

CONCENTRATION OF URANIUM WITH A CHELATE FORMING SORBENT BASED ON COPOLYMER OF MALEIC ANHYDRIDE WITH STYRENE CONTAINING 2-AMINOPHENOL-4,6-DISULFO FRAGMENTS

Elnara Alirzayeva*

Department of Ecological Chemistry, Baku State University, Baku, Azerbaijan

Abstract. The sorption capacity of a chelating sorbent based on a copolymer of maleic anhydride with styrene in relation to uranium has been studied. The conditions of concentration in a static mode are determined. A sorbent was obtained by modifying a copolymer of 2-aminophenol-4,6-disulfo in the presence of formaldehyde. It was found that the obtained sorbent has a high sorption capacity with respect to uranium. The possibility of desorption of uranium (VI) by solutions of various mineral acids has been studied. It revealed that multiple use of the regenerated sorbent for concentration is possible.

Keywords: Sorption, uranium, concentration, desorption.

***Corresponding Author:** Elnara Alirzayeva, Department of Ecological Chemistry, Baku State University, Z.Khalilov, 23, AZ1148, Baku, Azerbaijan, Tel.: (+994) 507310884, e-mail: ella.3108@list.ru

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1. Introduction

Uranium is a highly undesirable impurity in many environmental objects. Due to its toxicity, the determination of its presence and separation is an urgent task. A large number of different methods (chromatographic, sorption) are used for the separation of microquantities of uranium. Numerous compounds have been proposed as sorbents for uranium - silicon dioxide polymers (Xiao *et al.*, 2016), biological-based sorbents (Zhou *et al.*, 2016), Na-bentonite (Zong *et al.*, 2015), triple magnetic composites, surface-ion-printed polymers (Shao *et al.*, 2015; Yuan *et al.*, 2016a; Yuan *et al.*, 2016b; Meng *et al.*, 2015), polyvinyl polymers (Hallaji *et al.*, 2015; Anagnostopoulos *et al.*, 2016). All these sorbents have certain disadvantages. Some of them strongly depend on the ionic strength of the solution (Xiao *et al.*, 2016; Zong *et al.*, 2015); for some sorbents, the maximum sorption occurs when heated to 45-50°C (Zhou *et al.*, 2016; Anagnostopoulos *et al.*, 2016), at room temperature their sorption does not occur; for some sorbents, the optimal sorption is achieved with prolonged contact (6-10 hours) (Zong *et al.*, 2015; Anagnostopoulos *et al.*, 2016), the sorption capacity is low.

Obtaining of sorbents with higher sorption properties in relation to uranium (VI) always remains an actual problem. The sorption properties of polymer sorbents mainly depend on the nature, position in the link, the number of functional analytical groups contained in the polymer, as well as on the physicochemical properties of the polymer matrix (Myasoedova & Savvin, 1984). Earlier, the sorption of uranium by chelating sorbents based on a copolymer of maleic anhydride with styrene containing fragments of p-amino benzoic acid and m-amino phenol was studied (Maharramov *et al.*, 2011; Basargin *et al.*, 2013).

In this work, we studied the possibility of using a chelating sorbent containing 2-aminophenol-4,6-disulfo fragments for the extraction of radionuclides from solutions of various compositions using uranium as an example. Its sorption properties in relation to uranium have been studied. Determination of uranium in solutions was carried out spectrophotometrically with the reagent 2',2,3,4-tetrahydroxy-3'-sulfo-5'-chloroazobenzene.

2. Materials and research methods

Sorbent. To study the sorption of uranium, a chelating sorbent containing 2-aminophenol-4,6-disulfo fragments was used.

Synthesis of a sorbent based on a copolymer of maleic anhydride with styrene. The radical copolymerization of maleic anhydride with styrene is 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 to constant weight. The copolymer yield is 95-97%. It is known from the literature that maleic anhydride forms a linear sequential copolymer with styrene with a molar ratio of 1:1. The calculated amount of formaldehyde and 2-aminophenol-4,6-disulfo is added to the resulting copolymer. The reaction is carried out in a sand bath with continuous stirring. Due to the fact that the reaction is carried out in an aqueous medium, the anhydride groups in the copolymer undergo hydrolysis (Alieva *et al.*, 2006).

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.

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

To create the required acidity, HCl fixanal (pH 1-2) and ammonia-acetate buffer solutions (pH 3-11) were used. To create a constant ionic strength, KCl (pure for analysis) was used.

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

The degree of extraction (R, %) and the sorbent capacity for the studied component (SC, mg/g) were calculated using the formulas:

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

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

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

To study sorption in a static mode, 2 ml of a 10^{-2} M aqueous metal solution was introduced into a test tube with a ground stopper, and the optimal pH was added to create the required acidity to a total volume of 20 ml. 0,05 g of sorbent was introduced into a test tube, closed with a stopper and vigorously stirred for 1–240 min, depending on the task at hand. The solution was separated from the sorbent by decantation.

The dependence of the desorption of metal from the surface of the modified sorbents from the acidity and concentration of the medium was studied under static conditions. A weighed portion of the modified sorbent weighing 0,05 g was placed in a 50 ml glass with an aqueous metal solution and left for three hours, stirring occasionally. After three hours, the sorbent was separated by decantation, and the concentration of desorbed uranium (VI) in the resulting filtrate was determined.

3. Research results and their discussion

The IR spectra of the obtained sorbent and polychelate were taken.

Sorbent: 3665-3108 cm^{-1} [stretching vibrations of the $-\text{OH}$ group in the carboxyl group, also stretching vibrations of the $-\text{NH}$ group (3361 cm^{-1})], 1737-1742 cm^{-1} (stretching vibrations of the $-\text{C}=\text{O}$ group in the carboxyl group), 1541-1507 cm^{-1} (stretching vibrations $\text{C}-\text{N}$ and bending vibrations $\text{N}-\text{H}$), 1602-1454 cm^{-1} (stretching vibrations $\text{C}-\text{C}$ in the benzene ring), 728-692 cm^{-1} (bending vibrations $\text{C}-\text{C}$ benzene ring).

Sorbent-U (VI): 3626-3101 cm^{-1} [stretching vibrations of the $-\text{OH}$ group in the carboxyl group, also stretching vibrations of the $-\text{NH}$ group (3325 cm^{-1})], 1720-1594 cm^{-1} (stretching vibrations of the $-\text{C}=\text{O}$ group in the carboxyl group), 1529-1500 cm^{-1} (stretching vibrations $\text{C}-\text{N}$ and bending vibrations $\text{N}-\text{H}$), 1595-1459 cm^{-1} (stretching vibrations $\text{C}-\text{C}$ in the benzene ring), 763-716 cm^{-1} (bending vibrations of $\text{C}-\text{C}$ benzene ring)

Analysis of the IR spectra showed that the synthesized sorbent is coordinated as a bidentate ligand. Comparison of the IR spectra of the sorbent and the complex formed in the sorbent phase shows that, upon complexation, shifts are observed in the vibration frequencies of the groups located in the sorbent units. Based on the frequency shifts of stretching vibrations of NH_2 and COO^- as compared with the spectra of ligands, it was concluded that in these compounds the metal is coordinated with amino and carboxyl groups.

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

The dependence of the degree of extraction of U(VI) by the sorbent on the pH of solutions is shown in Fig. 1. The maximum degree of extraction of uranium by the sorbent is achieved from a solution with pH 4. The time of sorption equilibrium does not exceed 3 hours. For all further experiments, the time to establish sorption equilibrium was 3 hours (Fig. 2).

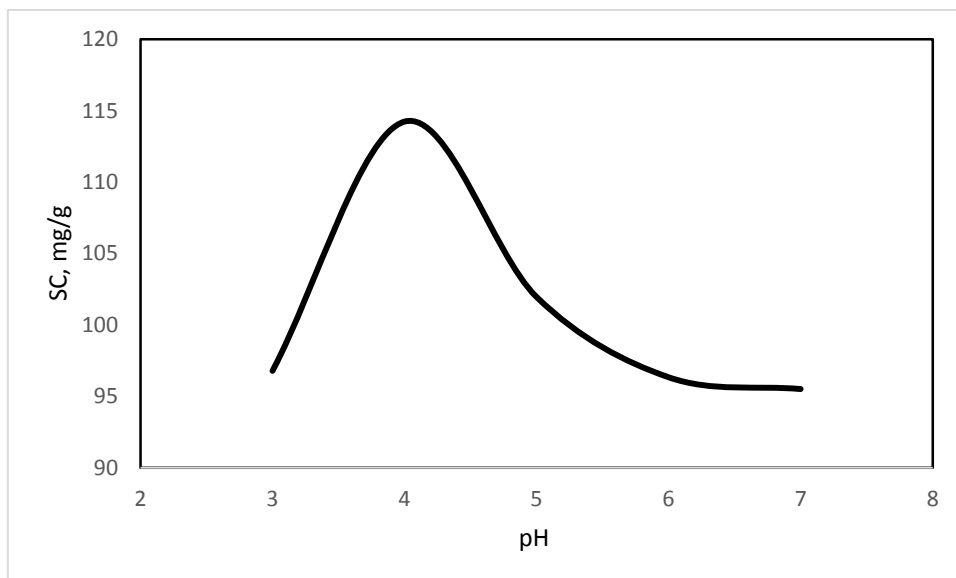


Figure 1. Dependence of the sorption of uranium (VI) on the pH of the medium ($m_{\text{sorb}}=30$ mg, $V=20$ ml, $\text{pH}=4$)

The influence of the ionic strength of the solution was studied by the photometric method. Uranium (VI) was sorbed from solutions containing 0,1-1,4 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 0,4 M.

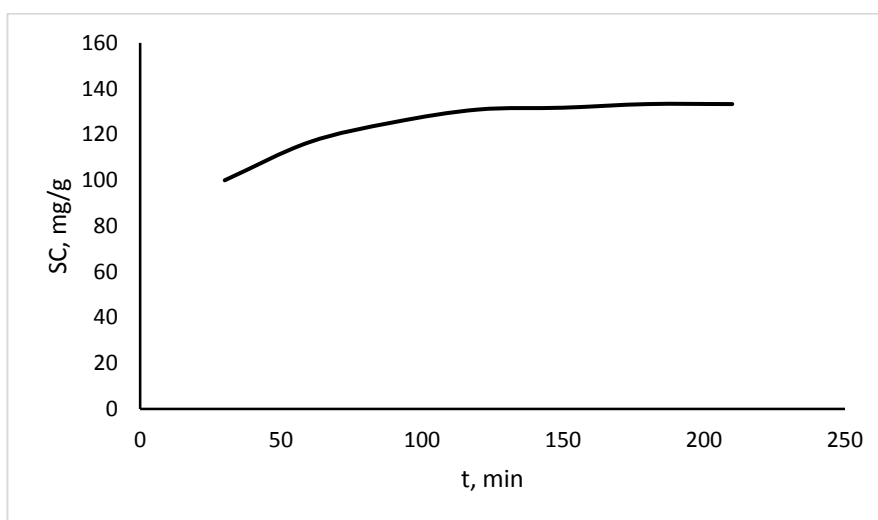


Figure 2. Dependence of the static capacity (SC) of the sorbent for uranium(VI) on the time of sorption

One of the main criteria for evaluating sorption equilibria are sorption isotherms, which determine the dependence of the sorption value of a substance on its equilibrium concentration in solution. Figure 3 is shown the isotherm of uranium sorption on the sorbent.

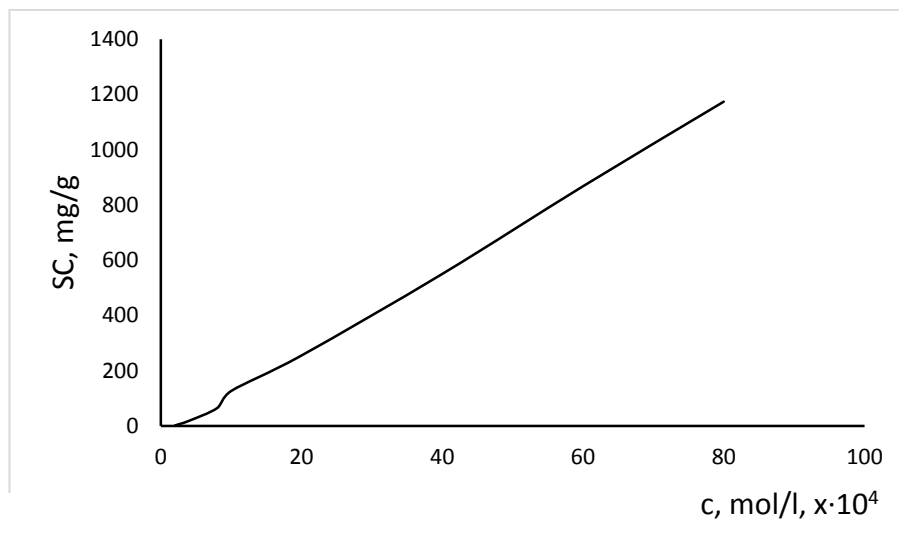


Figure 3. Sorption isotherm of uranium (VI) with the obtained sorbent:
 $m_{\text{sorb}}=30$ mg, $V=20$ ml, $\text{pH}=4$

With an increase of the concentration of uranyl ion in the solution, the amount of sorbed metal increases, and at a concentration of $8 \cdot 10^{-3}$ mol/l it becomes maximum ($\text{pH}=4$, $C_{\text{UO}_2^{2+}} = 8 \cdot 10^{-3}$ mol/l, $V_{\text{tot.}}=20$ ml, $m_{\text{sorb.}}=0,03$ g, $SC=1174$ mg/g).

The possibility of desorption of uranium (VI) by solutions of various mineral acids (HCl, HClO_4 , HNO_3 , H_2SO_4) has been studied. Data on the degree of uranium elution depending on the concentration of acids were obtained (Table 1).

Table 1. Influence of the concentration of different acids on the degree of extraction (%) of uranium ($n=5$)

Acid	Concentration, mol/l	Desorption rate, %
HCl	0,5	76
	1,5	81
	2,0	96
HClO_4	0,5	91
	1,0	94
	2,0	98
HNO_3	0,5	84
	1,0	89
	2,0	93
H_2SO_4	0,5	80
	1,5	86
	2,0	91

After determining the optimal concentration conditions, the method was successfully applied to determine trace amounts of uranium (VI) in seawater (coast of the Govsan settlement, Caspian Sea, Azerbaijan) with preliminary concentration (Table 2).

Performing analysis. 100 ml of the filtered analyzed sample was brought to the desired pH value by adding HNO_3 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 photometrically. The results were calculated assuming 100% uranium recovery.

The table shows that seawater contains 7.512 ± 0.106 µg/ml of uranyl ion. The correctness of the technique was checked by the "entered - found" method.

Table 2. Results of the analysis of seawater

Entered, µg / ml	Found $\bar{X} \pm \frac{t_{pS}}{\sqrt{n}}$, µg / ml
-	7,501±0,101
10	17,487±0,212
20	27,421±0,414

Note: sample volume – 100 ml; eluent volume – 5 ml;

$m_{\text{sorb}} = 100$ mg; $\lambda = 490$ nm, $l = 1$ cm, $p = 0.95$; $n = 5$

The data obtained showed that the synthesized sorbent can be used to concentrate uranium from solutions such as natural waters, which can be used for its radioanalytical determination. Multiple use of the regenerated sorbent for concentration is possible.

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