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OBTAINING OF PHOSPHORIC CATION-EXCHANGE RESIN FOR WASTE WATER TREATMENT

MUXAMEDJANOV TIMUR

Scientific researcher of Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Phone.: (0591) 191-1101, e-mail.: t.mukhamedjanov@uks.uz
**Corresponding author*

PULATOV KHAYRULLA

Professor of Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Phone.: (0593) 520-3660, e-mail.: hayrulla00796@gmail.com

NAZIROVA RANO

Professor of Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Phone.: (0588) 500-0551, e-mail.: kiyamova.malika@bk.ru

KHUSENOV ARSLONNAZAR

Professor of Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Phone.: (0590) 918-2564, e-mail.: sytk@tkti.uz

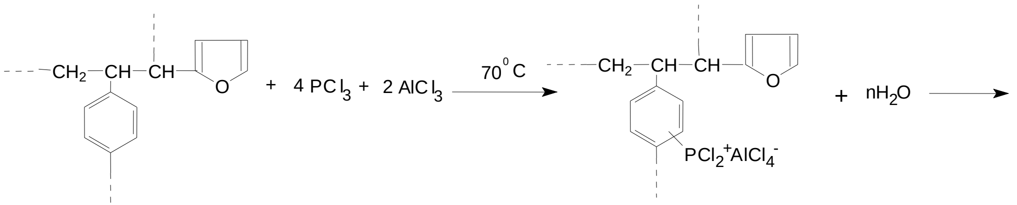
Abstract: The article presents the studies obtaining and research new polycondensation type phosphoric cation-exchange resin. The conditions for the phosphorylation of this polymer were selected from the experiments accumulated in relation to the phosphorylation reactions of low- and high-molecular compounds. The resulting polymer had an exchange capacity for a 0.1N NaOH solution – 5,5-5,6 mEq/g and contained 16,5% phosphorus. Based on the studies carried out, the optimal conditions for the synthesis of the styrene-furfural polymer are assumed to be: the reaction temperature is 90°C, the concentration of the ZnCl2 catalyst is 0.07 mol per mole of furfural, and the molar ratio of styrene to furfural is 1:1. There was studied an interaction of the cation exchanger in Na- and H-forms with solutions of salts of copper sulfate, nickel, cobalt, sodium chloride, calcium and uranyl nitrate. In order to elucidate the mechanicm of sorption of the cations of these metals, were taken the IR spectra of the cation exchanger in the H and Na form, saturated with copper ions. The less dissociated phosphoric acid groups, the stronger hydrogen bond forms phosphoryl oxygen with OH groups. Therefore, it can be expected that as the cation exchanger is saturated with sodium, the maximum of the band corresponding to the phosphorus-oxygen bond vibrations will slightly shift to longer wavelengths as a result of the destruction of the weaker hydrogen bond.

Keywords: OH groups, Na- and H-forms, styrene, phosphorus, NaOH.

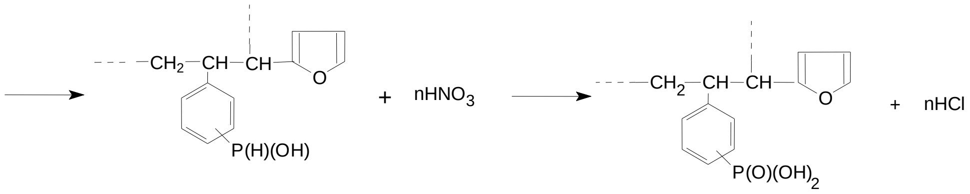
Introduction. One of the most important scientific directions is the purposeful development of new polymeric materials, including ion-exchange polymers with desired properties. The use of ion-exchange polymers in various industries requires the creation of ion exchangers with high thermal and chemical stability, resistance to the action of ionizing radiation and a number of specific properties. The creation of a wide range of domestic ion-exchange materials allows for a more complete extraction of metal ions from complex ores and various metallurgical products. Despite a significant number of studies devoted to the ion-exchange method for the extraction and separation of metals, the solution of this problem continues to be an important urgent task for the hydrometallurgical industry. In view of the widespread use of ion-exchange polymers in many areas of the national economy, science and technology, the requirements imposed by the industry on ion exchangers with regard to their thermal and chemical resistance, radiation resistance, mechanical strength, selectivity to certain metal ions, etc. are increasing. These requirements are no longer met by such universal ion exchangers as KU-1, KU-2, SBS, etc., despite the fact that they have high rates of sorption and kinetic properties [1]. Among the known ion exchangers, an important place from the physicochemical point of view is occupied by phosphorus-containing ion exchangers [2]. These ion exchangers have a number of valuable properties, such as high selectivity, thermal and chemical resistance, radiation resistance, etc., which allows them to be used in many areas of industry and the national economy [3]. At present, a large amount of experimental material has been accumulated for obtaining various types of phosphorus-containing ion exchangers [3]. The study of the properties of these ion-exchange polymers made it possible to outline the main ways of their use in many fields of science and industry [4].

Object and methods of research. The object of the study was a polycondensation type phosphate cation exchanger based on a styrene-furfural polymer, which is obtained by the following method: the styrene-furfural polymer previously swollen in phosphorus trichloride was placed in a three-necked flask with a stirrer and a reflux condenser and phosphorylated with phosphorus trichloride as a catalyst using aluminum (anhydrous). The molar ratio of the reagents polymer: aluminum trichloride: phosphorus trichloride = 1: 2: 4. The reaction was carried out at 75°C for 6 hours, after which the ion exchanger was stripped of phosphorus trichloride and washed with humidified alcohol, decreasing the concentration successively to 50, 30, 20%, and then washed with cooled distilled water until the wash water was neutral. To determine the dynamic exchange capacity (DEC), a sample of ion exchangers from the flask was transferred into a cylinder with a capacity of 100 sm3 and a layer of ion exchangers was compacted by tapping the hard surface of the bottom of the cylinder until sedimentation ceased. The volume of the ion exchangers was brought to 100 sm3 and with the help of distilled water the ion exchanger was transferred into the column, making sure that it was drained from the column, leaving a layer with a height of 1-2 sm above the level of the ion exchangers. The ion exchanger in the column was washed with distilled water, passing it from top to bottom at a rate of 1,0 dm3/h. In this case, the ion exchanger was washed from acid (according to methyl orange). When a working solution of 0.1 N concentration was passed through a column with ion exchanger, the filtrate was collected in cylinders with a capacity of 250 sm3. In the second and subsequent saturation cycles, before the appearance of ions of the working solution in the filtrate (determined after the first cycle), the filtrate was collected in 100 and 250 sm3, respectively, the concentrations of the working solution. After the ions of the working solution appeared in the proportion of the filtrate, the total volume of the filtrate was calculated. To determine the full dynamic exchange capacity, the solution was continued to flow until the concentration of the filtrate became equal to the concentration of the working solution. In this case, the saturation control is carried out by titrating the sample with an acid solution with a mixed indicator until the color changes. The value of the static exchange capacity (SEC) for calcium, magnesium, copper, nickel, and cobalt ions was calculated for ion exchanger samples in contact with a solution of calcium, copper, nickel, and cobalt salt and a model solution for seven days. To record IR spectra on a Specord IR 75 spectrophotometer, individual weighed portions of ion exchangers were treated with nickel sulfate solutions and model solutions with different pH values. Then, according to [5], KBr tablets were prepared and tested.

Results and their discussion. In [6], we showed the possibility of obtaining new sulfonic cation exchangers based on a new previously unknown styrene-furfural polymer. Proceeding from this, considering it very promising in terms of achievements in the field of synthesis of ion exchangers, we used a styrene-furfural polymer as a polymer matrix in the reaction of polymer-analogous transformations in order to obtain phosphorus-containing cation exchangers. The conditions for the phosphorylation of this polymer were selected from the experiments accumulated in relation to the phosphorylation reactions of low- and high-molecular compounds [7]. The reaction scheme for obtaining a phosphate cation exchanger by phosphorylation of a styrene-furfural polymer with its subsequent oxidation in nitric acid can be represented as follows:



Hydrolysis reaction



Reaction of the oxidation of the cation exchanger with nitric acid

The resulting polymer had an exchange capacity for a 0.1N NaOH solution – 5,5-5,6 meq/g and contained 16,5% phosphorus. In order to increase the exchange capacity, i.e. conversion of phosphine groups into phosphine, the polymer after washing with water was contacted for 7 hours at a temperature of 60°C with concentrated nitric acid. As a result, most of the phosphinic acid groups are oxidized to phosphinic acid groups. At the same time, the phosphorus content in the polymer does not change, the exchange capacity increases to 7,6-8,0 meq/g [8-10]. Table 1 shows the main properties of the phosphate cation exchanger obtained at different molar ratios of styrene to furfural.

Table 1. Influence of the ratio of the starting materials on the properties of the resulting cation exchanger.

Indicators		Unit of measurement	The molar ratio of styrene to furfural		
			1:2	1:1.5	1:1
Bulk weight		g/ml	0.68	0.6	0.5
Specific volume		ml/g	2.2	2.8	3.5
Static exchange capacity:					
0.1 N NaOH of solution		meq/g	5.6	6.5	7.0
0.1 N NaCl of solution		-//-	0.8	0.9	1.0
0.1 N solution of CaCl$_2$	H-form	-//-	2.6	3.0	3.2
	Na-form		2.8	3.2	3.6
0.1 N solution of MgCl$_2$	H-form	-//-	2.6	3.0	3.4
	Na-form		2.8	3.4-4.2	3.6-4.2
0.1 N solution of CuSO$_4$	H-form	-//-	1.8	2.0	2.4
	Na-form		2.0	2.2	2.8
Mechanical strength		%	99.5	99.0	99.0

From the data in Table 1 it can be seen that the phosphate cation exchanger with the best properties was obtained at a molar ratio of styrene to furfural of 1: 1. Based on the studies carried out, the optimal conditions for the synthesis of the styrene-furfural polymer are assumed to be: the reaction temperature is 90°C, the concentration of the ZnCl$_2$ catalyst is 0.07 mol per mole of furfural, and the molar ratio of styrene to furfural is 1: 1.

For phosphate cation exchangers, various types of metal bonds with ionogenic groups of the ion exchanger are characteristic: ionic bonds, mixed ion-coordination bonds and purely coordination bonds. The type of bond is determined by the ability of a particular metal to form donor-acceptor complexes and the degree of dissociation of the ion exchanger. For metals capable of complexation, the formation of ion-coordination bonds with a uniform distribution of electron density over the four-membered cycle is possible. It was of interest to study such properties of the studied phosphate cation exchanger, such as its sorption capacity for copper, nickel, calcium, sodium, cobalt and uranyl ions, which are important in modern technology, to reveal the influence of various factors on the sorption process of these cations, as well as the mechanicm of their sorption with using IR spectroscopic analysis. For this purpose, the interaction of the cation exchanger in Na- and H-forms with solutions of salts of copper sulfate, nickel, cobalt, sodium chloride, calcium and uranyl nitrate was studied. The research results are shown in Table 2 [10-12].

Table 2. Sorption of metal cations by phosphate cation exchanger.

0.1 N solutions	H-form			Na- form	
	pH solutions	Sorbed, mg-eq/g	Partition coefficient, ml/g	pH solutions	Sorbed, mg-eq/g
NaOH	13	6.6-7.6	184	-	-
NaCl	8.13	0.8-1.0	11.5	-	-
$CaCl_2$	6.5	1.1-1.2	120	6.5	3.57-3.6
$CuSO_4$	4.8-5.0	1.2-1.3	66	4.8-5.0	1.75-1.8
$CuSO_4$	11	2.64-2.7	733	11	3.08-3.1
$CuSO_4$	-	-	-	2.35	1.0-1.1
$NiSO_4$	7.6	1.1-1.2	20	2.25	1.0
$NiSO_4$	10	2.0-2.1	84	3.8	3.6
$NiSO_4$	-	-	-	7.6	2.0
$NiSO_4$	-	-	-	10	3.75-3.8
$CoSO_4$	8	2.0-2.05	35	2.36	0.8-0.9
$CoSO_4$	-	-	-	3.18	2.4
$CoSO_4$	-	-	-	8	2.65

The data in Table 2 indicate the effect of the nature of the cation on the sorption capacity. It was found that the studied cations are sorbed by the cation exchanger differently and, according to their ability to sorption, can be arranged in the following order:

$$\mathbf{Ni^{2+} > Cu^{2+} > Co^{2+} > Na^{+}}$$

In order to elucidate the mechanicm of sorption of the cations of these metals, we took the IR spectra of the cation exchanger in the H and Na form, saturated with copper ions. According to the literature data, the vibration frequencies for phosphoric acid groups are in the range of 700-2560 sm^{-1}. In the spectrum of the cation exchanger in the H-form, bands are observed at 1150 sm^{-1}, corresponding to stretching vibrations of the phosphorus-oxygen bond. The absorption band at 1150 sm-1 does not disappear in the spectrum of the cation exchanger in the Na-form. The tested cation exchanger contains phosphoric acid groups differing in their acidic properties pK1 = 2.8; pK2 = 7.5 [13-14]. The less dissociated phosphoric acid groups, the stronger hydrogen bond forms phosphoryl oxygen with OH groups. Therefore, it can be expected that as the cation exchanger is saturated with sodium, the maximum of the band corresponding to the phosphorus-oxygen bond vibrations will slightly shift to longer wavelengths as a result of the destruction of the weaker hydrogen bond. In the spectrum of the cation exchanger in the H-form, there are not sharp broad bands in the range of 2600-2860 sm^{-1}, 2100-2600 sm^{-1} related to the stretching vibrations of P-OH linked by hydrogen bonds. These bands disappear in the spectrum of the sodium-saturated cation exchanger. When considering the spectra of the cation exchanger saturated with metal ions, in contrast to the spectrum of the cation exchanger in the H-form, bands appear at 1060 sm^{-1} for uranyl and 1055 sm^{-1} for copper and nickel [15].

Conclusion. Phosphorylation of a styrene-furfural polymer has been used to obtain and investigate a phosphate cation exchanger characterized by high thermal-chemical resistance and mechanical strength. The structure and properties of the obtained cation exchanger were studied using chemical methods of analysis in combination with IR spectroscopy, potentiometry, photocalorimetry, etc. It was shown that ions of copper, nickel, cobalt and uranyl ion are sorbed by phosphoric acid cation exchanger due to ion exchange and partly due to the formation of coordination bonds with an ionic group of a cation exchanger. The analysis of the data obtained indicates that the studied phosphate cation exchanger is sufficiently high. sorption ability to ions of the tested metals.

List of used literature

1. A.A. Yuldashev, F.B. Igitov, T.T. Tursunov, Kh.L. Obtaining of polycondensation type anion-exchange polymer, Journal of Advanced research in dynamical and control systems, Special issue, **7**, pp.2125-2132, (2020)
2. U.I. Sharipova, R.A. Nazirova, Kh.L. Pulatov, B. Kedelbayev, Study properties of phosphate cation exchanger, International Journal of Advanced Research in Science Engineering and Technology, **12**, pp.56-59, (2019)
3. A.A. Yuldashev, Sh.A. Mutalov, Kh.L. Pulatov and etc. Polycondensation anion-exchange polymers, Science and education, **1**, pp.25-34, (2020)
4. A.A. Yuldashev, Sh.A. Mutalov, Kh.L. Pulatov and etc. Sorption of molybdenum ions by anion exchangers of polycondensation type, Composition materials, Special issue, pp.160-162 (2020)
5. Kh.L. Pulatov, S.M. Turabjanov, Sorption properties of ion-exchange resins of the polycondensation type, Universum: Technical sciences, **12**(33), (2016)
6. I.A. Geyvandov, A.N. Visloguzov and etc. Calculation of the concentration of ions Ca^{2+}, Mg^{2+} and Na^{+} in the cation exchanger and the solution in equilibrium with it according to experimental data, Bulletin of the North Caucasus State Technical University, Series "Physicochemical", **1** (8), Stavropol: SevKavGTU, pp. 84-90, (2004)
7. Kh.L. Pulatov, S.M. Turabjanov and etc. Study of the sorption capacity of phosphate cation exchanger, Universum: Technical sciences, **3** (48), (2018)
8. A.G. Kasikov, N.S. Areshina, I.E. Malts, T.R. Zinkevich, M.A. Mikhailenko, Sorption purification of solutions of copper-nickel production using ion exchangers "Purolite", Sorption and chromatographic processes, **5**, 11, pp.689-693 (2004)
9. M.A. Sinyakova et al. Features of sorption of copper (II) and aluminum (III) by various cation exchangers, Applied Chemistry, **3**, 73, pp. 388-390 (2000)
10. Kh.L. Pulatov, S.M. Turabjanov, Investigation of the possibility of obtaining ion exchangers for wastewater treatment based on secondary products of chemical enterprises, Chemical Industry, 5, pp. 231-235 (2017)
11. A.A. Yuldashev, Sh.A. Mutalov and etc. Weakly basic anion-exchange polymers, Chemistry and chemical technology, **2**, pp. 31-33 (2018).
12. Vignoli Claudio Nogueira, Bah́e Jackeline M.C.F., Marques M̓onica R.C. Evaluation of ion exchange resins for removal and recuperation of ammonium-nitrogen generated by the evaporation of landfill leachate, Polym.Bull., **12**, pp. 3119-3134, (2015)

13. Rajindar Singh, Development of Hybrid Processes for High Purity Water Production, Emerging Membrane Technology for Sustainable Water Treatment, Chapter **13**, pp. 327-357, (2016)

14. Kh.L. Pulatov, S.M. Turabjanov, T.T. Tursunov, R.A. Nazirova Furfural based policondensation type sulfonic acid cation-exchange resin, Austrian Journal of Technical and Natural Sciences, **5-6**, pp. 75-80. (2016)

15. Kh.L. Pulatov, S.M. Turabjanov, T.T. Tursunov, R.A. Nazirova Obtaining of phosphoric acid cation-exchange resins for wastewater treatment from heavy metal ions, Proceedings of the International conference on integrated innovative development of Zarafshan region: achievements, challenges and prospects, Navai, 26-27 October, pp.365-369, (2017).

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