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Furfural based cation-exchange resin

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By polycondensation of styrene with furfural obtained new polymer which can be used as a polymeric matrix for introduction ionogenic groups. Methods of the chemical analysis, IR- and mass-spectroscopy confirm structure of obtained polymer. By sulfonation of styrene-furfural polymer obtained and researched the sulfonic acid cation-exchange resin with high chemical and thermal, and mechanical durability.

Keywords: cation-exchange resins, sorption, furfural, styrene, polycondensation, sulfonation

I. INTRODUCTION

Obtaining of ion-exchange resins and areas of their application extends now fast rates. From the ecological point of view, it is defined by the practical and theoretical importance of ion-exchange polymers in various areas of a science and technics. Application of ion-exchange polymers leads to simplification of processes of division of mixes of ions, demineralization and softening of waters, clearing and concentration of solutions of ions of colour and rare metals which contain in industrial and waste waters of hydrometallurgical manufactures.

Despite considerable number of the researches devoted to ion-exchange method of extraction and division of metals from various solutions, softening of waters, the decision of these problems continues to remain a paramount problem for a hydro iron and steel industry and water preparation. [1]. For manufacture creation ion-exchange polymers in our Republic there is a raw-material base - a waste and secondary raw materials petrochemical, chemical, agricultural, cotton scrape and the hydrolytic industry. The enterprises agricultural, cotton scrape and the hydrolytic industry of our Republic are the richest sources of cheap, accessible and large-tonnage by-products being the basic and perspective raw materials for obtaining of various polymers including ion-exchange resins with the improved indicators of the basic properties [2]. Perspectivity and validity of a choice of this product as initial raw materials for creation of ion-exchange resins it is caused by presence in its structure heterocyclic furan nucleus which allows to obtain polymers with universal thermal-chemical stability and mechanical durability. Noted also has defined statement of the given work having for an object receptions new earlier not described in the literature sulfonic acid cation-exchange resins with in advance set properties, by sulfonation of new styrene-furfural polymer. The task in view decision has allowed, to obtain sulfonic acid cation-exchange resins, possessing enough in high exchange capacity to ions of heavy metals at high thermal-chemical stability and mechanical durability [3].

II. EXPERIMENTAL

On obtaining of sulfonic acid cation-exchange reins as a polymeric matrix for introduction sulphonic-acid groups we had been used polymer obtained by polycondensation of furfural with styrene. Use instead of divinyl benzene furfural is caused on the one hand by availability of the last in the conditions of our Republic, and the raised thermal-chemical stability of some cation-exchange resins, owing to presence in structure of a polymeric matrix of aromatic ring and furan cycles. For elimination of internal pressure and improvement of kinetic properties of cation-exchange resins, polymer preliminary subjected to swelling in ethanol, dichlorethane, dimethylformamide, and the concentrated sulfuric acid. The greatest degree of swelling to 180 % at T=25°C was observed on using of sulfuric acid. It has been studied the nature influence sulphonating agent on degree of sulfonation. We had been used the concentrated sulfuric acid and 5 % solution of oleum. On using of the last in the course of reaction of sulfonation of polymer is strongly crushed, i.e. becomes fragile.

On the basis of the spent researches of influence of various factors on process sulfonation of styrene-furfural polymer following conditions of reaction are established: mole parity of styrene to furfural is 1:1, duration of reaction of 6-7 hours, temperature of sulfonation 70°C, sulfonating agent - the concentrated sulfuric acid, used preliminary bulked up polymer in concentrated sulfuric acid.

III. RESULTS AND DISCUSSION

Good results of size of exchange capacity on 0.1 N solution of NaOH - 3 mg-ekv/g and on 0,1 N solution of NaCl - 3 mg-ekv/g have been received at usimg in quality of sulfonating agent the concentrated sulphuric acid. Influence of duration and temperature of reaction to degree of transformation of polymer, i.e. degree of sulfonation has been investigated. Properties of sulfonic acid cation-exchange resin obtained in optimum conditions are resulted in table 1.

TAB. 1. Physicochemical parameters of cation-exchange resin KU-FS

Indicators		Unit of measure	Mole ratio of styrene to furfural		
			2:1	1.5:1	1:1
Bulk weight		g/ml	0.68	0.6	0.5
Specific volume		ml/g	2.5	2.8	3.4
Static exchange capacity (SEC):					
on 0.1 N solution of NaOH		mg-ecv/g	3.2	3.4	3.6
on 0.1 N solution of NaCl		mg-ecv/g	2.6	2.8	3.4
on 0.1 N solution of $CaCl_2$	H-form	mg-ecv/g	2.6	3.3	4.4
	Na- form		3.8	4.4	5.2
on 0.1 N solution of $MgCl_2$	H- form	mg-ecv/g	1.6	2.0	3.6
	Na- form		2.0	2.4	4.8
on 0.1 N solution of $CuSO_4$	H- form	mg-ecv/g	0.9	1.5	3.8
	Na- form		1.0	2.0	4.2
Mechanical durability		%	99	98.5	99

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The obtained data of the chemical analysis have shown, that values of bromic numbers correspond for: initial furfural - 161.0, oligomer - 178.5, outcast polymer - 175.8, i.e. values of bromic numbers of the last differs from value of bromic number initial furfural a little. According to the received data, it is possible to assert, that double connections -CH=CH- furan cycle don't participate in polycondensation reaction.

Data received by the chemical analysis will be co-ordinated with results mass and IR-spectroscopic researches. So mass spectroscopic researches of structure of polymer show, that the available peak of an ion with mass unit equal 183 corresponds to molecular weight of an elementary link of styrene-furfural polymer. Peaks of ions with weight unit equal 85 and 98 it is described by the formula of a following structure (fig. 1).

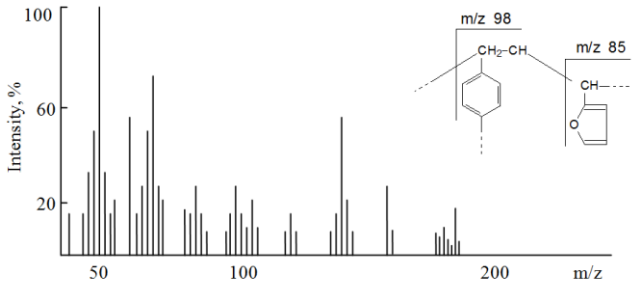
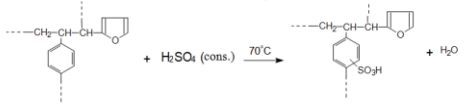


FIG. 1. A mass spectrum outcast styrene-furfural polymer

Peaks of ions of small intensity obviously specify in presence of insignificant quantities of not reacted initial components of reaction of styrene and furfural. IR-spectra of initial furfural and the obtained outcast polymer have shown characteristic strips in the field of 1030-1050 sm^{-1} corresponding to fluctuations of interfaced double communications of a heterocycle of furfural. Strips of absorption in the field of 1690-1670 sm^{-1} corresponding aldehydic group of furfural, in a spectrum of outcast polymer are absent. The received researches allow to draw a conclusion that reaction of polycondensation of styrene with furfural proceeds under the following scheme:

On the IR-spectrum of sulfonated polymer of a strip of absorption in the field of 1260-1150 sm^{-1}, 1060-1010 sm^{-1}, according to literary data, correspond to SO_3H-groups. Obtained sulfonic acid cation-exchange resin is monofunctional. In the IR-spectrum of sulfonic acid cation-exchange resin is absent strips of absorption in the field of 2600-3200 sm^{-1}, 3400 sm^{-1} corresponding fluctuations hydroxyl and carboxylic groups. Strips deformation fluctuation -C-H- in the field of 900-860 sm^{-1} correspond 1,3 replaced benzene ring of styrene and in 800-860 sm^{-1} - 1,3,4 replaced benzene ring of styrene [4].

Proceeding from it sulfonic acid cation-exchange resin and the reaction scheme of sulfonation of styrene-furfural polymer it is possible to present structure as follows:



From the basic chemical properties of ion-exchange resin the great value has ion-exchange ability which characterizes ion-exchange resins for the purpose of an estimation of their operational properties. Its size, basically, depends on quantity ionogenic groups of ion-exchange resin, their degrees of dissociation, and also the nature and concentration of exchanging ions.

As is known, at strong acid resins value of pH environments is practically does not influence of size of exchange capacity. Static exchange capacity of obtained sulfonic acid cation-exchange resin defined on absorption of ions of sodium as in neutral, and the alkaline environment.

Besides defined exchange capacity of cation-exchange resin in the Na-form on calcium and magnesium ions. In table 2 values of size of exchange capacity and size of a seeming constant dissociation of active groups of cation-exchange resin (pK_H) are resulted.

For an establishment of functionality and their degree of dissociation there has been made the curve potentiometric titration. The seeming constant of dissociation (pK) of ionogenic groups cation-exchange resin, found of a titration curve on Grissbakh is equal pK_H=1.8-2.2. Value of pK - a seeming constant of dissociation also testifies, that obtained cation-exchange resin concerns group of strong acid ion-exchange resins.

Presence of SO_3H-groups at structure of obtained cation-exchange resin is confirmed with absorption IR-spectra of sulfonated polymer. So SO_3H-groups in a spectrum of sulfonated polymer are characterised by a strip of absorption in the field of 1200 sm^{-1} that will be co-ordinated with literary data. From given tab. 2 it is visible, that size of exchange capacity of cation-exchange resin received of a curve potentiometric titration, calculated under the content of sulphur and practically differ from values of static exchange capacity a little.

TAB. 2. Exchange capacities of sulfonic acid cation-exchange resin

Ioniogenic group of cation-exchange resin	Exchange capacity, mg-ecv/g:					pK
	The theoretical	Under the content of % of sulphur	On titration curves	Static exchange capacity		
				on 0.1 N solution of NaOH	on 0.1 N solution of NaCl	
	3.8	3.53	3.4 – 3.5	3.4 – 3.6	3.2 – 3.4	1.8 – 2.2

As is known, in many regions of our Republic used in a life and on manufacture water has high rigidity which sometimes reaches to 12 mg-ekv/l instead of according to standards - 2 mg-ekv/l. For the purpose of use possibility cation-exchange resins KU-FS in water preparation processes, investigated its sorption ability to ions of calcium, magnesium, sodium from the waters brought by us for research from some areas of the Surkhandarya area and Karakalpakstan [5]. Cation-exchange resin is tested in H- and Na-forms. Results of researches are resulted in table 3.

TAB. 3. Application of cation-exchange resin in processes of demineralization of waters

Cation exchange resin KU-FS	Shurchi district of Surkhandarya		Muynak district of Karakalpakistan		Tahiatash district of Karakalpakistan	
	Hardness of water, mg-ecv/l:					
	before	after	before	after	before	after
at H-form	12.2	4.05	10.7	3.2	11.0	3.8
at Na-form		2.2		2.5		2.4

From table 3 data it is visible, that at use of the examinee cation-exchange resina KU-FS in processes of softening waters, hardness of water after contact with cation-exchange resin corresponds to requirements of standards.

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IV. CONCLUSIONS

By polycondensation of styrene with furfural obtained new polymer which can be used as a polymeric matrix for introduction of ionogenic groups. Methods of the chemical analysis, IR- and mass spectroscopy confirm structure of the obtained polymer. By sulfonation of styrene-furfural polymer obtained and investigated sulfonic acid cation-exchange resin, differing high thermal-chemical stability and mechanical durability. On the basis of the spent researches of optimum conditions of obtaining cation-exchange resin are defined. The structure and properties of obtained cation-exchange resin is investigated with application of chemical methods of the analysis in a combination with IR-spectroscopy, potentiometry, photocolorimetry, etc. It is established, that obtained cation-exchange resin is nonfunctional, contains only sulphonic-acid group, that allows to use it in processes of an ionic exchange in neutral and alkaline environments.

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