

PRECONCENTRATION OF URANIUM(VI) BY CHELATE-FORMING SORBENT ON THE BASIS OF MALEIC ANHYDRIDE-METHACRYLIC ACID COPOLYMER

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Abstract. The sorption ability of a chelating sorbent based on a copolymer of maleic anhydride with methacrylic acid in relation to uranium was studied. The sorbent was obtained by modifying the copolymer with 1,1,3-Triphenylguanidine guanidine in the presence of formaldehyde. The dependence of the sorption capacity on the acidity of the solution was studied. At pH 6, the degree of sorption passes through a maximum. With an increase in the concentration of uranium (VI) in the solution, the amount of the sorbed metal increases, and at a concentration of $8 \cdot 10^{-3}$ mol/l, it becomes maximum (Sorp.cap. = 968 mg/g). The influence of ionic strength on the sorption of uranium(VI) was studied. Studies have shown that the ionic strength up to 1.2 mol/l does not affect the sorption, after 1.2 mol/l the increase in the ionic strength at the beginning gradually, and then sharply reduces the sorption. Desorption of sorbed uranium ions was also studied. The effect of various mineral and organic acids on desorption of ions was studied. Maximum desorption of uranium occurs in H_2SO_4 .

Keywords: preconcentration, uranium, sorbent, 1,1,3-Triphenylguanidine guanidine, desorption.

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1. Introduction

Analysis of natural and industrial objects in order to determine individual components is carried out using various chemical and physicochemical methods (Ali & Nouh, 2019; Choi & Nho, 2000; Khalili, & Al-Banna, 2015; Gunathilake *et al.*, 2015; Zhang *et al.*, 2016; Kobuke *et al.*, 1990; Fan *et al.*, 2012; Metilda *et al.*, 2005; Li *et al.*, 2016). However, these methods do not always allow the determination of trace amounts of radioactive elements in objects of complex composition. All these sorbents have certain disadvantages. Some of them have a low sorption capacity (Ali & Nouh, 2019; Choi & Nho, 2000; Khalili, & Al-Banna, 2015; Gunathilake *et al.*, 2015; Kobuke *et al.*, 1990) some sorbents absorb radioactive elements as much as possible when heated to 45-60° C, but at room temperature the sorption of metal does not occur (Fan *et al.*, 2012; Metilda *et al.*, 2005; Li *et al.*, 2016); for some sorbents, optimal sorption is achieved with prolonged contact (20–78 hours) (Zhang *et al.*, 2016).

Publications of recent years indicate that the copolymer of maleic anhydride with styrene is a promising matrix for the production of chelating sorbents (Bahmanova, 2020, Basargin *et al.*, 2013; Hajieva *et al.*, 2019; Maharramov *et al.*, 2011).

In this work, we propose new methods for the sorption-spectrophotometric determination of microamounts of uranium(VI). It is known from the literature (Upor *et al.*, 1985) that chelating ligands containing donor oxygen and nitrogen atoms or two neighboring oxygen atoms are suitable for the concentration of radioactive elements. In

this regard, the proposed methods are based on the preliminary concentration of uranium(VI) from natural and industrial objects using polymer chelating sorbent containing fragments of 1,1,3-Triphenylguanidine.

2. Materials and research methods

Sorbent. To study the sorption of uranium, a chelating sorbent containing fragments of 1,1,3-Triphenylguanidine guanidine was used. Sorbent synthesized by the procedure (Mamedova *et al.*, 2004).

For use in the analysis, sorbent granules were ground in an agate mortar and sieved through a sieve (0.14 mm). The identification of sorbents was carried out by IR spectroscopy.

Solutions. The initial solution of uranium (VI) was prepared by dissolving an exact weighed portion of the metal salt $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (chemically pure) in distilled water (Korostelev, 1964). Working solutions were obtained by appropriate dilution of the initial solutions.

Determination of uranium(VI) in solutions was performed spectrophotometrically with the reagent - 2',2,3,4-tetrahydroxy-3'-sulfo-5'-chloroazobenzene. It was synthesized by the azo coupling of a diazotized amine with pyrogallol in a slightly acidic medium according to the procedure (Gambarov, 1984). To create the necessary acidity HCl (pH 1-2) and ammonium acetate buffer solutions (pH 3-11) were used. In order to create a constant ionic strength, KCl (pure for analysis) was used.

The study of metal sorption. The sorption isotherm of the metal was obtained under static conditions at 20 ° C. The sorption capacity of the sorbent and the degree of metal extraction were calculated by its residual concentration in solution by the spectrophotometric method (Bulatov & Kalinkin, 1972). Spectrophotometric measurements were performed using Lambda Perken Elmer spectrophotometer and KFK-2 photoelectric colorimeter.

Degree of extraction (R,%) and static capacity (Stat. cap.) of the sorbent for uranium(VI) was calculated by the formulas:

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

$$CE = \frac{(C - [C]) \cdot V}{m}$$

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

When studying sorption in a static mode, 2 ml of a 10^{-2} M aqueous metal solution was injected into a test tube with a ground stopper, pH 6 was added to create the necessary medium to a total volume of 20 ml. Then, 0.05 g of sorbent was added, the tube was closed with a stopper and vigorously stirred for 1-240 min, depending on the task. The solution was separated from the sorbent by decantation. The dependence of metal desorption from the surface of modified sorbents on the acidity and concentration of the medium was studied under static conditions. A portion of the sorbent, saturated with 0.05 g of uranium(VI), was placed in a 50 ml beaker with a solution of the desorbing solution and left for three hours, stirring occasionally. After three hours, the sorbent was separated by decantation and the concentration of desorbed uranium (VI) was determined in the resulting filtrate.

3. Research results and discussion

In the present work, the main attention was paid to the study of the influence of pH of the medium, time, ionic strength, metal concentration in solution on the sorption of uranium(VI), as well as the kinetic properties of sorbents.

The dependence of the static capacity of the sorbent for uranium(VI) is shown in Fig. 1.

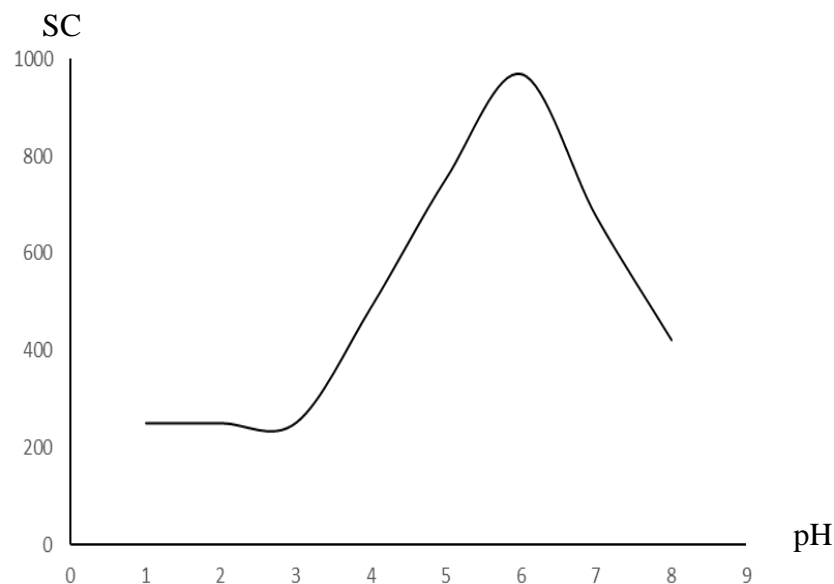


Figure 1. Dependence of the static capacity (SC.) of the sorbent for uranium on the pH of the solution. $m_{\text{sorb}} = 30 \text{ mg}$, $V = 20 \text{ ml}$

From figure 1 it can be seen that the maximum sorbent capacity for uranium(VI) is reached at pH 6.

Fig. 2 shows the dependence of Stat.cap. of uranium(VI) on the time of sorption.

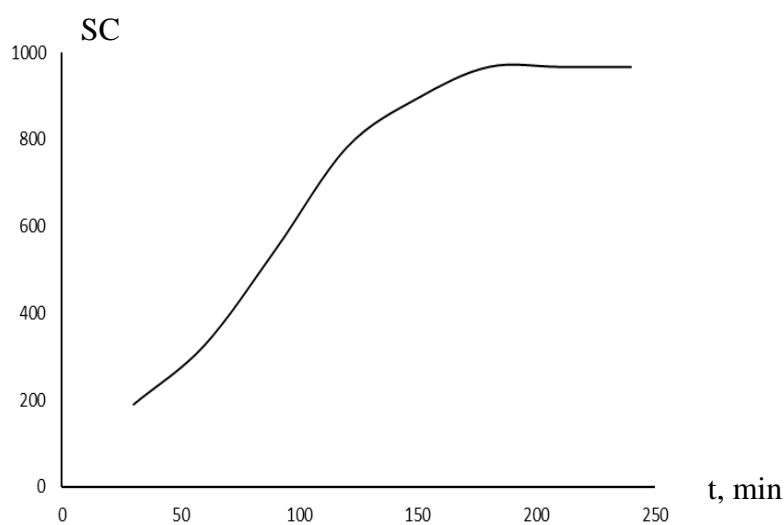


Figure 2. Dependence of the static capacity (SC) of the sorbent for uranium(VI) on the time of sorption

It is seen that the sorption equilibrium is established after 3 hours. In this regard, in all further experiments, the time to establish the sorption equilibrium was 3 hours.

The influence of the ionic strength of the solution. Uranium (VI) was sorbed from solutions containing 0.1-2.0 M KCl. The results of the study showed that a significant decrease in metal sorption occurs from KCl solutions with a concentration of more than 1.2 M (Table 1).

Table 1. The influence of the ionic strength of the solution on the sorption of uranium (VI): $m_{\text{sorb}} = 30 \text{ mg}$, $V = 20 \text{ ml}$, $\text{pH}=6$

$\mu, \text{ mol/l}$	0,2	0,4	0,6	0,8	1,0	1,2	1,4	1,6	1,8	2,0
CE, mg/q	968	968	968	968	968	968	897	64	41	26
								2	8	3

For the synthesized sorbent, the sorption isotherm of uranium (VI) was determined, which determines the dependence of the static capacity on the equilibrium concentration of uranium in solution (Fig. 3).

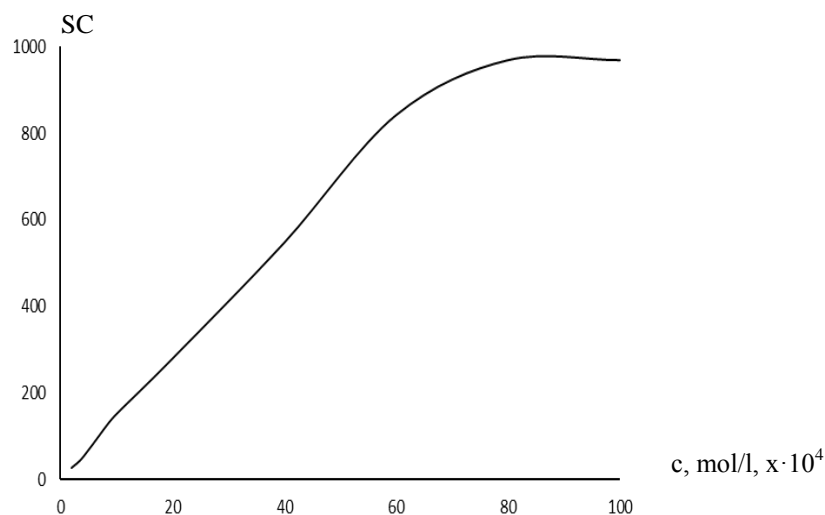


Figure 3. Sorption isotherm of uranium (IV) with a sorbent: $m_{\text{sorb}} = 30 \text{ mg}$, $V = 20 \text{ ml}$, $\text{pH} = 6$

From Fig. 3 it can be seen that with an increase in the concentration of uranium ion in the solution, the capacity of the sorbent increases. When the concentration of uranium is higher than $8 \cdot 10^{-3} \text{ mol/l}$, the capacity reaches a maximum value ($\text{SC} = 968 \text{ mg/g}$).

Desorption of uranium (VI). The results of the desorption of uranium (VI) with solutions of various mineral acids (HCl , HClO_4 , HNO_3 , H_2SO_4) under static conditions are shown in Table 2.

The results showed that the highest degree of desorption is observed when using solutions of H_2SO_4 with a concentration of 2 mol/l.

Thus, this study has shown the possibility of using a maleic anhydride with methacrylic acid copolymer matrix modified with 1,1,3-Triphenylguanidine for sorption-photometric determination of uranium (VI).

Table 2. Desorption of uranium (VI) with solutions of various mineral acids under static conditions: $m_{\text{sorb}} = 50$ mg, $V = 60$ ml, contact time - 3 hours.

Acid	Concentration, mol/l	Degree of desorption, %
HCl	0,5	78
	1,0	83
	1,5	88
	2,0	91
HClO ₄	0,5	84
	1,0	90
	1,5	92
	2,0	92
HNO ₃	0,5	74
	1,0	79
	1,5	83
	2,0	85
H ₂ SO ₄	0,5	84
	1,0	90
	1,5	95
	2,0	96

Sorbents used to determine the trace amounts of uranium (VI) have higher sorption properties (sorption capacity, analysis time, concentration temperature, influence of foreign ions on sorption) compared with those known in the literature (Ali & Nouh, 2019; Choi & Nho, 2000; Khalili, & Al-Banna, 2015; Gunathilake *et al.*, 2015; Zhang *et al.*, 2016; Kobuke *et al.*, 1990; Fan *et al.*, 2012; Metilda *et al.*, 2005; Li *et al.*, 2016). They can be reused after regeneration.

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