

CONCENTRATION OF URANIUM(VI) WITH A CHELATE-FORMING SORBENT

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The sorption properties of a modified sorbent based on a maleic anhydride-styrene copolymer with respect to uranium(VI) have been studied. The main quantitative characteristics of metal ion sorption are determined. A sorbent containing fragments of molon acid hydrazide for the selective extraction of uranium(VI) from solutions is proposed. The optimal sorption conditions were determined. The degree of extraction of uranium(VI) under optimal conditions exceeds 95%. A technique for the sorption-photometric determination of uranium(VI) in sea water has been developed

Keywords: uranium (VI), concentration, copolymer, sorbent, sorption, determination

INTRODUCTION

Sorption methods have found wide application for the preconcentration of radionuclides. Chelating sorbents are of particular interest as sorption material. More efficient is the use of modified forms of the copolymer of maleic anhydride with styrene. For example, chelating sorbents, which are matrices on which organic compounds are fixed [1–18]. Recent publications indicate that the copolymer of maleic anhydride with styrene is a promising matrix for the preparation of chelating sorbents [19–28].

The main goal in the present work is to study the conditions for the preconcentration of uranium(VI) with a new chelating sorbent containing molon acid hydrazide fragments, followed by the determination of these ions by photometric spectrometry to extract uranium(VI) from sea water.

EXPERIMENTAL

Sorbent. To study the sorption of uranium, a chelating sorbent containing fragments of molon acid hydrazide was used.

Synthesis of sorbents based on copolymer of maleic anhydride with styrene.

Radical copolymerization of maleic anhydride with styrene was carried out in a benzene solution in a water bath (75-80°C) for 140 minutes. Azobisisobutyronitrile recrystallized in ethanol was used as an initiator. The resulting copolymer was washed with benzene and dried in an oven at 50°C until a constant weight was obtained. The output of the copolymer is 95-97%. From the literature it is known that maleic anhydride forms with styrene a linear sequential copolymer with a molar ratio of 1:1. The calculated amount of formaldehyde and the corresponding amine was added to the obtained copolymer. The reaction was carried out in a sand bath with continuous stirring. Due to the fact that the reaction was carried out in an aqueous medium, the anhydride groups in the composition of the copolymer undergo hydrolysis [29].

As a result of the interaction of formaldehyde and amine, an unstable carbonylamine is formed in the system. The resulting carbonylamine interacts with the carboxyl groups of the macromolecule, and the introduced amine fragment enters the macromolecule [29]. For use in the analysis, the sorbent granules were ground in an agate mortar and sieved through a sieve (0.14 mm). The sorbents were identified by IR spectroscopy. IR spectra were recorded on a LUMOS IR Fourier microscope (BRUKER, Germany) in the wave frequency range 600–4000 cm⁻¹.

Solutions. The initial solution (2.38 g/l) of uranium (VI) was prepared by dissolving an accurate weight of the metal salt UO₂(NO₃)₂•6H₂O (chemically pure) in distilled water [30]. Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), Sr(II) solutions, Zn(II) was prepared by dissolving accurate weights of metal chlorides in 1 M hydrochloric acid. Working solutions were obtained by appropriate dilution of the stock solutions.

To create the required acidity, fixanalHCl (pH 1–2) and ammonium acetate buffer solutions (pH 3–11) were used. In order to create a constant ionic strength, KCl (analytical grade) was used. The determination of uranium in solutions was carried out by the spectrophotometric method using the reagent - 2,2',3,4-tetrahydroxy-3'-sulfo-5'-chloroazobenzene.

Study of metal sorption. Metal sorption isotherms were obtained under static conditions at 20°C. The sorption value and the degree of metal extraction were calculated from their equilibrium concentration in the solution by the spectrophotometric method [31]. Spectrophotometric measurements were performed using a Lambda Perken Elmer spectrophotometer and a KFK-2 photoelectric colorimeter.

The degree of extraction (R,%) and the value of sorption (a_s, mg/g) for the studied component were calculated using the formulas:

$$R = \frac{(C - [C])}{C} \cdot 100$$
$$a_s = \frac{(C - [C]) \cdot V}{m}$$

where C and [C] are the initial and residual (equilibrium) concentrations of the adsorbate, respectively, mg/l; V is the volume of the solution, l; m is the mass of the sorbent, g.

When studying sorption in a static mode, 4.76 mg of U(VI) metal aqueous solution was introduced into a test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the required acidity to a total volume of 20 ml. 0.05 g of the sorbent was added to a test tube, closed with a cork, and intensively stirred for 1–240 min, depending on the task. The solution was separated from the sorbent by filtration.

To study the effect of the amount of sorbent on the amount of sorption of uranium(VI) ions at pH 5, different amounts of sorbent (10,20,30,40, and 50 mg) and the same volume of solution (20 ml) containing 4.76 mg of metal ions were added.

The dependence of metal desorption from the modified sorbent surface on acidity and eluent concentration was studied under static conditions. A portion of the modified sorbent weighing 0.05 g was placed in a 50 ml beaker with a metal solution and left for three hours with occasional stirring. After three hours, the sorbent was separated by filtration. The concentration of desorbed uranium (VI) was determined in the obtained filtrate.

Performing the analysis. 100 ml of the filtered analyzed sample was adjusted to the required pH by adding HNO₃ and passed through a minicolumn with a sorbent at a flow rate of 1.0 ml/min. The sorbed metal ions were eluted with 5 ml of 2 M HClO₄ at a rate of 1.0 ml/min. The uranium concentration in the eluate was determined by the photometric method. The results were calculated assuming 100% uranium recovery.

RESULTS AND DISCUSSIONS

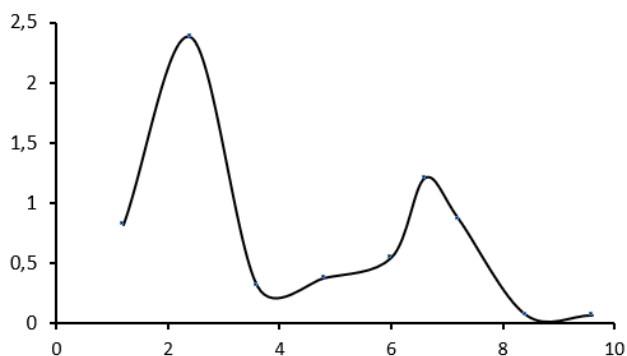
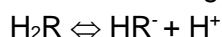


Figure 1. Differential titration curve of the sorbent.

From fig. 1 it can be seen that the resulting sorbent contains two different ionogenic groups. So the ionization of the sorbent occurs in two stages:



The ionization constant of the sorbent was calculated by the modified Henderson-Hasselbach equation [32].

By measuring the pH value of the solutions over the sorbent for each value of α , we plotted the dependence $\text{pH} = f\left(\lg \frac{\alpha}{1-\alpha}\right)$. The parameters $m(\text{tg}\alpha = m)$ were calculated from the value of the tangent of the slope of the straight line.

The graphical definition of the ionization constant of the sorbent is shown in Figure 2.

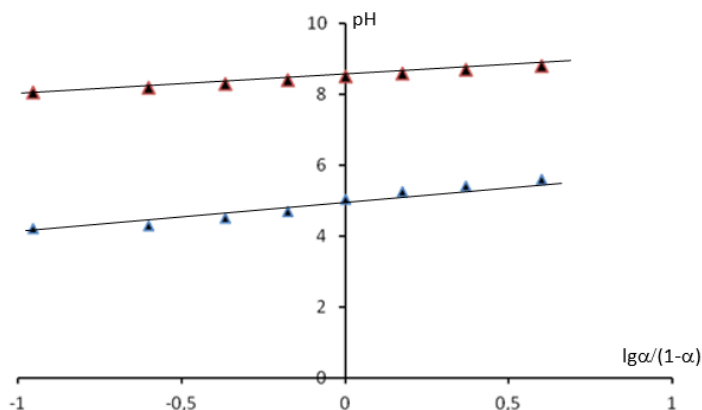


Figure 2. Graphical determination of the sorption ionization constant: $pK_1(\text{graph})=4.90$, $pK_2(\text{graph})=8.60$, $m_1=0.995$; $m_2=0.488$; (pK_1 - characterizes the ionization of carboxyl groups, pK_2 -deprotonization of amine groups)

Influence of pH on sorption. The study of the effect of pH (in the range of 1-8) on the preconcentration of uranium(VI) ions under static conditions showed that the quantitative extraction of metal ions is achieved at pH 4.

At low pH values (1–3) of the liquid phase, the low degree of extraction can be associated with the protonization of the functional groups present in the sorbent phase and the low degree of polymer swelling.

At such pH values, U(VI) ions are in the form UO_2^{2+} [33]. With an increase in the pH of the liquid phase, the degree of swelling of such polymeric sorbents increases. The maximum degree of uranium extraction by sorbents is achieved from solutions with pH 4. It was also found that at pH 4, the maximum metal sorption is achieved using 30 mg of the sorbent (Table 1).

Table 1. Influence of the amount of sorbent on the degree of extraction of uranium(VI): $C_{UO_2^{2+}}=238 \text{ mg/l}$, $V=20 \text{ ml}$, $pH=4$

m, mg	10	20	30	40	50
R, %	23	49	80	80	80

All further studies were carried out at pH 5.

Effect of time on sorption. It was found that the sorption equilibrium in the "sorbent - liquid phase" system is achieved after 2 hours of contact (Fig. 3). For all further experiments, the time to establish the sorption equilibrium was 2 hours.

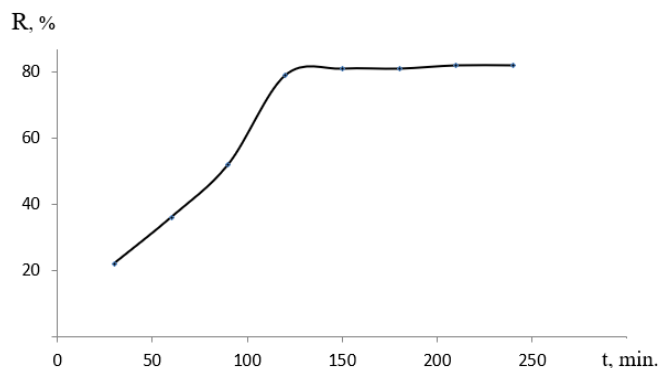


Figure 3. Dependence of the degree of extraction of uranium(VI) on time.

Influence of ionic strength on sorption. It is known [34] that the ionic strength of the solution significantly affects the flexibility of the solid-phase matrix and the state of the functional groups of the analytical reagent, in connection with this, the dependence of the analytical signal on the ionic strength was studied. An increase in ionic strength to 0.6 does not affect sorption. Its subsequent increase from 0.6 to 1.4 leads to a significant decrease in the sorption value. All further experiments were carried out in solutions with an ionic strength of 0.8.

Influence of uranium (VI) concentration. The study of the dependence of the sorption capacity on the concentration of uranium (VI) showed that the sorption value changes with the concentration of the uranyl ion. The sorption isotherm of uranium (VI) shows a steep rise in the initial linear section, the convexity of the isotherm curve, which indicates a high sorption (Fig. 4).

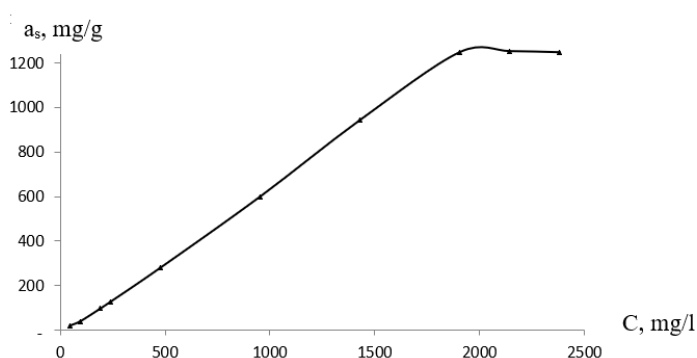


Figure 4. Isotherm of sorption of uranium (VI) by the obtained sorbent: $m_{\text{sorb}}=30$ mg, $V=20$ ml, $\text{pH}=4$

So, with an increase in the concentration of the uranyl ion in the solution, the amount of sorbed metal increases, and at a concentration of 1252 mg/l it becomes maximum ($\text{pH}=5$, $V_{\text{tot.}}=20$ ml, $m_{\text{sorb.}}=0.05$ g)

Study of the desorption of the absorbed uranyl ion from a polymeric sorbent. To select a suitable eluent, various acids were tested - HClO_4 , H_2SO_4 , HNO_3 , HCl . It was found that the desorption capacity of HClO_4 is higher than that of other acids; this may be due to the fact that perchlorate ions do not form complexes with metals, including uranium. A study of the influence of the HClO_4 concentration showed that U(VI) ions are maximally desorbed at a volume of 5 ml and a concentration of 2 M perchloric acid (Table 2).

Table 2. Effect of concentration and volume of eluent on the degree of desorption (%) of uranium

concentration and volume HClO_4	degree of desorption, %
0,5 M 5 ml	84
10 ml	86
1,0 M 5 ml	91
10 ml	93
1,5 M 5 ml	93
10 ml	96
2,0 5 ml	97
10 мл	97

Note: $n=5$, $p=0,95$

After determining the optimal preconcentration conditions, the developed method was successfully applied to determine the microquantities of uranium(VI) in sea water (the coast of the Govsan settlement, the Caspian Sea, Azerbaijan) with preliminary preconcentration (Table 3). The table shows that sea water contains 7.306 ± 0.101 $\mu\text{g/ml}$ of uranyl ion. The correctness of the technique was checked by the "introduced - found" method (Table 3).

Table3. Sea water analysis results.

introduced, mkq/ml	found $\bar{x} \pm \frac{t_p s}{\sqrt{n}}$, mkq/ml
-	7,306 \pm 0,101
10	16,489 \pm 0,127
20	27,299 \pm 0,318

Note: sample volume 100 ml; eluent volume 5 ml; $m_{\text{cop6}}=100$ mg; $\lambda=490$ nm, $l=1$ sm, $p=0,95$; $n=6$

CONCLUSION.

A new sorbent based on a copolymer of maleic anhydride with styrene was synthesized by modification with molon acid hydrazide in the presence of formalin. The resulting sorbent was used to extract uranium from sea water. The optimal conditions for the sorption of uranium on the sorbent are determined. The sorbent used to determine trace amounts of radioactive metal has higher sorption properties (sorption capacity, analysis time, concentration temperature, influence of foreign ions on sorption) compared to those known in the literature [1–18]. The data obtained showed that the proposed sorbent can be used to preconcentrate uranium from solutions such as natural waters. It is possible to reuse the regenerated sorbent for preconcentration.

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