

## The Investigation of the Nitro-Containing Cross-Linked Copolymers of Maleic Anhydride and Styrene as Chelating Sorbents for Extracting Uranyl-Ions from Water Systems

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### Abstract

Copolymers of maleic anhydride and styrene were synthesized by block-radical polymerization. The structures of cross-linked copolymers were determined by IQ-spectroscopy. Based on the obtained structure, the shape of cross-linked copolymer, which was used as a sorbent and the structure of uranyl-ions which is in hydrated form in water solution forms the chelating structure due to free electron pair of nitrogen, oxygen and recoverable ions. Detection of the best conditions of sorption of uranyl-ions by cross-linked copolymer was carried out in the experiments by varying pH at different time intervals.

**Keywords:** PEPA copolymers; Maleic anhydride; Polymers

### Introduction

As the title implies the article describes the results of investigation of purification water systems from uranyl-ions by the cross-linked with PEPA copolymers of maleic anhydride and styrene [1,2].

There are determined the high sorption properties of these substances to the uranyl-ions in the wide interval of the concentration and shown the opportunity of the reusing (after desorption of bound ions of hydrochloric or sulfuric acid) [3,4].

The modern technologies, which related with purification of natural and waste water from ions of heavy metals, radionuclides and other ecological dangerous compositions, there are widely used sorption methods.

Nowadays by this aim there are used chelating sorbents of polymer type. Also they are proposed in the analytic chemistry for the deciding tasks such as separating, concentrating and determining micro quantities at the different objects [5,6].

The article reports results of our investigation of studying the copolymers of maleic anhydride and styrene, which are cross-linked by PEPA, as sorbent for extracting uranyl-ions from water solutions.

### Experimental Part

Copolymers of maleic anhydride and styrene (yield~98%) were synthesized by block-radical polymerization by known method [7]: at the temperature 80°C in the presence of initiator of dinitryl azoisobutyric acid (1%) during 5 hours.

Curing of synthesized copolymers was developed by their interaction with PEPA at 40-60°C. Quantity of taken PEPA and copolymer was (0.2-0.3):1 mol.

Curing (cross-linked) part separated from solution part by extracting boil mixture of benzene and acetone in the device of Soxhlet (yield 98.5%).

The structures of cross-linked copolymers were determined by of IQ-spectroscopy. IQ-specters were shot in the device Specord-45-I.R.

At the IQ-spectra there are determined the following characteristic bands: 1648 (-NH-CO), 1700(C=O), 1622 (-C<sub>6</sub>H<sub>5</sub>), 3300 (-COOH).

As it is shown on the IQ-specters conclusions are drawn that

curing copolymers of PEPA was by opening of anhydride ring into the copolymer, mainly, with formation of the following structures:

The results of TG and DTA-analyses of cross-linked copolymers, which were carried on the device STA 449 F<sub>3</sub> Jupiter- NETZSCH (Leading Thermal Analyses), were confirmed their high thermal properties (mass losing at temperature 210,410 and 680°C respectively 10.1, 65.0 and 85.2%).

Into their structure they contain of potential important for complexing groups such as -NH, -CO, -COOH, through which the reaction of complexing with uranyl-ions and their extraction from water solutions.

By the aim of revealing sorption chelating properties of above-mentioned cross-linked copolymers to uranyl-ions, laboratory investigations were carried by using water solutions of uranyl-nitrates at different concentrations.

Initial solutions were prepared by dissolution exact samples of uranyl-nitrate in distilled water. Also we prepared ammoniac buffer solutions by mixturing the counted volumes 0.1M CH<sub>3</sub>COOH CO, 1M CH<sub>3</sub>COONH<sub>4</sub>, NH<sub>4</sub>OH and using fiksansols of HCl and NaOH.

Experiments were carried out as follows: in the teflon cup of 100 ml capacity loading definite amounts of copolymer and an aqueous solution of a predetermined concentration uranyl-sulfate. Further, the mixture was added 10 ml 0.1M buffer solution and its volume brought to 50 ml (dilution with distilled water). The system is maintained at room temperature for a certain time, after which the aqueous solution is determined by the content of UO<sub>2</sub><sup>2+</sup> ions.

In the static conditions, the systems, which consist of water solutions of uranyl-nitrates and copolymers, was aged at 25°C during 24 hours. In

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the end of standing the water solution was filtered and into this activity of isotopes of uranium such as  $^{235}\text{U}$  and  $^{238}\text{U}$  was determined.

Desorption of uranyl-ions, which related with sorbent, was carried out at room temperature also into the static regime during 24 hours by mineral acid (HCl or  $\text{H}_2\text{SO}_4$  in different concentration). Quantity of taken uranyl-containing sorbent is 50 mg. Based on activity of isotope  $^{238}\text{U}$  (after sorption) we can judged about extraction degree of these ions.

Concentration of  $\text{UO}_2^{2+}$  ions in water systems (before and after sorption) was determined by  $\gamma$ -spectroscopy HPGe with germanium detector (made in USA).

## Results and Discussion

As it known, the nature of sorbent, initial concentration in solution, pH, diffusion speed, containing the functional groups into structure of sorbent and other many factories influence to the process of sorption.

Based on the structure of cross-linked copolymer, which we used as a sorbent and the structure of uranyl-ions, which usually are in water solutions in the hydrated form, obviously, chelate structures were formed due to free electron pair of nitrogen, oxygen and recoverable ions.

The initial concentration of uranyl ions and their state in solution, also pH of solution are the main factors, from which the process of sorption largely depends.

By the aim of to identify the influence of concentration of uranyl-ions to the sorption capacity of sorbent (SCS), and also the degree of binding of these ions (R) the series of experiment were carried out in the alkaline medium (pH 11). The containing of uranyl-ions into water solution was changed in wide interval (from  $21.2 \pm 0.4$  till  $318.0 \pm 6.6$  mg/g).

The results of investigations for learning the influence of concentration of uranyl-ions in initial solution on the values of  $\text{SCSUO}_2^{2+}$  and (R%) are shown in the table.

As it is shown at the Table 1, the process of sorption proceeds as in diluted solutions as in concentrated solutions. Their extraction rate from solutions with concentration from 21.2 till 212 mg/l is 95%.

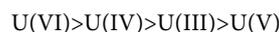
When we increased the concentration from 265 to 318 mg/l the R was 89.0 and 82.5%, but  $\text{SCSUO}_2^{2+}$  regularly increasing with increasing of concentration of uranyl-ions in initial water solution.

So, we can say about opportunity of using our sorbent in wide interval of concentration of uranyl-ions into water systems.

At the pH 12 the influence of weight of sorbent on value of  $\text{SCSUO}_2^{2+}$  and R was investigated. The initial concentration of uranyl ions into water solution in these experiments was  $636 \pm 1, 3$  mg/l, but the activity of isotope  $^{235}\text{U}$   $144 \pm 3$  Bq/l. Those results are shown on the Table 2.

As it is shown on the Table 2, the weight of sorbent give certain influence on the extraction rate of uranyl-ions (R) from water solution and  $\text{SCSUO}_2^{2+}$ . By increasing of weight of sorbent from 10 till 275 mg the amount of bind uranyl-ions was increasing from 33.1 till 99.0%, but the value of  $\text{SCSUO}_2^{2+}$  was decreasing from 1061.3 till 114.4 mg/l.

In water solution the uranyl salts could be in hydrate view. According to the stability of the valence state of uranium, they are arranged in the following sequence [8,9]:



The stability of high positive charge of U(VI) and U(V) was by formation of uranyl- ( $\text{UO}_2^{2+}$ ) and uranoil- ( $\text{UO}_2^+$ ) ions. Obviously, the ions of both type participated in the process of complexing with cross-linked copolymer.

By the aim of detection of the best conditions of sorption of uranyl-ions by cross-linked copolymer there were also carried out the experiments in different pH (from 1 till 13).

The influence of pH on SCS is shown in Figure 1. As it is shown on Figure 2, on the curve of dependence of SCS on pH of water solution, the best data of sorption properties of cross-linked copolymer, which we use as sorbent, were found in weakly acid medium (pH~6) and strongly alkaline medium (pH=12).

As it is known, the task, from which the opportunity of practical using the sorbent most depended, was the developing of convenient ways of desorption the bond ions.

As our investigations showed the desorption of bond uranyl-ions could carried out into mineral acid (HCl,  $\text{H}_2\text{SO}_4$ ). The results of these investigations are shown in the Tables 3 and 4.

The investigations have shown that by the dependence of concentration of mineral acid, which was used, we can achieve the high desorption rate.

Thus, when we used the hydrochloric acid as desorbent in the 1.5-2.0 mol/l concentration, the maximum of desorption rate of ions achieved 99-99.3%, at the same time when we use the sulfuric acid the full desorption achieved in 2.0 mol/l concentration.

As further studies have shown that the regenerated sorbent can be reused.

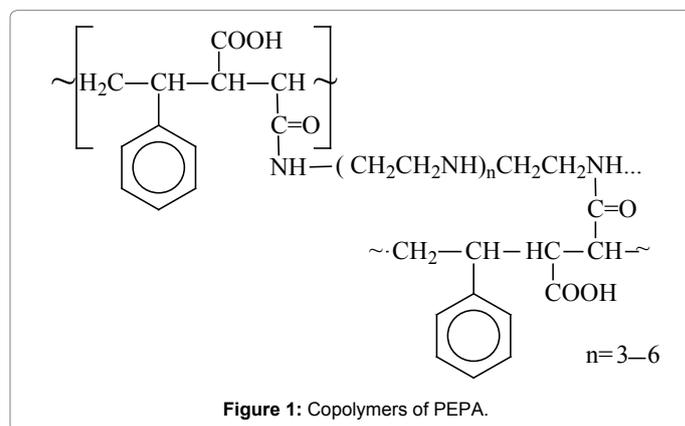


Figure 1: Copolymers of PEPA.

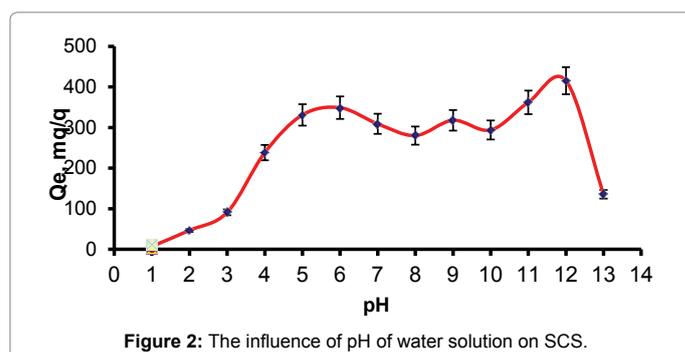


Figure 2: The influence of pH of water solution on SCS.

Concentration of uranyl-ions in water solution, mg/l		Activity of isotope $^{235}\text{U}$ in water solution, Bq/l		SCSUO <sub>2</sub> <sup>2+</sup> mg/g	R %
Before sorption	After sorption	Before sorption	After sorption		
21.2 ± 0.4	0.4	4.8	0.1	20.8	97.9
42.4 ± 0.8	3.5	9.6	0.8	38.9	91.7
106.0 ± 2.2	4.0	24.0	0.9	102.0	96.3
159.0 ± 3.3	6.6	36.0	1.5	152.4	95.8
212.0 ± 4.4	11.1	48.0	2.5	200.9	94.8
265 ± 5.5	29.2	60.0	6.6	235.8	89.0
318 ± 6.6	55.7	72.0	12.6	262.3	82.5

Table 1: The influence of concentration of uranyl-ions on the indicators of sorption.

The sorbent mass, mg	Activity of isotope $^{235}\text{U}$ in water solution, Bq/l	Concentration of UO <sub>2</sub> <sup>2+</sup> -ions in water solution after sorption, mg/l	SCSUO <sub>2</sub> <sup>2+</sup> mg/g	R %
	After sorption			
10	636 ± 1.3	425.8	1061.3	33.1
20	-	318.9	792.8	49.9
40	-	213.8	527.8	66.4
50	-	158.1	477.9	75.1
75	-	126.3	339.8	80.1
100	-	80.4	277.8	87.4
125	-	74.2	224.7	88.3
150	-	60.1	192	90.6
175	-	51.2	167.1	91.9
200	-	34.5	150.4	94.6
225	-	20.3	136.8	96.8
250	-	9.3	125.3	98.5
275	-	6.6	114.4	99

Table 2: The influence of mass of sorbent on the indicators of sorption process.

Concentration of HCl, mol/l	Concentration of desorption ions, mg/l	Desorption rate %
-	4.40	1.2
5 × 10 <sup>-4</sup>	35.38	17.4
7.5 × 10 <sup>-4</sup>	58.05	28.5
10 × 10 <sup>-4</sup>	74.64	36.7
5 × 10 <sup>-3</sup>	123.29	60.6
10 × 10 <sup>-4</sup>	96.67	47.5
0.05	159.50	78.4
0.1	180.94	88.9
0.3	168.88	83.0
0.75	181.92	89.4
1.5	202.09	99.0
2.0	201.33	99.3

Table 3: The influence of concentration of HCl on the desorption rate. (SCSUO<sub>2</sub><sup>2+</sup> initial sorbent 230 mg/g).

Concentration of H <sub>2</sub> SO <sub>4</sub> , mol / l	The concentration of desorbed ions, mg / l	Degrees of desorptions %
-	3.6	1.2
5 × 10 <sup>-4</sup>	42.02	20.7
7.5 × 10 <sup>-4</sup>	78.29	38.5
10 × 10 <sup>-4</sup>	82.27	40.4
5 × 10 <sup>-3</sup>	98.63	48.5
10 × 10 <sup>-4</sup>	144.19	70.9
0.05	178.04	86.5
0.1	188.42	92.6
0.2	203.4	100

0.35	199.92	98.3
0.75	203.42	100
1.5	203.02	99.8
2	203.42	100

**Table 4:** The influence of H<sub>2</sub>SO<sub>4</sub> on the desorption rate. (SCSUO<sub>2</sub><sup>2+</sup> initial sorbent 230 mg/g).

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