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SORPTION OF IONS STRONTIUM WITH NEW COMPLEX - FORMING IONITES ON THE BASIS OF EPOXYACRYLATES AND COMPLEXONES

Abstract. Polycondensation of glycidylmethacrylate, acrylonitrile and nitrilotrimethylphosphonic acid (NTPA), oxyethylidene diphosphonic acid (OEDA) complexes gave new complexing chelating ion exchangers with a static exchange capacity of 0.1 N HCl 3.64 and 3.43 mg-equiv / g. The sorption of Sr²⁺ ions by complex-forming cation exchangers of GMA-AKN-OEDA, GMA-AKN-NTFA was studied by the classical polarography method under static conditions. The sorption of strontium ions under static conditions from a solution of strontium chloride depending on their concentration and pH, as well as the time of their contact with ion exchanger was studied. It was found that they possess high kinetic and sorption characteristics and surpass the known industrial ionites in their absorbing capacity.

Key words: complexing ion exchangers, sorption, strontium ions, chelates, complexones, sorption capacity.

The element of strontium is the main source of pollution of the environment, in most cases due to the testing of nuclear weapons and the nuclear industry. Excessive content of strontium ions in living organisms becomes a real threat of the development of the level disease (Kashin-Bek disease), which is revealed in joint disease, increased brittleness and bone deformity. In the regions (East Siberia, Northern China, and North Korea) that are endemic for the abundance of strontium in soil and water, the level pathology is observed not only in humans, but mainly among animals.

Strontium is one of the most difficult and widely spread radionuclides. The specific feature of strontium isotopes is low sorbability and the high migration ability due to it in the environment. Sorption processes on mineral and organic components of soils have a large effect on the regularities of migration of strontium compounds. Sorption of radionuclides is often determined not by individual soil components, but by their complex action, since humus substances can be sorbed on the surface of natural aluminosilicates, oxides and hydroxides of iron, aluminum, etc., can be precipitated, which must be taken into account when assessing the migration of radionuclides in the environment.

For chelating-forming sorbents, a particularly important characteristic is the sorption capacity, which is caused by the interaction of the metal with the complexing groups of sorbent, which determine its selective properties. Therefore, to characterize the sorption capacity of complex-forming sorbents, the sorption capacity is determined under the conditions which the sorbent interacts with metal mainly to chelating groups [1-3].

Among the chelating-forming ion exchangers, phosphoric acid cation exchangers are advantageously distinguished by such practically important properties as a sufficiently high exchange capacity, thermochemical and radiation resistance, mechanical strength of the polymer matrix, increased selectivity

to many metal ions. Due to these qualities, they find wide application for the separation and concentration of ions in hydrometallurgy, nuclear technology. They, obviously, will acquire great practical significance in the new fields of science and technology [4].

A sorption-ionometric technique for removing strontium from water has been developed. The technique can be extended to study the adsorption of various substances from other environmental objects and with the use of other sorbents, for the purification of water from strontium ions, the flasks of the Astrakhan region, which possess a high sorption capacity with respect to strontium, are used, the developed method for water purification is used at the enterprise Astrakhan Oil and Gas Company (Astrakhan Region, Kharabalinsky District) [5].

In nuclear power, under conditions of normal operation of nuclear power plants, emissions of radioisotopes onto the environment are insignificant. In accidents, especially large ones, radionuclide emissions, including strontium radioisotopes, can be very dangerous for the environment. Therefore, studying the sorption of Sr^{2+} ions remains an urgent problem.

The purpose of this work is to study the sorption of strontium ions by new phosphorus-containing ion exchangers based on glycidyl methacrylate (GMA), acrylonitrile (ACN) and nitrilotrimethylphosphonic acid (NTPA), oxyethylidenediphosphonic acid (OEDP).

Experimental part

The extraction of Sr^{2+} ions by the GMA-AKN-NTFK and GMA-AKN-OEDP ion exchangers in the H-form (grain size 0.5-1 mm) was studied under static conditions at a sorbent: solution ratio of 1: 400, temperature 20 ± 2 °C, varying the concentration of strontium ions in SrCl_2 solutions and from 0.206 to 2.277 g / l and their acidity in the pH range from 1.6 to 5.9 by adding 0.1N solutions of HCl or NaOH. The duration of contact between the sorbent and the solutions was from 0.5 h to 7 d. For the preparation of model solutions, the $\text{SrCl}_2 \cdot 5\text{H}_2\text{O}$ salt of the qualification "h.ch" was used. The sorption capacity (SC) was calculated from the difference in the initial and equilibrium concentration of solutions, which was determined by the classical polarography method against a background of 0.5 M NH_4Cl in the recovery wave of Sr^{2+} ($E_{1/2} = -0.16$ V). The polarograms were recorded on a universal polarograph PU-1 in a thermostated cell at a temperature of 25 ± 0.5 °C using a mercury dropping electrode. Oxygen from the analyzed solutions was removed by blowing argon for 5 minutes. A saturated calomel electrode served as the reference electrode.

Results and its discussion

Chelate-forming sorbents often have a complex chemical structure. In addition to chelating groups, they contain other reactive groups. These can be acidic or basic groups. Often, the chelating sorbents are polyampholytes.

Acid-base properties of chelating-forming sorbents are an important characteristic of them and to a large extent determine their selectivity. The sorption properties of chelating sorbents are affected by the state of all ionogenic groups of sorbents.

To establish the acid-base properties of polymeric sorbents, the potentiometric titration method is widely used. This method makes it possible to establish the presence of certain groups in the polymer sorbent, and in some cases also their concentration, to calculate the dissociation constants of ionogenic groups and the total exchange capacity of the sorbent [6].

Potentiometric studies were performed to evaluate the acid-base properties of synthesized polyelectrolytes. The results are shown in Figure 1,2. As can be seen from Fig. 1, the potentiometric curve of this ion exchanger has two inflections, this indicates the presence of two unlike active groups, characteristic of polyfunctional ion exchangers. The acid-base properties of synthesized ion exchanger based on the double copolymer GMA-AKN and nitrilotrimethylphosphonic acid (NTFK) (Figure 2) indicate the presence of two kinks of the obtained new ion exchanger on the curves, indicating a medium-acid character, and also indicate their polyfunctionality.

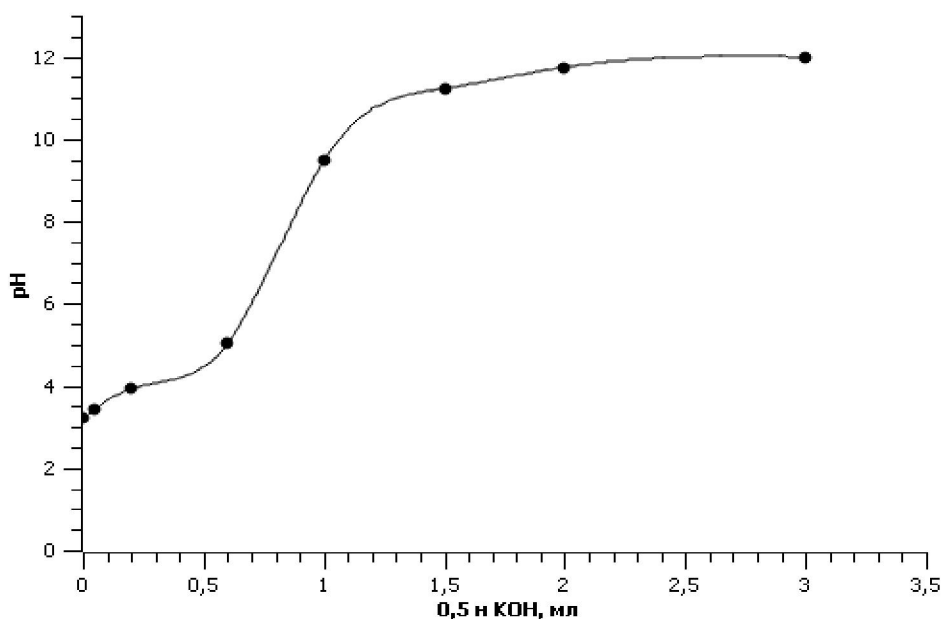


Figure 1 - Curves of potentiometric titration of ion exchanger based on the copolymer of GMA-AKN and OEDP

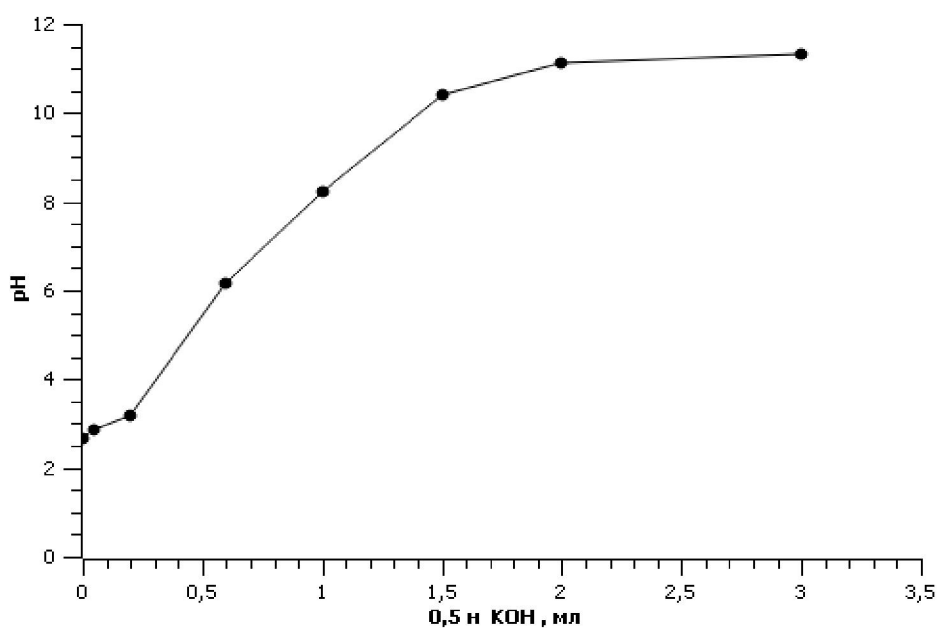


Figure 2 - Curves of potentiometric titration of ion exchanger based on the copolymer of GMA-AKN and NTFP

The sorption properties of complexing phosphorus-containing ion exchangers based on the copolymers GMA-AKN: NTFP and GMA-AKN-OEDF with respect to strontium ions were studied.

Figure 3 shows isotherms of sorption of strontium ions, showing the dependence of SC ion exchangers on the equilibrium concentration of Sr^{2+} in solutions. It can be seen that with the increase in the concentration of strontium ions in solutions of SrCl_2 from 0.175 to 2.057 g / l, the sorption capacity (SC) of the ion exchanger GMA-AKN-NTFP for strontium ions increases from 56.8 to 358.4 mg / g and SC of the sorbent GMA- AKN-OEDP increases from 37.6 to 315.2 mg / g.

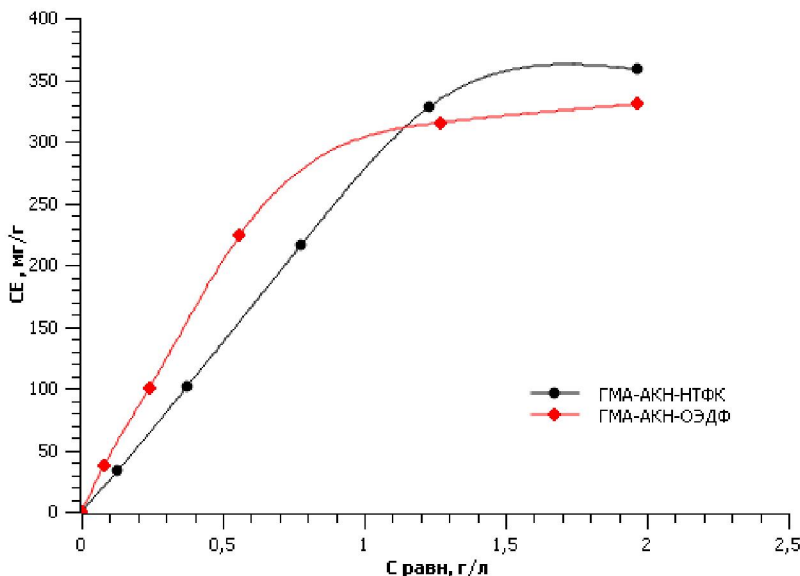


Figure 3 - Isotherms of sorption of Sr^{2+} ions from a solution of SrCl_2 ($\text{pH} = 5.8$) by the ions of GMA-AKN-NTFP and GMA-AKN-ODEF in H^+ form. The duration of the contact is 7 days.

It is known that selective ion exchanger sorbs metal ions, which depends on the pH of the medium, with change in which metal ions in solutions can be in different ionic states. The results of studies of the sorption capacity of chelating-forming ion exchangers based on GMA-AKN-NTFP and GMA-AKN-ODEF on strontium ions on pH are presented in Fig. 4. The pH was taken at intervals from 1.6 to 5.9. As can be seen from Fig. 3, in the pH range from 1.6 to 3.5, the maximum sorption capacity of the GMA-AKN-NTFP ion exchange (SC is 437.6 mg / g) is observed. As the acidity of the SrCl_2 solution decreases, pH 3.5-5.9, the sorption capacity of the ion exchanger gradually decreases. The sorption capacity of the GMA-AKN-ODEF ion in Sr^{2+} ions, from pH 1.6 to 3.5, is constant and amounts to 458.6 mg / g, and with the pH 4.6-6.9 SC of ion exchanger for Sr^{2+} ions begins to decrease by 358, 8 mg / g, respectively. Reduction of SC with increasing alkalinity of the medium is due, obviously, to competitive sorption of protons (H^+).

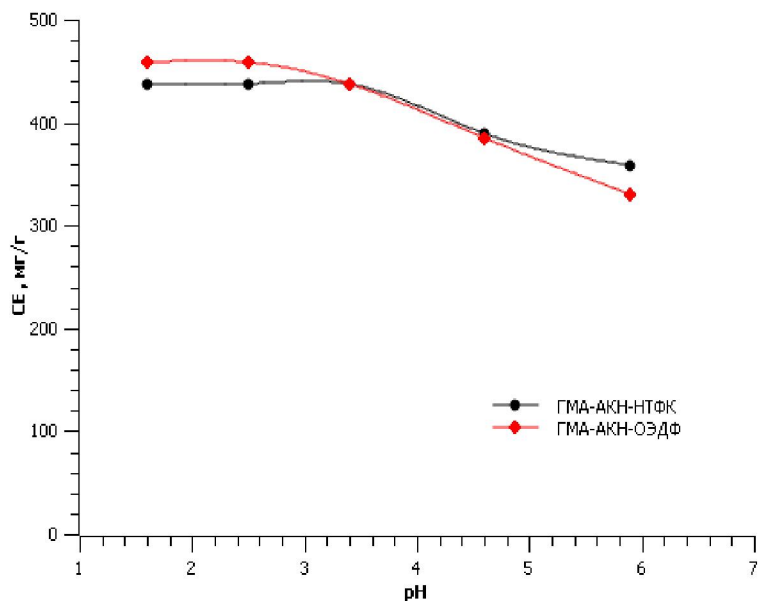


Figure 4 - Dependence of the sorption of chromium ions Sr by the ion exchangers GMA-AKN-NTFP ($C = 1.926 \text{ g / l}$) and GMA-ACN-ODEF ($C = 2.016 \text{ g / l}$) on the acidity of SrCl_2 solutions.

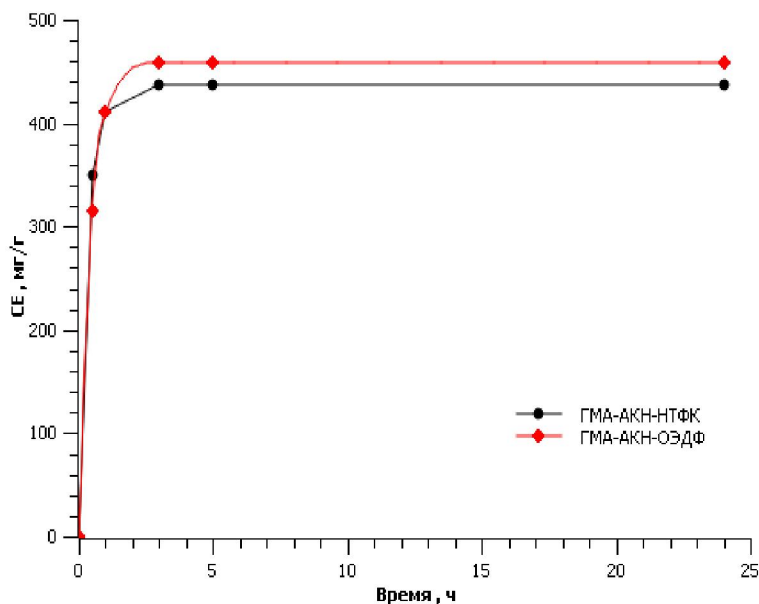


Figure 5 - Kinetic curves of sorption of Sr ions by ion exchangers of GMA-AKN-NTPK ($C = 1.926 \text{ g/L}$, $\text{pH} = 3.4$) and GMA-AKN-NTFP ($C = 2.016 \text{ g/L}$, $\text{pH} = 3.4$) versus time duration of contact with a solution of SrCl_2

The degree of saturation of the ion exchanger with the absorbed ions depends on the contact time of the sorbent with solutions. From figure 5, where the dependence of the SC of the ion exchanger GMA-AKN-NTFP on the time of its contact with a solution of SrCl_2 ($\text{pH} 3.4$, concentration of $\text{Sr}^{2+} 2.016 \text{ g/l}$ ions), it follows that the equilibrium is established after 2 hours and the kinetic curves of sorption of strontium ions the state of the GMA-ACN-ODEF ion-exchange resin and that between the model SrCl_2 solution containing 2.016 g/l of Sr^{2+} ions and having a pH of 3.4 occurs two hours later. Consequently, this ion exchanger has good kinetic properties.

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ЭПОКСИАКРИЛАТ ПЕН КОМПЛЕКСОНДАР НЕГІЗІНДЕГІ ЖАҢА КОМПЛЕКСТҮЗГІШ ИОН АЛМАСТЫРҒЫШТАР АРҚЫЛЫ СТРОНЦИЙ ИОНДАРЫН СОРБЦИЯЛАУ

Аннотация. Глицидилметакрилат (ГМА), акрилонитрил (АКН) және нитрилотриметилфосфон қышқылы мен оксиэтилендифосфон қышқылының поликонденациясы арқылы статикалық алмасу сыйымдылығы 0,1 н НСІ ерітіндісі бойынша 3,64 және 3,43 мг-экв/г болатын жаңа хелатты комплекстүзуші ион алмастырғыш шәйрлер синтезделіп алынды. Классикалық поляриграф әдісімен статикалық жағдайда стронций иондарын Sr^{2+} ГМА-АКН-НТФК және ГМА-АКН-ОЭДФ катиониттерімен сорбциясы зерттелді. Статикалық жағдайда стронций хлориді ерітіндісінен стронций иондарын сорбциялаудың ерітіндінің концентрациясына, рН ортасына, сондай ақ иониттің әсер ету уақытына қатынасы зерттелді. Бұл иониттер жоғары кинетикалық және сорбциялық сипаттамалары бар және оның сіңіру сыйымдылығы жоғары, өндірістік шайыр екені анықталды.

Тірек сөздер: комплекстүзуші ион алмастырғыштар, сорбция, стронций ионы, хелат, комплексондар, сорбциялық сыйымдылық.

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СОРБЦИЯ ИОНОВ СТРОНЦИЯ НОВЫМИ КОМПЛЕКСООБРАЗУЮЩИМИ ИОНИТАМИ НА ОСНОВЕ ЭПОКСИАКРИЛАТОВ И КОМПЛЕКСОНОВ

Аннотация. Поликонденсацией глицидилметакрилата, акрилонитрила и комплексонов нитрилотриметилфосфоновой кислоты (НТФК), оксиэтилендифосфоновой кислоты (ОЭДФ) были получены новые комплексообразующие иониты хелатной структуры со статической обменной емкостью по 0,1 н раствору НСІ 3,64 и 3,43 мг-экв/г. Методом классической полярографии в статических условиях изучена сорбция ионов Sr^{2+} комплексообразующими катионитами ГМА-АКН-ОЭДФ, ГМА-АКН-НТФК. Исследована сорбция ионов стронция в статических условиях из раствора хлорида стронция в зависимости от их концентрации и рН, а также времени их контакта с ионитом. Установлено, что они обладают высокими кинетическими и сорбционными характеристиками и превосходят по своей поглощающей способности известные промышленные иониты.

Ключевые слова: комплексообразующие иониты, сорбция, ионы стронция, хелаты, комплексоны, сорбционная емкость.