layer[2].

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Specific fields, such as thermal power, nuclear energy, chemical production, and radio electronics, as well as technologies for obtaining highly purified substances, especially energy carriers like pure water and solvents, rely on ion exchange methods.

The majority of ion exchange materials are used predominantly in the water supply sector (60-90% of total production volume). Sorption methods also play a significant role in resource conservation and protection technologies for processing and extracting mineral and organic resources. Certain quantities of ion exchange resins are employed in chromatographic processes.

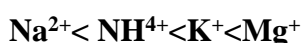
Ion exchange methods can be used to separate ions, molecules, macromolecules, and certain particles in colloidal systems (with sizes ranging from 10^{-6} to 10^{-2} mm). Modifikatsiyalangan strukturali ion almashinuvchi polimerlarni olish usullari.

High-capacity, highly selective, chemically stable, and mechanically robust synthetic ion-exchange materials play a crucial role in the development of many industrial sectors. These materials not only enhance technological processes but also reduce energy consumption, labor intensity, and production costs.

Deterioration of water quality in water sources and secondary contamination during transport means that water often does not meet the required standards. Therefore, it is necessary to purify water before using it in technological cycles. Water used in technological processes must meet specific quality standards. Ion exchange sorbents are widely used to improve water quality [3]

The ion exchange method for water softening relies on the cation exchange properties of cation exchangers, where the active groups of the cation exchanger are pre-charged and exchange with calcium and magnesium cations in the water to be softened. During this reaction, the cation exchanger replaces ions in the water with ions absorbed by the cation exchanger. The most important factors are the properties of the cation exchanger, the composition of the water, and the conditions of the process. These factors are interrelated and determine the rate of the ion exchange reaction. The exchange reaction between the ions in the water and the cation exchanger is ensured by the diffusion of ions from the solution into the cation exchanger and from the cation exchanger into the water. The process is governed by the laws of diffusion and mass action.

When softening water containing calcium and magnesium ions, these ions diffuse into the cation exchanger, while sodium ions diffuse from the cation exchanger into the water. As a result of the exchange reaction, calcium and magnesium replace sodium in the cation exchanger, while sodium replaces calcium and magnesium in the softened water. The ion exchange between the cation exchanger and the solution is an equivalent reaction. The amount of Na^+ ions expelled from the cation exchanger is equivalent to the amount of Ca^{2+} and Mg^{2+} ions removed from the solution. The ion exchange process is not only equivalent but also reversible, as the rate of ion exchange expelled from the cation exchanger and the rate of ions entering from the solution are equal under equilibrium conditions. Cases of equivalent reversibility occur when other reactions accompany ion exchange in the water, such as oxidation-reduction, physical adsorption of molecules, and others. For ammonium purposes, the primary task for conducting Na^+ , NH_4^+ , and NH_4^+ cation exchange processes is to maximize the use of the cation exchanger's ion exchange capacity. This, in turn, enhances the efficiency of the ion exchange process, which depends on the ionization of the cation exchanger's active groups. The ion exchange properties of the cation exchanger significantly impact the nature of water softening. Any cation can be fully saturated, but the operational capacity depends on which specific ion is absorbed. The absorption rate follows a specific order:



Each cation in this series was rapidly absorbed by the preceding cation. Currently, artificially obtained materials are used as cation exchangers. Among the most widely used cation exchangers is sulfougol, primarily because it is easy to obtain and inexpensive. As a result, sulfougol is widely used in thermal power engineering for water preparation. Besides sulfougol, modern times see extensive use of ion exchangers such as resins—ionites, high-molecular-weight compounds consisting of high-molecular-



mass molecules. Ionites are solid, practically insoluble in water, mechanically strong, and chemically stable substances. The ion-exchange property of ionites in water treatment is explained by the presence of active groups fixed within the high-molecular compounds' framework, just like natural substances. Thus, each ionite is an insoluble ion with either a positive or negative equivalent, surrounded by oppositely charged mobile ions. The most commonly used synthetic cation exchangers in water purification are KB-4-P2, KU1G, and KU-2-8. These have a significantly higher working exchange capacity compared to sulfonogols [4].

The KU-2-8 brand cation exchanger is utilized for water desalination in water supply, chemical and food industries, hydrometallurgy, and several other production fields. Although the ion exchange efficiency of this cation exchanger is high, saturation with heavy metal ions (such as iron, manganese, copper, zinc, lead, etc.) frequently occurs during water softening processes. For instance, even though the static exchange capacity of KU-2-8 cation exchanger is 1.720 mg-eq/gram according to its passport, its capacity for colored metals decreases to 0.012 mg-eq/gram when treating high-hardness saline waters. To solve this issue, cation exchange sorbents modified with various functional groups can be used, such as carboxyl, amino, phosphoric acid, alkylthiophosphoric, sulfo groups, and others. Modified sorbents have demonstrated high selectivity towards heavy metal ions. Increasing the concentrations of functional groups on the ionite surface enhances its sorption capacity. This can be achieved by chemically and thermally processing the ionite. Conducting research on creating universally selective ionites through modification methods is one of the most interesting directions today [5].

The purpose of this research is to improve the sorption of heavy metals by modifying the universal KU-2-8 sulfo-cation exchanger through the impregnation of titanium dioxide from mineral acid solutions.

Standard KU-2-8 granules are spherical in shape, yellowish or white, and for this experiment, 50 grams of the cation exchanger were placed in a three-necked flask equipped with a reflux condenser, thermometer, and stirrers. Acid solutions with concentrations of 5%, 10%, 15%, 20%, and 30% were added to the flask along with 1 to 10 grams of titanium dioxide. The reaction mass was heated to 50-60°C and stirred for 120 minutes. Then the mixture was cooled to room temperature and left for 3 days. The resulting mass was washed with distilled water until a neutral reaction was achieved.

Before and after modification, cation exchanger samples were washed with a 5% sulfuric acid solution, then washed with distilled water until neutral, and dried in an oven at 80-90°C. The samples were analyzed using SEM.

Various methods can be used for modifying the surface of sorbents, including plasma treatment, interfacial polymerization, adsorption methods, chemical or physical modification, and others. Usually, modification involves applying an additional layer to the sorbent's surface. Additionally, certain methods, such as "ion implantation," can alter the chemical structure of the surface of granular sorbents [143]. In this work, the adsorption method was used, where the sorbent is immersed in a solution containing the modifier for a certain period to form a new layer on its surface. As a result, 5 grams of TiO₂ uniformly dispersed in a 20% nitric acid solution creates a new layer on the surface of KU-2-8 cation exchanger granules.



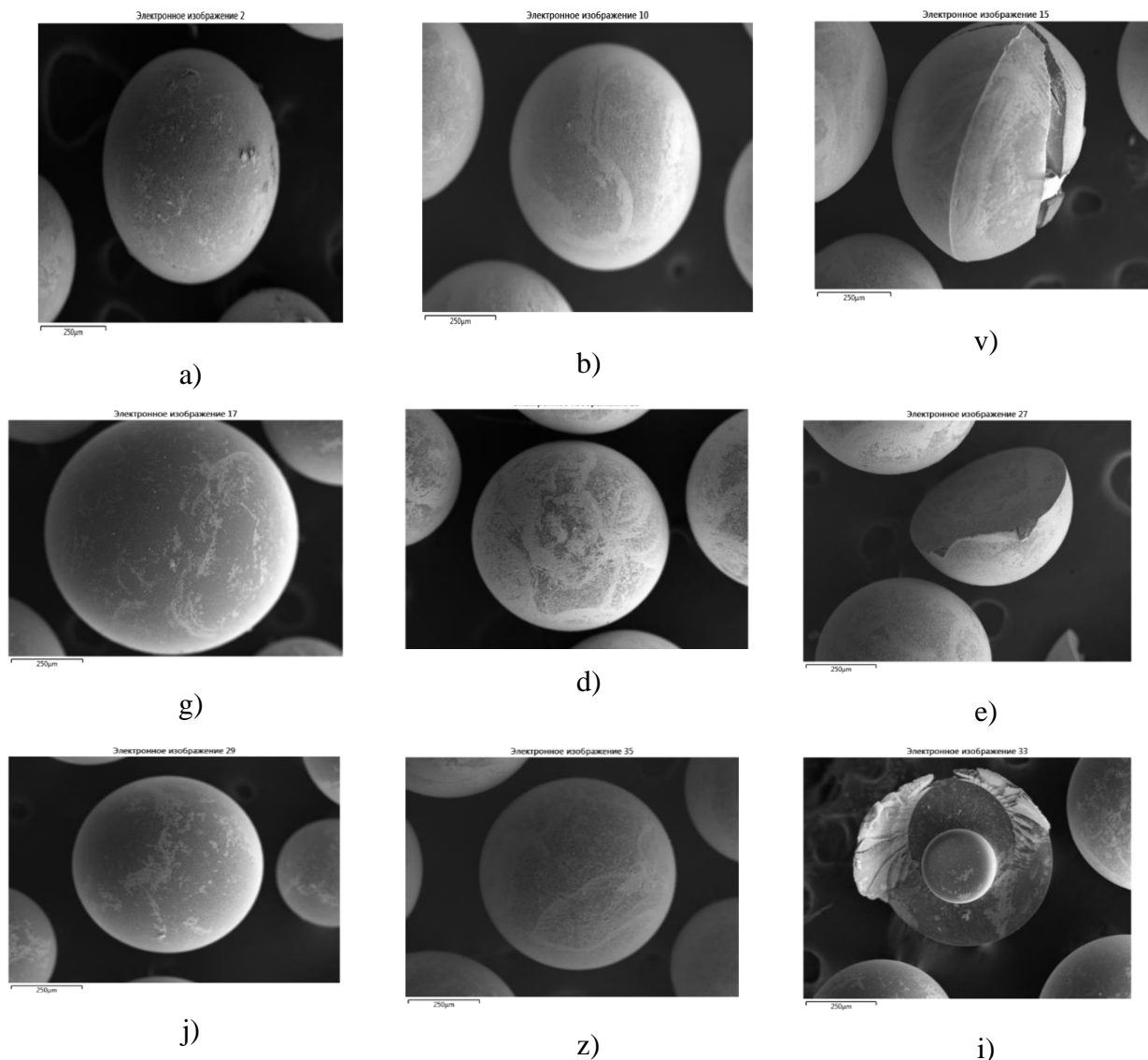
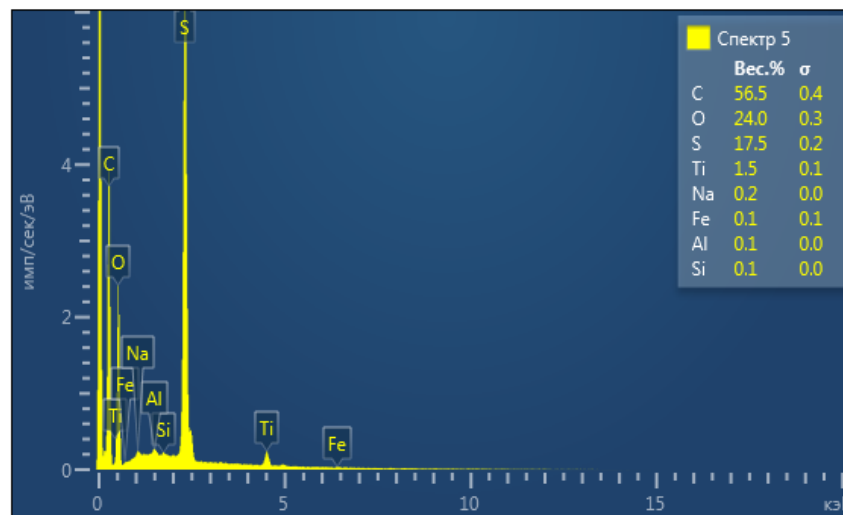


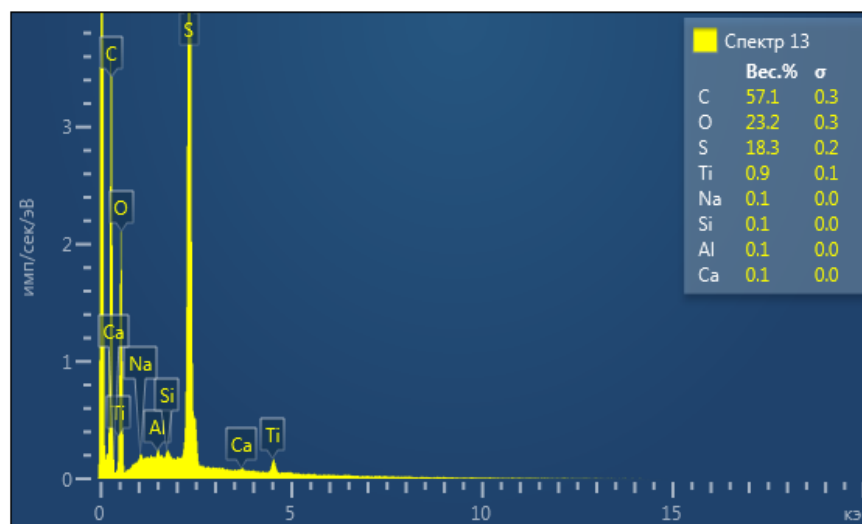
Figure 1 shows SEM images of soaked sample granule surfaces magnified 500 times (scale 250 μm). Resin particles soaked in acids: 1g 20% HCl (a), 5g 20% HCl (b), cross-section of 5g 20% HCl(v); 1g 20% HNO₃ (g), 5g 20% HNO₃ (d), cross-section of 5g 20% HNO₃ (e); 1g 20% H₂SO₄ (j), 5g 20% H₂SO₄ (z), cross-section of 5g 20% H₂SO₄(i).

Due to different amounts of the modifier (from 1 gram to 5 grams) and varying immersion times in hydrochloric acid solution, the surface structure of the tested sorbent granules was different. Additionally, the surface morphology varied depending on the concentration of the solvent. [6]

For example, it was found that the surface was much smoother in 20% acid compared to 5% acid. Increasing the acid concentration led to an increase in granule density. When the granule was immersed in a 20% nitric acid solution, SEM images showed the adsorption of the modifier on the surface of the cation exchanger.



A)



B)

Figure 2 shows element analysis spectra: a) 20% HNO₃ with 5 grams of TiO₂; b) 20% HCl with 5 grams of TiO₂.

When 5 grams of granules were immersed in nitric acid solution, it was found that the surface had a much smoother morphology with larger diameter particles. The results with 20% sulfuric and hydrochloric acids were less effective, indicating a lower formation of titanium salts. Elemental analysis using EDS can determine the type and molar mass of cations. The images show that in sample (a), there are eight different types of cations, with varying intensities of signals from carbon, oxygen, sulfur, and titanium ions, with titanium being the most prominent. Additionally, signals from sodium, aluminum, silicon, and iron were very small. In the second sample (b), all metals from the first sample (a) were present, but the signal for titanium in the 20% hydrochloric acid solution was smaller. The results for the a-sample cation exchanger were consistent with literature data [144; pp. 724-729]. Iron, silicon, and aluminum are common particles always present in water as trace elements [7].

The functional groups and microstructure of the standard KU-2-8 and the modified KU-2-8-SO₃-Ti(OH)₃ new ion-exchange polymer were studied using IR spectroscopy, scanning electron microscopy (SEM), elemental analysis, and potentiometric methods.



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