

SYNTHESIS OF CARBOXYLATE TYPE SORBENT BASED ON COOLIGOMERS OF 2-PROPENYLPHENOL AND FORMALDEHYDE AND STUDY OF THEIR FUNCTIONAL PROPERTIES FOR SORPTION OF URANYL IONS IN MODEL SYSTEMS

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Abstract: *Alkaline synthesis of double co-oligomers of 2-propenylphenol and formaldehyde (synthons) was carried out at 92-95⁰C, for 3 hours and ratio of 1:2.5 mol (their yield are 93% of theory) Interaction of maleic anhydride with the obtained oligomers at 80⁰C in the presence of 0.5% benzoyl peroxide for 10 hours produced copolymers of a three-dimensional cross-linked structure (with a yield of 90%). By treating them with hot water, a sorbent was obtained to contain both propenyl and carboxylate fragments in the structure - active centers of chemisorption. The functional sorption properties of the copolymer were studied under static conditions, in model water systems. The influence of the pH of the medium, the concentration of uranyl ions and the exposure time on the degree of their sorption at room temperature were studied and it was found that the best results are achieved at pH 6 and for 24 hours (R=93%). Uranyl ions can be easily desorbed with mineral acid and the crosslinked copolymers can be reused.*

Keywords : *formaldehyde, 2-propenylphenol, oligomers, uranyl ions, sorption, desorption*

Introduction

The development of effective sorption methods for the purification of water systems from heavy metals, radionuclides, and other environmentally hazardous substances is one of the priority areas of chemical science [1–4]. Sorption methods based on the use of cross-linked polymeric materials with various active adsorption sites, such as amino, sulfo, carboxy, and other groups, occupy an important place among them [5]. They can be used alone or in combination with inorganic modifiers to isolate and even concentrate trace amounts of ions from environmental objects, which is often impossible when using other purification methods.

While developing new sorption polymeric materials, the main attention is paid to the availability of used monomers, solvents, and other excipients, as well as the simplicity of the technology for implementing their synthesis processes. In this regard, syntheses using various alkenylbenzenes, maleic anhydride, acrylonitrile, formaldehyde, and other available compounds attract the greatest attention of researchers [6,7].

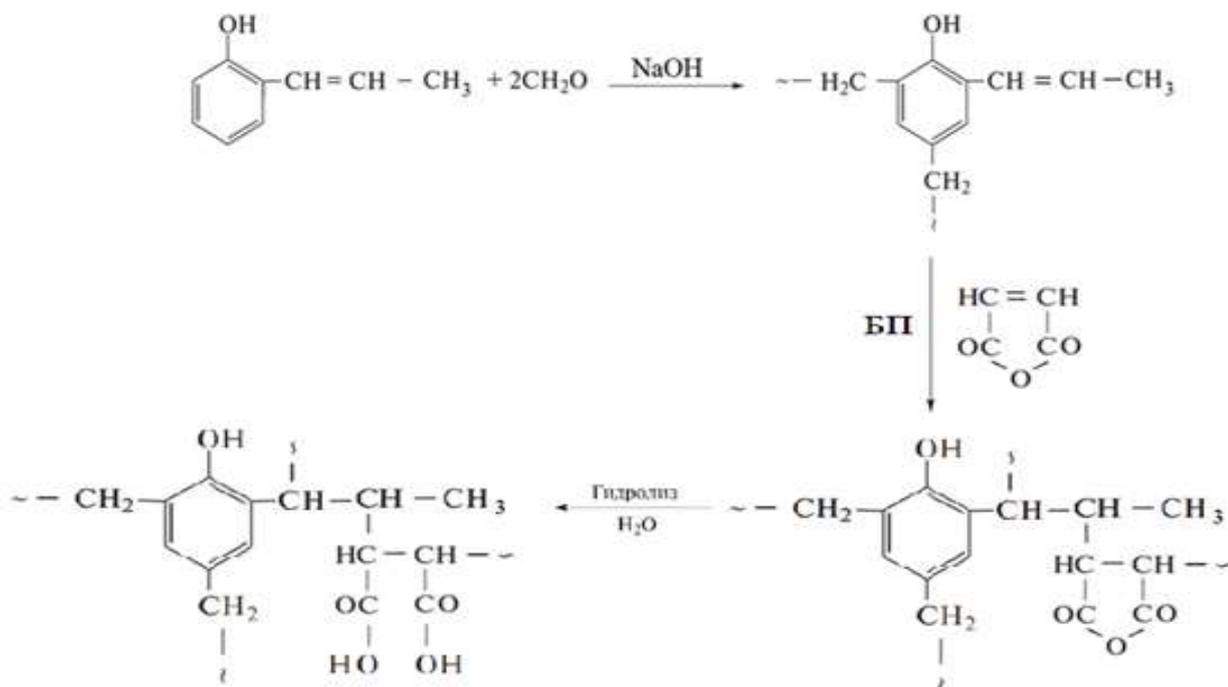
The work [8] describes the synthesis of phenol-formaldehyde co-oligomers based on phenol and formaldehyde, which are further used to obtain a cross-linked material. First, the interaction of o-benzoyl-benzoic acid chloride with phenol in the presence of a ZnCl₂ catalyst synthesizes 3-phenyl-3(4)-hydroxyphenyl phthalide which is then introduced into the polycondensation reaction with formaldehyde in the presence of catalytic amounts of ammonia at their various ratios (from 5:95 to 40:60% wt). In this case, phenol-formaldehyde co-oligomers of the resole type are formed, which are used as raw materials for the synthesis of heat-resistant cross-linked copolymers.

Composite polymeric material intended for the adsorption of uranyl ions from natural and waste waters, as indicated in [9], can be synthesized by graft copolymerization of polyacrylamide and chalkocarboxylic acid.

Our studies have previously shown [10] that effective sorbents for the extraction of uranyl ions from aqueous systems are cross-linked copolymers based on alkenyl-substituted phenols, formaldehyde, and maleic anhydride.

This article presents the results of the synthesis of cross-linked copolymers containing phenol hydroxyl, propenyl and carboxylate fragments in the structures; results of the study of their functional sorption properties with respect to uranyl ions from model aqueous systems under static conditions (depending on the pH of the medium, the concentration of uranyl ions, time, and other factors) on sorption capacity of the sorbent (SCS) and, finally, the degree of their extraction (R, %).

The synthesis of cross-linked copolymers was carried out according to the scheme below:



Experimental part

During the work we used:

- 2-propenylphenol, obtained by a known method [11], $T_{\text{melt}} 36.5\text{-}37^\circ\text{C}$
- formalin (37% formaldehyde aqueous solution)
- maleic anhydride - reactive, recrystallized from a benzene solution, $T_{\text{melt}} 54^\circ\text{C}$.

a) Synthesis of double co-oligomers of 2-propenylphenol and formaldehyde

To three-necked flask equipped with a thermometer, a stirrer, and a reflux condenser 13.4 g (0.1 mol) of 2-propenylphenol and 0.2 g (0.005 mol) of NaOH dissolved in 10 ml of water were added. The mixture was heated to $40\text{-}45^\circ\text{C}$, then 20.8 ml of formalin was added to the mixture, and co-oligomerization was carried out with stirring for 3 hours at a temperature of $92\text{-}95^\circ\text{C}$. Upon completion of the process, the mass was washed several times with warm distilled water and dried under vacuum. The yield of double co-oligomers is ~ 19.4 g (93% of theory). They are solids with grey color, highly soluble in acetone, cyclohexanone, ethanol. M.p. $110\text{-}115^\circ\text{C}$.

The structures of double co-oligomers and obtained cross-linked copolymers were confirmed by IR spectroscopy data. The IR-spectra on a Varian 3600 FI-IR spectrophotometer (Bruker, Germany). The absorption bands at 647, 723, 754, 802, 883 cm^{-1} belong to the bending vibrations of aromatic CH bonds characteristic of the aromatic ring of 2-propenylphenol, the absorption bands at 1146, 1212 cm^{-1} refer to the bending and stretching vibrations of C–O -groups, absorption bands at 1372 cm^{-1} - to bending vibrations of C–H bonds at CH_2 and CH_3 , bands at 2875, 2925, 2962, 3332 cm^{-1} – to stretching vibrations of the OH group.

To determine the molecular weight of the synthesized co-oligomers and MWD fractions, laboratory studies were carried out on a Kovo gel chromatograph (Czech Republic) equipped with a

refractometric detector and two columns filled with Separon SQX adsorbent (particle size 7 μm , diameter 100 \AA). The process of separating cooligomers into fractions was carried out at a temperature of 25 $^{\circ}\text{C}$.

Separate fractions were eluted with a polar solvent (dimethylformamide). Its feed rate to the column was 0.3 ml/min. In the work, polyethylene glycol was used as a standard. For the determined molecular weight, a plot of $\lg M$ versus v_R was plotted. Calculations were proceeded from the equation [12]:

$$v = \frac{C_1 - C_2}{\lg M}$$

$$M_w = \sum_i M_i w_i \quad M_n = \frac{1/w_i}{\sum_i M_i}$$

where M_w is the average molecular weight;

M_n - number average molecular weight;

M_i - molecular weight corresponding to the i -th area;

w_i - is the mass fraction of the i -th part.

b) Structuring of double co-oligomers of 2-propenylphenol and formaldehyde with maleic anhydride

The process of structuring (crosslinking) of co-oligomers with maleic anhydride was carried out in glass ampoules in the presence of benzoyl peroxide initiator. Calculated amounts of cooligomers, maleic anhydride, and benzoyl peroxide were loaded into the preliminarily prepared ampoules. The ampoules were cooled with dry ice, evacuated and sealed in a stream of nitrogen, then were transferred to an ultrathermostat (at a temperature of 80 $^{\circ}\text{C}$), where they were kept for 5–6 h.

Upon completion of the structuring process, the crosslinked copolymers were separated from the soluble ones in a Soxhlet apparatus by treatment with boiling benzene.

c) Hydrolysis of the synthesized cross-linked copolymers with water

The crosslinked copolymers were treated with hot distilled water for 2 hours in order to open the anhydride groups and obtain structures containing succinic acid fragments.

The structure of the obtained carboxylate type crosslinked copolymer material was confirmed by IR spectroscopy data. The structure of the resulting carboxylate type crosslinked copolymer was confirmed by IR spectroscopy data. The absorption bands at 753, 815, 883 cm^{-1} refer to bending vibrations of aromatic CH bonds characteristic of the aromatic ring of 2-propenylphenol, the absorption bands at 1147, 1206 cm^{-1} refer to bending and stretching vibrations of the C–O group, absorption at 1376, 1463 cm^{-1} - to bending vibrations of C–H bonds at CH_2 and CH_3 , bands at 1650, 1714 cm^{-1} – to stretching vibrations of the C=O group, bands at 2928, 2964, 3388 cm^{-1} to the stretching vibrations of the OH group.

d) Method for determining the sorption properties of cross-linked copolymers (with respect to uranyl ions)

To reveal the possibility of using the synthesized cross-linked copolymers as a sorbent for the extraction of uranyl ions from model aqueous systems, a HPGe γ -spectrometer (with a germanium detector, manufactured by Canberra, USA) was used.

To assess the effectiveness of their action, the content of 238U and 235U isotopes in an aqueous solution (before and after sorption) was measured under specified conditions [13]:

$$A_{U_{235}} = \lambda_{U_{235}} N_{U_{235}} = \frac{\ln 2}{T_{1/2}^{U_{235}}} N_A \frac{m^{U_{235}}}{M_{U_{235}}},$$

$$A_{U_{238}} = \lambda_{U_{238}} N_{U_{238}} = \frac{\ln 2}{T_{1/2}^{U_{238}}} N_A \frac{m^{U_{238}}}{M_{U_{238}}},$$

Where $A_{U_{235}}$ and $A_{U_{238}}$ is the activity of radionuclides ^{235}U and ^{238}U , respectively, $\lambda_{U_{235}}$ and $\lambda_{U_{238}}$ are the half-lives of radionuclides ^{235}U and ^{238}U , respectively, N_A is the Avogadro number, $m^{U_{235}}$ and $m^{U_{238}}$ are the masses of radionuclides ^{235}U and ^{238}U respectively, $M^{U_{235}}$ and $M^{U_{238}}$ are the atomic masses of radionuclides ^{235}U and ^{238}U , respectively, $T_{1/2}^{U_{235}}$ и $T_{1/2}^{U_{238}}$ are the half-lives of radionuclides ^{235}U and ^{238}U respectively.

$$R = \frac{C_0 - C}{C_0} \cdot 100 \% \quad \text{CEC} = \frac{m_{\text{погл}}}{m_{\text{сорб}}} \cdot 1000 \text{ mg/g} \quad [14]$$

C_0 - concentration of uranyl ions in solution before sorption, mg/L

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

R - is the degree of sorption, %

m_{sorb} - is the mass of the taken sorbent; mg

$m_{\text{погл}}$ is the mass of the extracted substance; mg

SCS - is the sorption capacity of the sorbent, mg/g

Results and its discussion

The results of gel chromatographic studies showed that synthesized by us the double co-oligomers of 2-propenylphenol and formaldehyde are comparatively low molecular weight compounds. The average molecular weights of M_w and M_n are respectively 5580 and 1440 (M_w / M_n 3.87) According to MWD, ~65% falls on the relatively high molecular weight (M_w 7040, M_n 5050, M_w / M_n 1.57), low molecular weight part is ~ 35% (M_w 760, M_n 580, M_w / M_n 1.31). This can obviously be explained by the effect of phenolic hydroxyl on the termination of growing cooligomeric chains during the synthesis of double cooligomers of 2-propenylphenol and formaldehyde.

The structures of the obtained cooligomers contain reactive propenyl groups, which can easily participate in the reaction of radical copolymerization with maleic anhydride in the presence of various initiators, in particular benzoyl peroxide (through the intermediate formation of a donor-acceptor complex with charge transfer). Apparently, the reaction of graft copolymerization occurs first, and three-dimensional structures are formed at the late stages of transformations. As is known, the density of the network is dependent not only upon the structure of the initial co-oligomers (synthons), but also on the nature of the cross-linking comonomer, in particular, maleic anhydride, and, finally, on the structuring conditions. They have high thermal properties, as evidenced by the results of DTA and TG analyses.

Table 1 shows the results of studies into the influence of the pH of the medium of the initial concentration of uranyl ions and the duration of the process, the degree of their extraction (R ,%) from the model aqueous system, as well as the static capacity (CEC) of the used crosslinked copolymer. It found that a high degree of sorption (93%) with an initial concentration of uranyl ions of 155.2 mg/l is achieved at pH 6, time 24 h. SCS is 240.7 mg/g. A further increase in pH to 7–8 leads to a decrease in the degree of sorption of uranyl ions to an average of ~75%, while the SCS is ~195.0 mg/g. With a further increase in pH to 10-13, a sharp decrease in sorption occurs. Thus, the

results of these studies showed that pH 6 can be considered the best conditions for the extraction of uranyl ions from an aqueous solution.

Table 1. Effect of medium pH and uranyl ion concentration on R and SCS (initial uranyl ion concentration 155.2 mg/l)

pH	Concentration of uranyl ions in water solution after sorption, mg\L	Sorption degree of uranyl ion (R,%)	SCS , mg/g
1	143.1	7.8	20.2
2	120.9	22.1	57.2
3	88.1	43.2	111.8
4	54.6	64.8	167.7
5	20.7	86.7	224.2
6	10.8	93.0	240.7
7	36.6	76.4	197.7
8	38.9	74.9	193.8
9	91.2	41.2	106.7
10	101.3	34.7	89.8
11	116.4	25.0	64.7
12	109.7	29.3	75.8
13	135.4	12.8	33.0
14	115.6	25.5	66.0

The results of these studies showed that the effective degree of recovery is achieved in a slightly acidic environment (pH 6).

Table 3 shows the results of studies to identify the duration of the process of sorption of uranyl ions (initial concentration of 155.2 mg/L, pH 6). With a further increase in the exposure time to 27 and 30 hours, the indicators of the sorption process practically do not change.

It was established that the process of trapping uranyl ions by cross-linked copolymers was also significantly affected by the holding time. A 50% degree of their extraction is achieved in 4-5 hours. The maximum degree of extraction (more than ~93%) occurs for at a duration of 24 hours. Obviously, the process of binding uranyl ions by a carboxylate copolymer is preceded by their diffusion.

Table 2. Influence of duration on the process of sorption of uranyl ions (pH 6, initial concentration of uranyl ions 155.2 mg/L)

Time, hours	Concentration of uranyl ions in water solution after sorption, mg\L	Sorption degree of uranyl ion (R,%)	SCS , mg/g
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0.25	144.3	7.0	18.2
0.5	136.2	12.2	31.7
1	121.5	21.7	56.2
2	102.3	34.1	88.2
4	76.8	50.5	130.7
6	51.2	67.0	173.3
8	45.1	70.9	183.5
10	32.6	85.3	204.3
12	29.7	80.9	209.2
20	14.2	90.9	235.0
24	10.7	93.1	240.8
27	10.8	93.0	240.7
30	10.7	93.1	240.8

Table 3 shows the results of studies into the influence of the concentration of uranyl ions in an aqueous solution of their extraction (R) and SCS (at pH 6, time 24 hours).

As can be seen, depending upon the initial concentration of uranyl ions, the degree of their extraction (R) varies from 63.2 to 93%. At low concentrations (38.0 and 45.6 mg/l), R does not exceed ~63-66%, the maximum value of R (93%) is achieved when using a solution containing 140.6 mg/l of uranyl ions, while SCS is 217.8 mg/g. With a further increase in their concentration to 197.4 and 260.1 mg/L, the sorption indices average 70%. Thus, the synthesized sorbent can be used both in dilute and concentrated solutions.

Table 3. Effect of the initial concentration of uranyl ions in aqueous solution on R and CEC (pH 6, sorption time 24 h)

A ₀ , Bk\L	A, Bk\L	C ₀ mg\L	C _e , mg\L	R,%	SCS, мг/г
22.5	7.6	38.0	12.8	66.3	42.0
27.0	9.9	45.6	16.8	63.2	48.0
44.0	8.3	74.4	14.1	81.1	100.6
83.1	5.8	140.6	9.9	93.0	217.8
116.7	34.8	197.4	58.9	70.2	230.9
153.9	45.7	260.1	77.4	70.3	304.6

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2-PROPENİLFENOL VƏ FORMALDEHİD ƏSASINDA KARBOKSİLAT TIPLİ SORBENTİN SİNTEZİ VƏ MODEL SİSTEMLƏRDƏ URANİL İONLARINA QARŞI ONUN XASSƏLƏRİNİN ÖYRƏNİLMƏSİ

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Xülasə: 2-propenilfenol və formaldehidin (sintonların) ikiqat sooliqomerlərinin qələvi iştirakında sintezi 92-95⁰C temperaturda, onların nisbəti 1:2.5 mol götürülməklə 3 saat müddətində aparılmışdır. Çıxım ~93% təşkil edir. Malein anhidridinin sintez olunmuş sooliqomer ilə 80⁰C temperaturda 0.5% benzoil peroksid inisiatoru iştirakı ilə 10 saat ərzində qarşılıqlı təsiri tikili sopolimer əmələ gətirir. Çıxım ~90% təşkil edir. Onları qaynar su ilə bir neçə dəfə yuyaraq, daha sonra asetonla ekstraksiya edərək, strukturunda aktiv kimyəvi sorbsiya mərkəzləri - həm propenil, həm də karboksilat fraqmentləri olan sorbent alınmışdır. Sopolimerin sorbsiya xassələri statik şəraitdə, model su sistemlərində tədqiq edilmişdir. Mühitin pH-ı, uranil ionlarının qatılığı və zamandan asılılığının onların sorbsiya dərəcəsinə təsiri öyrənilmiş və müəyyən edilmişdir ki, ən yaxşı nəticə pH 6-da və 24 saat ərzində əldə edilir (R = 93%).

Uranil ionları mineral turşu ilə asanlıqla desorbsiya edilə bilər və tikili sopolimer təkrar istifadə edilə bilər.

Açar sözlər: formaldehid, 2-propenilfenol, oliqomerlər, uranil ionları, sorbsiya, desorbsiya

СИНТЕЗ КАРБОКСИЛАТНОГО СОРБЕНТА НА ОСНОВЕ СООЛИГОМЕРОВ 2-ПРОПЕНИЛФЕНОЛА И ФОРМАЛЬДЕГИДА И ИССЛЕДОВАНИЕ ЕГО ФУНКЦИОНАЛЬНЫХ СВОЙСТВ ПО ОТНОШЕНИЮ К УРАНИЛ-ИОНАМ В МОДЕЛЬНЫХ СИСТЕМАХ

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Аннотация: Осуществлен щелочной синтез двойных сополимеров 2-пропенилфенола и формальдегида (синтонов) при соотношении 1:2.5 моль, температуре 92-95⁰С и времени 3 час (выход 93 % от теорет). Взаимодействием малеинового ангидрида с последними при температуре 80⁰С в присутствии 0.5% бензоилпероксида в течение 10 час получены сополимеры трехмерной сшитой структуры (с выходом 90 %). Обработкой их горячей водой получен сорбент, содержащий в структуре одновременно пропенильный и карбоксилатные фрагменты – активные центры хемосорбции. Исследованы функциональные сорбционные свойства сорбента в статических условиях в модельных водных системах. Изучено влияние рН среды, концентрации уранил-ионов и времени выдержки на степень их сорбции при комнатной температуре и выявлено, что наилучшие результаты достигаются при рН 6 и времени 24 час (R=93 %). Связанные уранил-ионы можно легко десорбировать минеральной кислотой и сшитые сополимеры повторно использовать.

Ключевые слова: формальдегид, 2-пропенилфенол, сополимеры, уранил-ионы, сорбция, десорбция