

SYNTHESIS AND CHARACTERIZATION OF ETHYLENEDIAMINE-STRUCTURED TERNARY CO-OLIGOMERS OF 4-ISOPROPENYLPHENOL, STYRENE AND MALEIC ANHYDRIDE AS A SORBENT FOR THE EXTRACTION OF URANYL IONS FROM AQUEOUS SYSTEMS

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The article presents the results of studies on the synthesis of a new sorption material with a cross-linked structure (with a yield 94%) based on a ternary co-oligomer of 4-isopropenylphenol (I), styrene (II) and maleic anhydride (III) - their structuring (crosslinking) with ethylenediamine. The process was carried out in a block, at a temperature of 80°C and a time of 3 hours. The ratio of co-oligomer and ethylenediamine is 1:2 mol. The initial co-oligomers were obtained by co-oligomerization of I, II and III at their equimolar ratio in the presence of the initiator di-tert-butyl peroxide (2% of the mixture of initial components). Temperature 140°C, time 10 hours. The gel chromatography data confirmed the formation of mainly co-oligomeric compounds under these conditions (87% are co-oligomers with Mw 575 and 980, and Mn 400 and 450, respectively). 13% are co-oligomers with Mw 3585 and Mn 2900.

A study of the sorption properties of three-dimensional copolymers as sorbents for the extraction of uranyl ions from model aqueous systems (depending on the pH of the medium, the initial concentration of the said ions, and the holding time of the system) in statistical mode showed that they are highly effective.

The degree of extraction (R) of uranyl ions at an optimal pH of 7 is more than 84.2%, while the sorption capacity (q) is 216.5 mg/g.

Keywords: uranyl ions, sorption, 4-isopropenylphenol, styrene, maleic anhydride, ethylenediamine.

INTRODUCTION

Protection of water-salt systems and other environmental objects from heavy metals and radioactive elements is one of the urgent problems of chemical science [1-6]. Numerous ion-exchange, precipitation, membrane, electrochemical and other methods developed in the world related to reducing the amount of toxicants in the water environment are often ineffective, insufficiently selective and difficult to regenerate.

For example, many ion-exchange materials are mainly effective in concentrated aqueous solutions of salts and other substances and do not have selectivity with respect to individual ions; they cannot be regenerated and reused, which creates additional environmental problems [7,8].

Membrane methods for cleaning water systems are considered promising. However, they are not without drawbacks (low strength properties, clogging of pores with a substance, difficulty of regeneration, etc.) [9-12]. Therefore, in recent years, technologies based on the use of sorption materials (synthetic, hybrid, natural) have been most preferable [10-12]. Of particular interest among them are cross-linked polymers and copolymers containing active chelating functional groups (NH₂, COOH, CO, C-NH₂, etc.) in their structures, which are the centers of adsorption of certain ions (or their mixtures). The processes of their synthesis are mainly based on the use of industrial monomers such as styrene, α -methylstyrene, acrylonitrile, maleic anhydride, inexpensive solvents and auxiliary materials [13-18].

The article presents the results of studies on the synthesis of ternary reactive co-oligomers of styrene and maleic anhydride with 4-isopropenylphenol (precursors) with subsequent reactions of their structuring (cross-linking) with ethylenediamine and the study of the functional sorption properties of the obtained three-dimensional copolymers in relation to uranyl ions in model aqueous systems (depending on the pH of the medium, the initial concentration of these ions, time, etc.).

EXPERIMENTAL

Synthesis of triple co-oligomers (precursors) was carried out in glass ampoules, in the absence of air at a ratio of 4-isopropenylphenol, styrene, maleic anhydride 1:1:1 mol, a temperature of 140°C for 10 hours, in the presence of the initiator DTPB (2% of the mixture). The yield of triple co-oligomers was 94%. Structuring (cross-linking) of co-oligomers was carried out thermally at 80-85°C in a rotor in a flask, in the presence of a cross-linking agent - ethylenediamine (at their ratio of the taken compounds 1:1 mol for 3 hours). Upon completion of the reaction, the mixture was treated with acetone (in a Soxhlet apparatus) in order to separate the soluble part from the cross-linked one. Cross-linked co-oligomers were dried in a vacuum drying oven at 50°C for 3 hours. Their yield is 94%.

In order to identify the possibility of using the synthesized products as a sorption material, laboratory studies were carried out in model systems obtained by dissolving certain amounts of uranyl nitrate in distilled water.

For the experiments, small teflon cups were used, into which a sample of the cross-linked material was loaded, weighed on an analytical scale, and 10 mL of the prepared aqueous solution of uranyl nitrite was added.

To create an environment with a given pH, a specially prepared buffer solution (10 mL) was used. For this, an ammonia solution and acetic acid were used. The system was maintained in static mode for a certain time at room temperature. The sorbent used was taken for sorption studies 30 mg.

After the end of the holding time, the solution was filtered and the activity of the ²³⁵U and ²³⁸U isotopes (Bq/L) was determined in it using an HPGe γ -spectrometer (manufactured by Canberra, USA). Based on the data on the change in the concentration of the indicated uranium isotopes (before and after sorption), the degree of sorption (R) was calculated, as well as the sorption capacity of the sorbent (q) using known formulas:

$$R = \frac{C_0 - C}{C_0} \times 100\% \quad q = \frac{C_0 - C}{m_{\text{sorb}}} V_{\text{sorb}}$$

C₀ - concentration of uranyl ions in solution before sorption, mg/L

C - concentration of uranyl ions in solution after sorption, mg/L

R - degree of sorption, %

m_{sorb} - mass of the taken sorbent, mg
 q - sorption capacity of the sorbent, mg/g

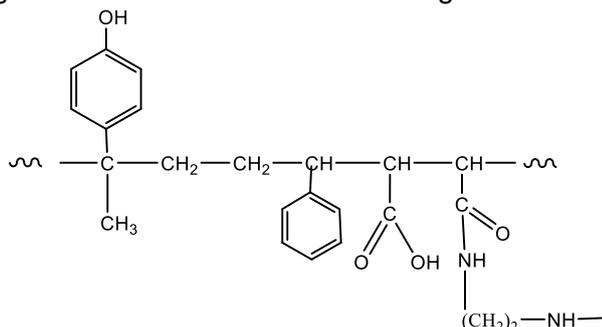
RESULTS AND DISCUSSION

The following characteristic absorption bands were found in the IR spectrum of ternary co-oligomers (cm^{-1}): 701, 703, 760, 828 (deformation vibrations of aromatic rings), 1211 (C-O bond); 1365, 1408, 2928, 2960 (deformation and stretching vibrations of the C-H bond) 1706, 1773 (C=O bond); 3232 (OH). Table 1 shows the MWD data of the co-oligomer

Table 1. MWD of oligomer

Fractions of the oligomer, %	MW		
	M_w	M_n	M_w/M_n
13	3585	2900	1,23
87	575	400	1,51
	980	450	2,17

As can be seen from Table 1, under the conditions of co-oligomerization, mainly (87%) low-molecular compounds are formed (about 575). Their formation can be explained by the breakage of growing chains under the influence of pH groups of 4-isopropenylphenol; the presence of a CH group at a short bond can also have a negative effect on this process. The process of hardening the co-oligomer with ethylenediamine apparently occurs by opening the anhydride ring with the formation of the following structures:



The structure of the obtained cross-linked copolymer is confirmed by IR spectroscopy data. IR spectrum, cm^{-1} : 700, 761, 831 (mono- and tri-substituted aromatic ring); 1385, 1452, 2928 (C-H); 1178 (C-N); 1235 (C-O); 1550, 1513 (amide group), 1770, 1696 (C=O), 3225 (OH).

The presence of NH, COOH, OH, CO and other functional groups in the structure of the synthesized cross-linked product - active centers of chemisorption of various ions made it possible to study them in the process of extracting uranyl ions from model aqueous systems. To identify optimal conditions, experiments were carried out at different pH, concentrations of uranyl ions and holding times of the cross-linked copolymer sample in the test medium. All experiments were carried out at room temperature.

Table 2 presents the results of the studies depending on pH for 24 hours. As can be seen, the best results for the maximum extraction of uranyl ions R and q are achieved at pH 8. Usually, the chemisorption process is preceded by diffusion of ions to the active centers, after which the complex formation process takes place.

As can be seen from the Table 3, the extraction process in the selected static uranyl ions mainly occurs for the first 4 hours. In this case, R is more than 85%, and the q is 218 mg/g. Therefore, the optimal condition can be considered pH 7 and a time of 4 hours.

An important factor influencing the sorption process is the concentration of uranyl ions in the aqueous solution. The results of studies to identify the effect of uranyl ion concentration on R and q values are given in Table 4.

Table 2. Effect of pH of the medium and concentration of uranyl ions on R and q, initial concentration of uranyl ions 154.3 mg/L

pH	Content of uranyl ions in aqueous solution after sorption, mg/L	Sorption degree (R, %)	q, mg/g
1	146,1	5,3	13,7
2	136,4	11,6	29,8
3	111,6	27,7	71,2
4	99,2	35,7	91,8
5	78,6	49,1	126,2
6	54,2	64,9	166,8
7	24,4	84,2	216,5
8	13,6	91,2	234,5
9	25,1	83,7	215,3
10	79,7	48,3	124,3
11	107,6	30,3	77,8
12	130,1	15,7	40,3
13	123,9	19,7	50,7
14	132,2	14,3	36,8

Table 3. The influence of the sorption time of the obtained sorbent on the degree of sorption and sorption capacity of the sorbent

Time, hour	Concentration of UO_2^{2+} in water solution after sorption, mg/L	Sorption degree (R, %)	q, mg/g
0,25	142,3	7,8	20,0
0,5	130,8	15,2	39,2
1	119,3	22,7	58,3
2	100,5	34,9	89,7
4	23,0	85,1	218,8
6	22,9	85,2	219,0
8	23,0	85,1	218,8
24	22,8	85,2	219,2

Table 4. Effect of uranyl ion concentration in an aqueous solution on R and q

A_0 , Bk/L	A, Bk/L	C_0 mg/L	C_e , mg/L	R, %	q, mg/g
22,6	9,314	38,0	8,3	78,2	49,5
27,1	10,53	45,6	8,9	80,5	61,2
44,3	11,0	74,4	14,6	80,4	99,7
83,6	11,96	140,6	20,4	85,5	200,3
117,4	31,11	197,4	27,8	85,9	282,7
154,8	54,8	260,1	83,1	68,0	295,0

As can be seen from Table 4, the sorption degree of cross-linked copolymers have calculated both in dilute and concentrated solutions of uranium salt. For example, at a concentration of uranyl ions of 38 mg/L, the degree of their extraction is more than 78%, at a concentration of 197.4 mg/l, about 86%, with the q of 282.7 mg/g. With a further increase in the initial concentration of uranyl ions to 260 mg/L, R decreases to 68%, although the q is 295 mg/g. In order to identify the mechanism of binding uranyl ions by the cross-linked material used, IR spectra were recorded (before and after sorption, Fig. 1 and 2).

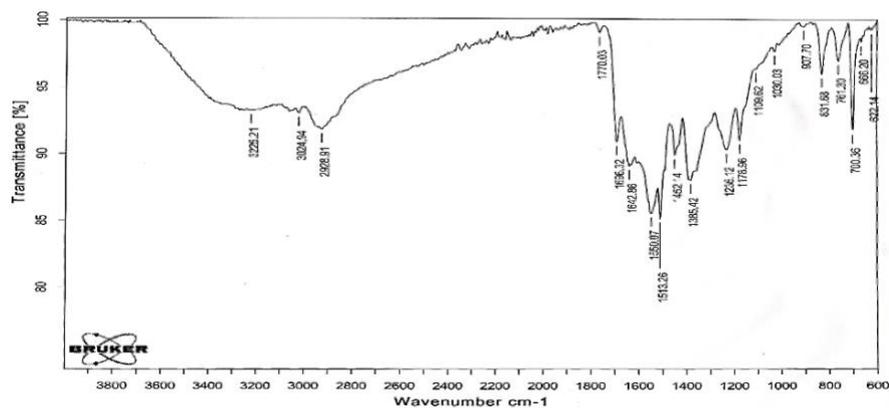


Figure 1. IR spectrum of the sorbent before sorption

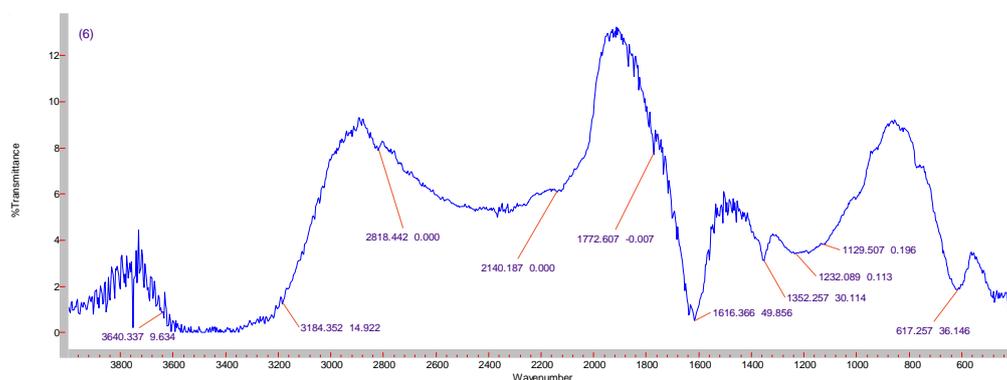


Figure 2. IR spectrum of the sorbent after sorption

Comparison of IR spectra before and after sorption of uranyl ions shows that the process of their extraction from the aqueous medium occurs due to the participation of functional groups (for example, complex formation).

Uranium salts in aqueous solutions are usually in hydrated form. The most stable are compounds of hexavalent uranium in aqueous solution in the form of uranyl ions [19], which behave as divalent cations. They are capable of forming complexes with chelate sorbents (for example, nitrogen-containing), which include amidoxime-modified styrene and acrylonitrile copolymers.

CONCLUSION

Thus, based on the results of comprehensive studies, it can be concluded that the sorption product obtained by the reaction of ethylenediamine with a triple co-oligomer of 4-isopropenylphenol, styrene and maleic anhydride has high sorption properties in an insignificant amount (30 mg) and the degree of its sorption at pH 7 is 84%, and the sorption capacity is 216.5 mg/g.

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