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PURIFICATION OF WATER FROM URANYL-IONS BY NEW SORBENT OF CARBOXYLATE TYPE

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The hydrolyzed ternary copolymer of styrene, maleic anhydride and 1,3-bis(2-propenylphenoxy)-propane was studied as sorbent for extraction of uranyl-ions out of aqueous systems. The influence of pH medium, concentration of uranyl-ions, quantity of sorbent, duration of sorption and other factors on main indices of the sorption process was analyzed. The analysis of isotherms of sorption of uranyl-ions was performed through the use of Langmuir and Freundlich's equations. The possibility of using the copolymer both in concentrated and diluted solutions established.
Keywords: *cross-linked copolymers, isotherms of sorption, regeneration, sorption, uranyl-ions*

INTRODUCTION

As is known, the development of effective methods of purification of aqueous systems from ions of heavy metals, radionuclides and other harmful substances is one of the priority directions of the chemical science [1-3].

In spite of the fact that recently there have been proposed the various sorption methods of purification from above-mentioned toxicants, an emphasis is laid on making new materials with high functional properties, especially as regards sorbents of complex-forming type which can be easily regenerated and reused [4].

Radionuclides in aqueous solutions are usually in the hydrolyzed form which largely accounts for their behavior in the sorption processes, ion exchange, extraction, etc. In the compounds, the uranium shows a valence state (from 2 to 6). However, in the aqueous medium, U(VI) is the most stable in the form of UO_2^{2+}-ions to create mononuclear and polynuclear hydroxocomplexes [5].

The works [6] revealed that for effective binding of UO_2^{2+}-ions from aqueous solutions it'd be appropriate to use the synthetic sorbent-hydrolized cross-linked copolymer of styrene, maleic anhydride and 1,3-bis-(2-isopropenylphenoxy)-butane developed by us.

The paper deals with the synthesis of cross-linked copolymer of styrene, maleic anhydride and 1,3-bis-(2-propenylphenoxy) propane to examine them as sorbent for purification of aqueous solutions from uranyl salts.

EXPERIMENTAL PART

The radical ternary copolymerization reaction of styrene, maleic anhydride and 1,3-bis-(2-propenylphenoxy)-propane (at their ratio 1:2:0,2 mol) was analyzed with a view of preparing a new sorbent with cross-linked structure. The last one was synthesized (Williamson reaction) through the interaction of 2-propenylphenol with 1,3-dibromopropane (in the presence of alcohol solution of KOH and promoter KY). The copolymerization was carried out in a medium of solvating solvent (200% of dioxane). As a template there was

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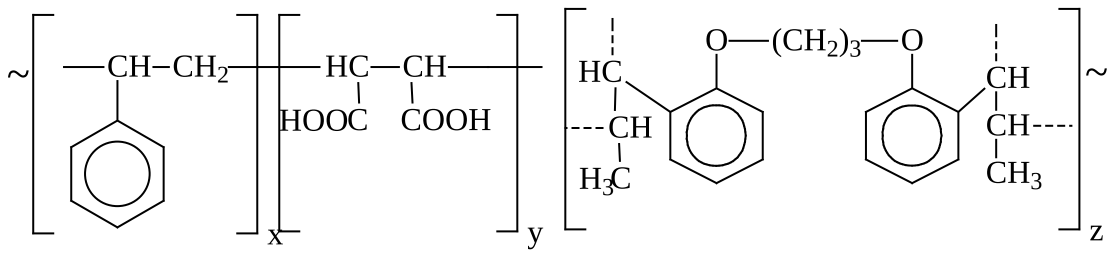
used a linear copolymer of styrene with maleic anhydride (4% per taken reagents).

The copolymerization process was carried out in the presence of initiator – dinitrile of azoizobutyric acid (1% per mixture of monomers), at temperature 80°C during 10 hours.

In the end of template synthesis aimed at separating a pore agent (linear copolymer of styrene with maleic anhydride) from cross-linked copolymer, it was extracted (at the Soxhlet apparatus) first by acetone, then by toluene. The cross-linked copolymers were dried up at temperature 40-50°C for 2 hours in the vacuum box with yield ~95% (thereof).

The last ones were further treated by hot water for 2 hours with the aim of opening anhydride rings and preparing a sorbent with carboxyl groups in their structure:



To reveal the possibility of use of last one as sorbent for extraction of uranium compounds, comprehensive laboratory explorations in static conditions were carried on model systems consisting of solutions with sertain concentration of uranyl sulfate in distilled water. To regulate pH medium, ammonia acetate solutions through mixing corresponding volumes of 0,1M CH_3COOH with 0,1M NH_3 were used. Also, fixanal HCl was used.

An estimation of sorption properties was carried out by determination of isotope ^{238}U activity in aqueous phase (before and after sorption) by γ-spectrometer HPGe with germanium detector (made in USA).

The influence of UO_2^{2+}-ions concentration of pH, quantity of sorbent, endurance time and other parameters on degree of their sorption (R, %) and sorption capacity of sorbent (SCS, mg/g) was analyzed.

Note that respective experiments were carried out as follows: some quantities of copolymer and aqueous solution of uranyl-sulfate of a given concentration are loaded into a teflon cup with capacity of 100 ml. Then, 10 ml of 0.1M buffer solution was added to the mixture and its volume brought to 50 ml (a dilution with distilled water). The system is kept at a room temperature for some time, after which in the aqueous solution it is determined a content of UO_2^{2+} ions. Based on the obtained data R and SCS are calculated. The equilibrium of sorption of uranyl ions on the synthesized sorbent was examined at 293 K under static conditions. The equilibrium concentration of the uranyl ion have also been determined by γ-spectrometer.

RESULTS AND DISCUSSION

Table 1 shows the results of research into the influence of pH medium on R and SCS (duration of endurance – 24 hours, quantity of sorbent – 20 mg). The concentration of UO_2^{2+}-ions in the initial solutions in these series made up 236 mg/l and the activity – ^{235}U Bq/l.

Table 1. Influence of pH of aqueous solution on R and SCS values

pH of solution	Activity of isotope ^{235}U after sorption, Bq/l	Concentration of UO_2^{2+}-ions in solution after sorption, mg/l	R, %	SCS, mg/g
1.0	120	236.0	0	0
2.0	109	214.4	9.2	54.1
3.0	104	204.5	13.3	79.7
3.85	89	175.0	25.8	152.4
4.8	65	127.8	45.8	270.4
5.7	31	61.4	74.0	236.6
6.2	30	57.2	75.8	436.9
8.0	32	62.9	73.3	432.7
9.0	92	181.5	23.1	136.2
10	120	236.0	0	0
11	115	226.2	4.2	24.6
12	120	236.0	0	0
13	117	230.1	2.5	14.8
14	118	232.1	1.7	9.8

In an effort to find the possibility of using the copolymer for UO_2^{2+}-ions concentration from diluted solutions, we have carried out further experiments where initial concentrations alternated in a wider range (2.4 mg/l to 778.8 mg/l). These studies were also carried out under static conditions at a room temperature and an optimum value of pH ~ 6. Duration of sorption was 24 hours. The obtained results are presented in Table 2.

Table 2. Influence of UO_2^{2+}-ions in the solution on R and SCS

Activity of isotope ^{235}U, Bq/l		Conc. of UO_2^{2+}-ions in water, mg/l		R,%	SCS, mg/g
before sorption	after sorption	before sorption	after sorption		
1.2	0.11	2.4	0.2	90.8	2.7
2.4	0.19	4.7	0.4	92.1	5.4
3.6	0.44	7.1	0.9	87.8	7.8
14.4	1.13	28.3	2.2	92.2	32.6
28.28	2.9	56.6	5.7	89.9	63.7
43.2	4.2	85.0	8.3	90.3	95.9
86.4	6.8	189.9	13.0	92.4	196.2
120.0	12.1	236.0	23.8	90.0	265.3
180.0	45.5	354.0	88.7	74.9	331.6
216.0	62.6	424.8	123.1	71.0	377.1
252.0	79.6	495.6	156.1	68.4	423.8
288.0	100.1	566.4	196.9	65.2	461.9
324.0	136.2	637.2	256.9	58.3	464.1
360.0	166.3	708.0	327.1	53.8	476.2
396.0	199.5	778.8	392.4	49.6	483.1

According to Table 2, the copolymer has high sorption properties in relation to UO_2^{2+}-ions both in concentrated and diluted aqueous solutions. A degree of extraction of UO_2^{2+}-ions from concentrated solution (with content ~ 190 mg/l UO_2^{2+}-ions) is 92.4% where SCS is

196.2 mg/g. Further increase of the ions concentration in the initial solution makes up to 236 mg/l and R to 90%, and SCS – to 265.3 mg/g. When used strongly concentrated solutions (content 708.0 and 778.8 mg/l UO_2^{2+}-ions), R value averages to ~50%.

To calculate the sorption constants, the well-known Freundlich and Langmuir equations were used.

An estimation of the distribution of uranyl-ions on heterogeneous sorption surfaces can be described by empirical Freundlich equation

$$q_e = K_F + C_c^n \quad (1)$$

where K_F – Freundlich constant characterizing the adsorption capacity

n – surface heterogeneity index; $0 \leq n \leq 1$

In $n \rightarrow 1$ a heterogeneity decreases and in n = 1, the Freundlich equation passes over to linear isotherm.

Table 3 presents the calculated parameters of the Freundlich sorption. The K_F and n constants were revealed from the linearized form of the equation

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where C_e – concentration of uranyl ions in the solution after sorption

q_e– quantity of uranyl ions relating to sorbent, mg/g

n – sorbent heterogeneity index

K_F – sorption capacity constant determined experimentally

Table 3. Parameters of Freundlich sorption

Activity ^{235}U before sorption, A_0, Bq/l	Activity ^{235}U after sorption, A, Bq/l	Concentration of uranyl-ions before sorption, C_0, mg/l	Concentration of uranyl-ions after sorption, C_e, mg/l	log C_e	SCS, q_e, mq/l	log q_e
1.2	0.11	2.4	0.2	0	2.7	0.081
2.4	0.19	4.7	0.4	0	5.4	0.069
3.6	0.44	7.1	0.9	0	7.8	0.111
14.4	1.13	28.3	2.2	0.347	32.6	0.068
28.8	2.9	56.6	5.7	0.756	63.7	0.090
43.2	4.2	85.0	8.3	0.917	95.9	0.086
86.4	6.6	169.9	13.0	1.113	196.2	0.066
120.0	12.1	236.0	23.8	1.377	265.3	0.090
180.0	45.1	354.0	88.7	1.948	331.6	0.267
216.0	62.6	424.8	123.1	2.090	377.1	0.326
252.0	79.6	495.6	156.5	2.195	423.8	0.369
288.0	100.1	566.4	196.9	2.294	461.9	0.426
324.0	135.2	637.2	265.9	2.425	464.1	0.573
360.0	166.3	708.0	327.1	2.515	476.2	0.687
396.0	199.5	778.8	392.4	2.594	483.1	0.812

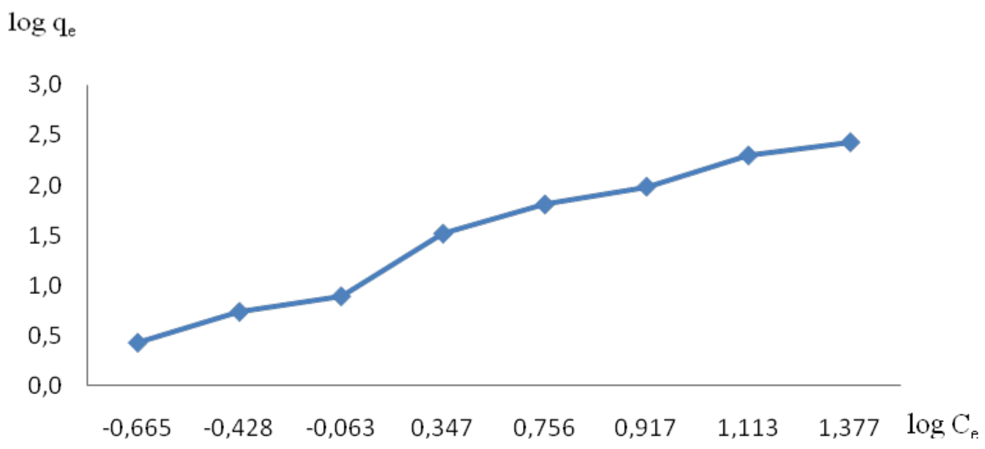


Fig. 1. Freundlich isotherm

To characterize the sorption process of uranyl-ions, the Langmuir isotherm was also built. The sorption isotherm constants were calculated by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} Ce \; ; \qquad q_e = \frac{Q_{\max} a_L C_e}{1 + a_L C_e}$$

C_e – concentration of uranyl-ions in the solution after sorption, mg/l
q_e – quantity of connected sorbent of uranium, mg/g
K_L – sorption constant l/g
a_L – constant characterizing the sorption energy l/mg
Q_{max} – maximum sorption capacity of the sorbent, mg/g

The same Table presents the Freundlich isotherm constant.
The Langmuir isotherm is shown in Fig. 2.

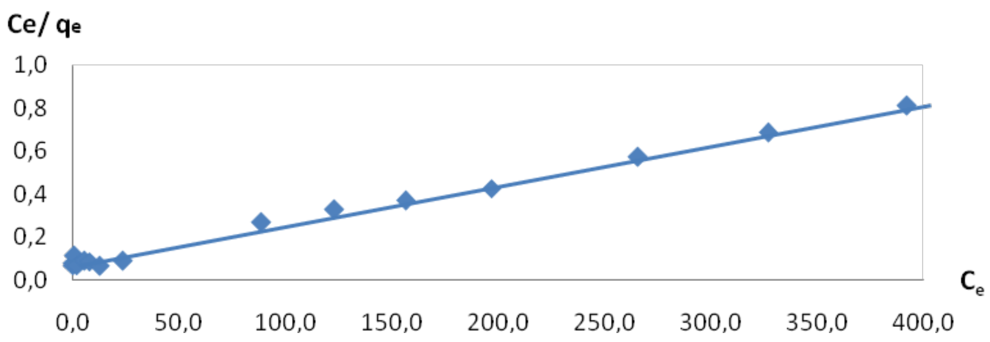


Fig. 2. Langmuir isotherm

An intercept at the intersection of a straight line with ordinate axis corresponds to 1 / KL.

According to the formula:

$$R_L = \frac{1}{1 + bC_0}$$

Where b (a_L) – Langmuir constant

C_0 – initial concentration of uranyl-ions in the solution, mg/l; were calculated $R_L$of Langmuir isotherm.

It should be noted that if this constant will take the values in the range $0<R_L<1$, the sorption process can be considered as profitable, at $R_L>1$ – unprofitable and in $R_L = 0$ – irreversible). The Freundlich and Lanqmuir isotherm constants are shown in Table 4.

Table 4. Freundlich and Lanqmuir isotherm constants

Sorbent	Freundlich isotherm constants			Lanqmuir isotherm constants			
	n	K_F	R^2	K_L, *l/g*	a_L, *l/mg*	R_L	Q_{max}, *mq/g*
Carboxylate containing copolymer	1.0026	12.31	0.989	13.61	0.0259	0.047	483.1

The data of Table 4 shows that the sorption process can be considered as profitable (RL = 0,047); maximum value of SCS (483.1 mg/g) = C_0 is reached at 778.8 mg/l.

To find the possibility of reusing the copolymer, the experiments on its regeneration through the use of hydrochloric acid of various concentrations were carried out. The process proceeded at room temperature under static conditions for 24 hours. The results of these experiments are presented in Table 5.

Table 5. Results of desorption of UO_2^{2+} -ions with hydrochloric acid (HCl)

Acid concentration, M	Activity of isotope ^{235}U in aqueous solution, Bk/l	Concentration UO_2^{2+} -ions in aqueous solution (after desorption), mg/l	Degree of sorption, %
0	1.25	2.46	1.2
0.00051	10.9	21.4	9.2
0.00075	19.5	38.35	16.5
0.003	28.5	56.25	24.2
0.005	39.5	77.68	33.5
0.001	56.7	111.41	48.0
0.05	75.4	148.29	63.9
0.1	85.6	168.35	72.5
0.3	102.9	202.37	87.2
0.75	110.2	216.73	93.4
1.5	114.4	225.0	96.9
2.0	112.4	221.05	95.3

As is seen from Table, when using diluted solutions of hydrochloric acid, a degree of desorption of UO_2^{2+}-ions doesn't exceed 24,2%.

When using an acid in the concentration (from 0.1 to 0.3 M), a degree of desorption of uranyl-ions is 72.5 and 87.2%, respectively. A maximum degree of desorption of UO_2^{2+}-ions (~ 97%) is attained when using an acid of 1M concentration.

CONCLUSION

Thus, the results of the analysis make it possible to recommend the cross-linked copolymer obtained by radical copolymerization of styrene, maleic anhydride and new cross-linking comonomer-1,3-bis-(propenylphenoxy)-propane as sorbent for effective purification of aqueous solutions from uranium salts.

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ОЧИСТКА ВОДЫ ОТ УРАНИЛ-ИОНОВ С ПОМОЩЬЮ НОВОГО СОРБЕНТА КАРБОКСИЛАТНОГО ТИПА

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Гидролизованный тройной сополимер стирола, малеинового ангидрида и 1,3-бис-(пропенилфенокси)пропана исследован в качестве сорбента для извлечения уранил-ионов из водных систем. Изучено влияние pH среды, концентрации уранил-ионов, количества сорбента, продолжительности сорбции и др. факторов на основные показатели

процесса сорбции. С применением уравнений Ленгмюра и Фрейндлиха проведен анализ изотерм сорбции уранил-ионов. Установлена возможность использования сополимера как в концентрированных, так и разбавленных растворах.
Ключевые слова: *сшитые полимеры, изотермы собции, уранил-ионы, регенерация*

SULU SİSTEMLƏRİN URANİL-İONLARDAN YENİ KARBOKSİLAT TİPLİ SORBENT VASİTƏSİ İLƏ TƏMİZLƏNMƏSİ

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Sulu sistemlərindən uranil-ionlarının təmizlənməsi üçün hidroliz olunmuş stirol, malein anhidridi, 1,3-bis-(propenilfenoksi)propan əsasında alınmış üçlü sopolimerindən sorbent kimi istifadə olunmuşdur. Sorbsiya prosesinin əsas göstəricilərinə mühitin pH-i, uranil-ionlarının qatılığı, sorbentin miqdarı, sorbsiya vaxtı və s. faktorların təsiri öyrənilmişdir. Lenqmür və Freyndlix tənliylərindən istifadə edərək uranil-ionlarının sorbsiya izotermlərinin təhlili aparılmışdır. Sopolimerin qatı və duru məhlullarda istifadəsinin mümkünlüyü təsdiq edilmişdir.
Açar sözlər: *tikili polimer, sorbsiya, uranil-ionları, sorbsiya izotermləri, regenerasiya*