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TECHNOLOGY FOR THE PRODUCTION OF ION-EXCHANGE POLYMERS BASED ON FURFURAL AND ITS DERIVATIVES AND THEIR APPLICATION IN THE TREATMENT OF WASTEWATER FROM HYDROMETALLURGICAL INDUSTRIES

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ABSTRACT

The article substantiates the feasibility of using furfural a product of the hydrolysis industry as a base monomer in the synthesis of ion-exchange resins. A methodology for obtaining new ion-exchange polymeric materials based on furfural as a secondary raw material is presented, along with the results of studies on their sorption, physicochemical, and operational characteristics. The identify cation of effective practical applications of the synthesized ion exchangers for the treatment of industrial wastewater and natural waters from chemical enterprises, including hydrometallurgical facilities, is of considerable scientific, technical, and applied significance.

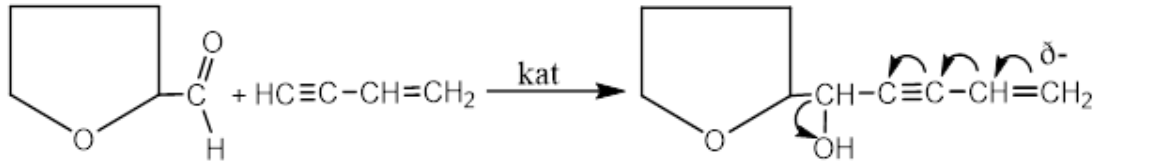
1. INTRODUCTION

The scale of industrial organic synthesis has now reached such proportions that the issue of the limited availability of natural oil and gas resources required to meet its demands is becoming increasingly urgent. Under the conditions of modern scientific and technological advances, polymer composite materials formed through the combination of components of different chemical nature represent a new class of materials that, in terms of overall performance characteristics, significantly surpass the properties of their individual constituents [1-3]. Owing to their composite characteristics, such materials exhibit unique physicomechanical, magnetic, and optoelectronic properties, high chemical and thermal stability, and enhanced resistance to various types of radiation. In recent years, the development of materials and compositions with predetermined properties containing phosphate groups has gained increasing importance.

Phosphate-containing natural compounds are components of widely used medicinal pharmaceuticals. Compounds with phosphate groups constitute not only the foundation of inorganic chemistry but also the fundamental basis of vital processes in living organisms. The ability of phosphate groups to undergo facile modification with organic compounds is of both practical and theoretical significance and has generated considerable scientific interest among researchers [4-6]. Foreign literature sources devoted to the synthesis and investigation of ion-exchange materials based on furfural and its derivatives are limited to a small number of publications and are predominantly of a patent nature [7-9]. One of the earliest studies aimed at the synthesis of ion exchangers focused on the production of carboxyl and sulfo-cationites through the polycondensation of furfural with β-furylacrylic acid, benzenesulfonic acid, and *n*-phenolsulfonic acid. These cationites contain carboxyl, sulfo, and phenolic hydroxyl groups. Although sulfo-cationites are produced from relatively inexpensive raw materials, such as lignin, the sulfation process is random in nature, resulting in ion exchangers with a disordered structure. Simultaneously, both ion-exchange and electro-exchange properties were observed in the polymer obtained through the polycondensation of polyhydric phenols with furfural [9-11]. This polymer is characterized by reducing properties, with a capacity to reduce trivalent iron to divalent iron of 6.5 mg-eq/g. To improve the kinetic characteristics during the synthesis of electro-ion-exchange polymers, pre-sulfonated phenols were used, which led to a slight increase in the reducing capacity up to 7.5 mg-eq/g. The use of furfural as a crosslinking agent in the production of ion-exchange materials and the analysis of the structure of these polymers will be considered in greater detail, as the results obtained can be applied in further studies on the synthesis of nitrogen-containing anion exchangers. Among the earliest works devoted to the synthesis of ion exchangers are studies on the production of carboxyl and sulfo-cationites through the polycondensation of furfural with *p*-furylacrylic acid, benzenesulfonic acid, and *n*-phenolsulfonic acid [12-14]. Moreover, one of the most dynamically developing areas of modern organic chemistry is the synthesis of highly reactive compounds through the introduction of unsaturated groups into the structure of organic molecules. The incorporation of a vinyl group opens virtually unlimited possibilities for the use of divinylfurfuryl ethers in the targeted organic synthesis of multifunctional furan compounds [15-17]. However, the widespread application of divinylfurfuryl ethers is limited by the lack of simple and technologically convenient methods for their synthesis. In contrast to alkyl vinyl ethers, they have been studied to a much lesser extent; their chemical properties are distinguished by specificity due to the presence of additional functional groups, which makes them prone to electrophilic and radical reactions. In this context, the synthesis of silsesquioxanes and (oligo)polymers, which enhance the mechanical strength and thermal stability of compositions, as well as the study of their properties and the development of technologies for producing ion exchangers based on them, becomes particularly important [18].

2. EXPERIMENTAL PART

In this study, the synthesis 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% (by monomer mass) of the initiator dinitrile-azobisiminodiacetic acid (DAA). The flask was equipped with a thermometer and placed on a magnetic stirrer, then heated at 85–120 °C for 2 hours. After the reaction was complete, the viscous, yellowish, and solidifying polymer Polyphos 1 was washed three times, purified, and dried to constant weight.

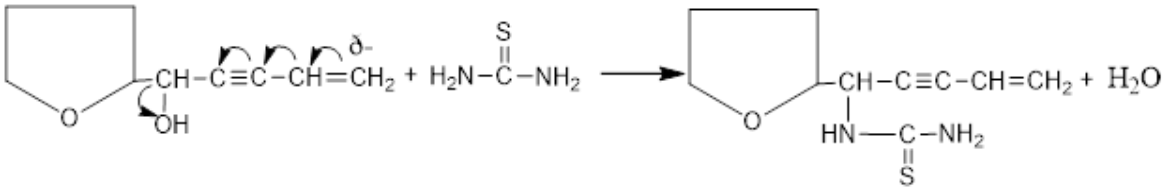


1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-ol

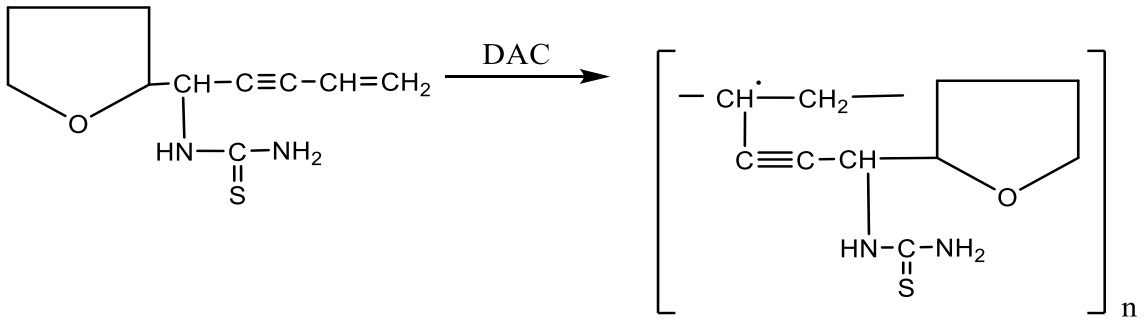
Data on the direct vinylation of furfuryl alcohols with vinylacetylene are extremely limited. Considering the potential of furfural to undergo the Cannizzaro reaction in an alkaline medium, furfuryl alcohol was chosen. The reaction to produce divinylfurfuryl ether was carried out using furfuryl alcohol and vinylacetylene in an alkaline system at room temperature and atmospheric pressure, resulting in the formation of 1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-ol.

The resulting intermediate compound possesses broad potential for modification with various substances. In particular, the introduction of compounds containing a non-bonded electron pair enables the synthesis of highly reactive compounds. Accordingly, the intermediate was modified with thiourea, sodium tripolyphosphate, and polysilicic acid to obtain an inorganic-organic ion exchanger. The reaction was carried out in the following sequence.

First, thiourea reacts with the hydroxyl group of the intermediate compound according to the following scheme.



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



To purify the obtained ion exchanger, an extraction method using various solvents was employed. The separation method, based on the differing solubilities of the starting, intermediate, and final products in various solvents, ensures a high level of substance purity. Accordingly, a solvent was selected that does not dissolve the final product but is capable of dissolving the starting and intermediate compounds. The extraction results are presented in the following table (table 1).

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Table 1. *Solubility of reagents and reaction products in various solvents*

Solvents	**Isopropyl alcohol**	**Octane**	**Isobutyl alcohol**	**Heptane**	**Toluene**	**Hexane**	**Amyl alcohol**	**Decane**	**Ethyl alcohol**	**Dimethylformamide (**
Substances										
Furfural	+	+	+	+	-	-	-	-	-	-
Vinylacetylene	+	+	+	-	+	-	-	-	+	-
Sodium tripolyphosphate	+	+	+	+	+	+	+	+	+	-
Product										
Polifos-1	+	+	+	-	+	-	-	-	-	+

When selecting a solvent for the extraction method, the solubility of the reagents and reaction products in various solvents was taken into account. Dimethylformamide proved to be the most suitable extractant for this reaction system due to its dipole moment and selective dissolving ability compared to other solvents. Moreover, the insolubility of the intermediate and starting compounds allowed the substance to be isolated in a pure form.

In the first layer of the extraction mixture, unreacted substances and ether-soluble components (KOH + DMSO + furfural) were identified, while in the second layer, the ether-insoluble synthesis product was found, which was 1-(1-(tetrahydrofuran-2-yl)pent-4-en-2-yn-1-yl)thiourea.

In dimethylformamide, the pure polymer was isolated using the extraction method, and its physical properties were studied. The viscosity of polydivinylfurfuryl sodium tripolyphosphate (before the addition of polysilicic acid) was measured using a HAAKE Viscotester 2 Plus viscometer and can be represented in the following graph.

3. Conclusion

The conducted studies confirm that the synthesis of ion-exchange polymeric materials based on furfural and its derivatives is both scientifically and practically justified and represents a promising direction. In the context of limited oil and gas resources, the use of furfural a product of the hydrolysis industry as a valuable monomer provides a resource-saving and economically efficient solution. The inorganic-organic ion exchangers obtained with the involvement of phosphate groups, thiourea, and polysilicic acid exhibit high reactivity. The presence of functional phosphate, thiocarbamide, and silicon-containing fragments in their structure enhances their sorption properties and complex-forming ability. It has been established that the intermediate compounds formed during the synthesis of divinylfurfuryl ether and its subsequent modification create an ordered structure during polymerization. The high efficiency of dimethylformamide as a selective solvent in the purification of the product by extraction has been demonstrated, allowing the isolation of a polymer with a high degree of purity. The obtained polymer, Polifos-1, exhibits favorable physicochemical characteristics, including

viscosity and stability. The incorporation of polysilicic acid contributes to increased mechanical strength and thermal resistance of the composite material. The results of the study indicate that the furfural-based phosphorus- and sulfur-containing ion-exchange polymers can be effectively used as sorbents for the treatment of wastewater from hydrometallurgical and chemical industry enterprises. They provide efficient removal of heavy metal ions through complexation and ion-exchange mechanisms.

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