Jomard
Publishing

ADSORPTION PROPERTIES OF URANIUM ON THE CHELATING SORBENT MODIFIED WITH ACETYLACETONE AND APPLICATION OF THE RESULTS TO WASTEWATER SAMPLES

F.N. Bahmanova[1*], E.N. Alirzaeva[1], N.T. Afandieva[1], N.T. Shamilov[1]

[1]Department of Ecological Chemistry, Baku State University, Baku, Azerbaijan

Abstract. Sorption of uranium (VI) from aqueous solutions has been experimentally carried out. For this purpose a polymeric chelating sorbent on the base of maleic anhydride styrene modified with acetylacetone has been synthesized. The sorption properties of synthesized chelating sorbent toward uranium ions have been studied. As a function of pH, contact time, effect of initial uranium ion concentration, ionic strength and other optimal conditions on the sorption behavior of uranium (VI) has been studied. The highestadsorption capacity of uranium ion on to this adsorbent is 613.5 mg g^{-1}. The maximum removal efficiency is 95.4%. At the final stage has been investigated the desorption process using inorganic and mineral acids as the desorbing agents. The influence of matrix components on concentration of microamounts of uranium (VI) has been studied. This type of sorbent shown a high selectivity and sensitivity on uranium extraction. The availability of using this sorbent for uranium separation has been successfully applied to the determination of micro amount of uranium (VI) in the water samples taken during oil extraction.

1. Introduction

Ion-exchange methods of separation and concentration of heavy metal ions have a great importance and occupy a leading position in the chemical analysis.

Uranium is one of the most important radioelements and one of the more common elements in the Earth's crust. Uranium occurs in seawater, and can be recovered from the oceans. Its contamination of water and soil is a matter of concern because of the high toxicity of the dissolved metal. It is a very toxic metal, because all three isotopes of it have a high radioactivity. So, removal and recovery of uranium ion is essential for protection of environment and human's life.

The UO_2^{+2} ions represent the uranium (VI) state and are known to form compounds such as uranium carbonate, uranium chloride and uranium sulfate. UO_2^{2+} also forms complexes with various organic chelating agents, the most commonly encountered of which is uranium acetate (Krajnak, 2014).

Uranium ion has a strong influence in human's life, being an ion of very radioactive element. In the majority it gets organs by drink water and in concentrations above the limit allowable concentration gradually destroyed human's tissues, causing several diseases. The recommended maximum admissible concentration for uranium in drinking water according to WHO (World Health Organization) is 15µg/L (Katsoyiannis, 2007). Separation and pre-concentration of this metal ion from solution

are extremely important from the point of view of its toxicity. Application of the results of these methods to the waste waters allows reducing the quantum of uranium for disposal.

In recent years the sorption behavior of uranium ion because of its toxicity is in the field of concern. Soluble salts of uranium have a high toxicity. Well known that soluble form of uranium compounds are a part of the water and sewage and can represent a serious environmental hazard for human's life. Taking into account the high toxicity of this element its pre-concentration for subsequent allocation is one of the urgent problems of modern analytical chemistry.

Adsorption is a surface phenomenon with general mechanism for organic and inorganic pollutants removal. (Rashed, 2013). According to the literature there are several preconcentration materials for uranium removal (Kulyukhin, 2016; Zeng, 2016; Zhou, 2016; Magerramov, 2011; Basargin, 2013). One of the most widely applied remediation techniques for contaminated waters is the use of sorbent materials (Handley, 2016).

Over the last years for extraction and concentration of uranium as a heavy and toxic element are widely used synthetic polymeric sorbents. These ion-exchange sorbents due to high adsorption capacity have a high value of selectivity. These analytical characteristics allow to using synthetic polymeric sorbents for extraction and concentration of uranium from water samples.

The aim of this work is to developed the ion-exchange method-sorption to extract of uranium ions from solutions. The sorption process has advantages such as a high degree of adsorption capacity, sensitivity and widely used to determine and identification toxic elements. For this process as a chelating sorbent a polymeric synthetic sorbent on the base of maleic anhydride styrene modified with acetylacetone was synthesized and its sorption properties toward uranium ions has been studied.

2.   Experimental

All chemicals used in analysis were of analytical reagent grade. In experiments for the preparation of 10^{-2} M uranium solution was used salt of uranium - uranyl nitratehexahydrated $UO_2 (NO_3)_2 \cdot 6H_2O$. A uranium stock solution containing 250 mg L^{-1} of U (VI) was prepared by dissolving 1.782 g of uranyl nitratehexahydrated and diluting to 250 ml using the distilled water. It was identified ion equilibrium concentration of U (VI) in a solution by photometric method - using a 10^{-3} M solution of the reagent 2, 2', 3, 4-tetrahydroxy-3'-sulfo-5'-chlorebenzene.

For photometric studies have been used 10^{-3} M metal solutions and for sorption studies -10^{-2} M. Solutions used for experiments were prepared with double distillled water. Ammonia-acetate buffer solutions (pH 3-11) were used to achieving the corresponding environment acidity. Solution of chemically pure KCl was used for achieving the constant ionic strength. 0.5M;1M;1.5M;2 M solutions of $HClO_4$, HCl, H_2SO_4 and HNO_3 was used as desorbing agents in desorption process. KOH solution used in desorption process was prepared from a chemically pure potassium hydroxide.

Polymeric chelating sorbent on the base of maleic anhydride styrene was synthesized by the known technique (Cutter, US4145375 A).

Apparatus

The optical density of the test solutions has been measured on phototocolorimeter КФК -2. pH of the solutions was measured using an ionomer И-130.For each experiment the contents of the sorption flasks were continuously stirred using a stirrer ORBITAL SHAKER TS-1. The sorbent was dried on evaporator ZymarkTurboVap LV.

3. Results and discussion

The effect of pH

The effect of medium acidity on the retention of uranium from aqueous solutions has been investigated. The appropriate pH of buffer solutions was adjusted using CH_3COOH and NH_4OH to achieve the desired medium acidity (3–8). At pH=5 separation of uranium ions is higher than at pH<5. After pH=5 with increasing of medium acidity the sorption of uranium ions will decreases. So, according to the results, the optimum pH value of the sorption is pH=5. Fig. 2 shows the dependence of the sorption capacity on the medium acidity.
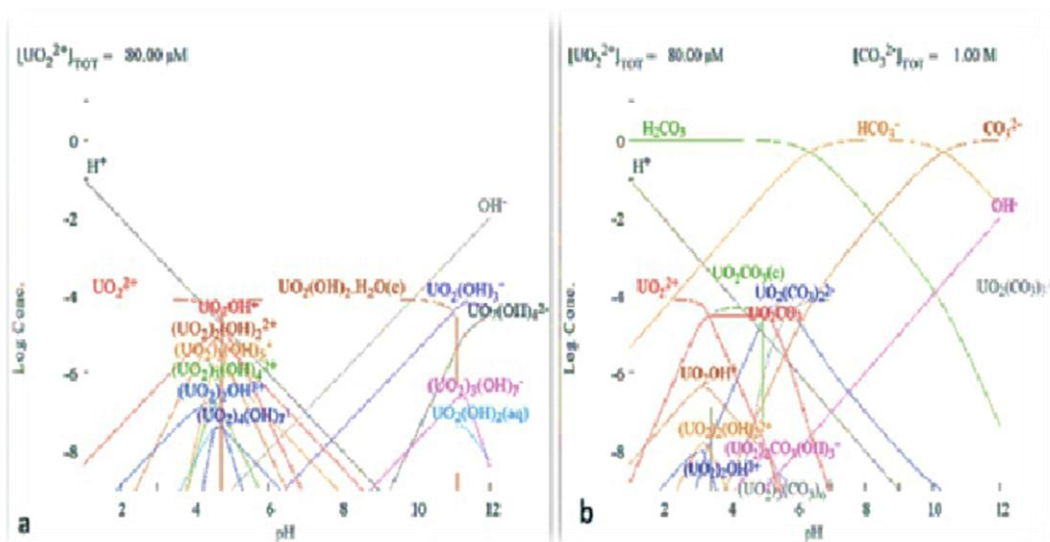

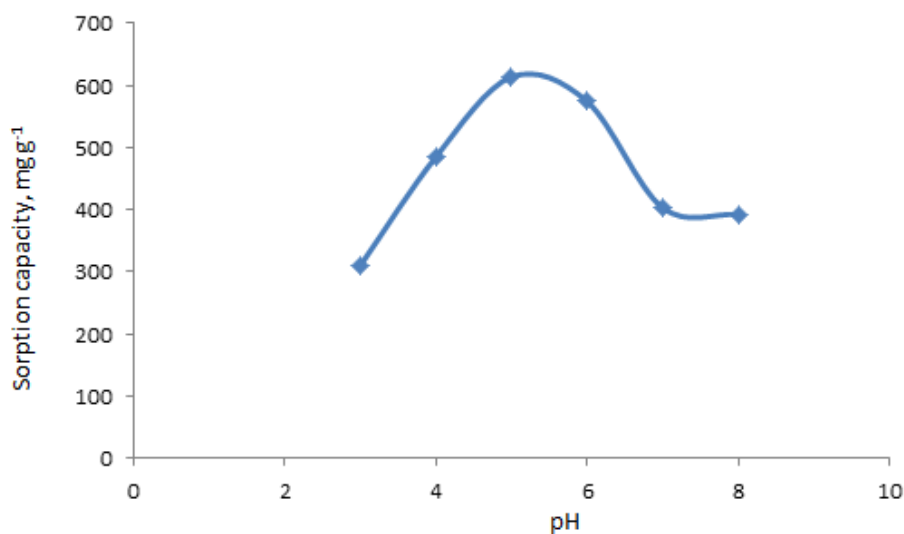**Figure 1.** Speciation of uranium at different pH (Bakatula, 2015).

Figure 2. . Influence of the medium acidity to the sorption process.
m_{sorb}= 30 mg, C_{UO2}^{2+}=10^{-2} mol L^{-1}, time=180 minutes

The effect of initial uranium concentration

Adsorption of uranium from aqueous solutions was studied as a function of metal concentration in the range of initial uranium concentration 0.2-8.0 mol L^{-1}. The amount of the sorbed uranium(VI) from aqueous solutions was determined. The results of the experiments show, that the amount of uranium adsorbed onto the surface of chelating polymeric sorbent increases with increasing initial uranium ions concentration and reaches maximum at $6 \cdot 10^{-3}$mol L^{-1} (pH= 5, $C_{UO_2^{2+}}$ =$6 \cdot 10^{-3}$ M, $V_{total.}$=20 ml, m_{sorb}=0,05 g, static capacity =613.5 mg g^{-1}).

The sorption capacity of the sorbent calculated by the equation:

$$Q = \frac{V(C0 - C)}{m}$$

where Q is adsorption capacity of sorbent (mg g^{-1}), V is the volume of solution (mL), C_o and C – concentrations of uranium (VI) before and after adsorption (mg/L), and m is the weight of sorbent (g).

The removal efficiency of uranium ions was calculated by the equation:

$$R\ (\%) = \frac{C_o - C_e}{C_0} \cdot 100\%$$

where C_0 and C_e are the initial and the equilibrium uranium concentrations (mg/L). The maximum removal efficiency of uranium with polymeric chelating sorbent on the base of maleic anhydride styrene modified with acetylacetone is 95.6%. Table 1 shows the sorption capacity and removal efficiency of uranium by the sorbent. Fig.3 shows the dependence of the sorption capacity on the initial concentration of the uranium ion.

Table 1. Removal efficiency (%) of U (VI) ions by the investigated chelating sorbent

$C_{Me},\cdot 10^{-3}$,mol L^{-1}	0.2	0.4	0.8	1.0	2.0	4.0	6.0	8.0
Sorption capacity, mg g^{-1}	17.5	58.2	105.78	152	300.5	545.8	613.5	599
R,%	55.9	91.7	83.3	95.6	94.7	86	89	86

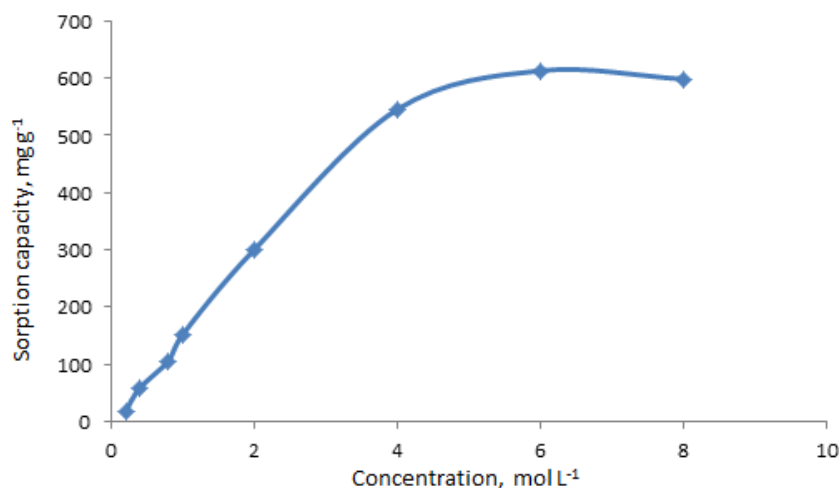**Figure 3.** Influence of the initial metal concentration to the sorption process. m_{sorb}= 30 mg, C_{UO2}^{2+}=10^{-2} molL^{-1}, pH=5, time=180 minutes

The effect of ionic strength

The effect of ionic strength on the sorption of uranium from aqueous solutions was studied by photometric method and found to be μ=0.4. After this value the sorption of uranium (VI) solution decreases. Solution of chemically pure KCl was used for achieving the constant ionic strength.

Effect of contact time on uranium retention

In order to study the dependence of uranium sorption from contact time in a sorption flask put 50 mg. of sorbent, added 12 mL. of uranium and 8 ml. of pH=5 solutions. Then the contents of the flask stirred using a a stirrer ORBITAL SHAKER TS-1. The removal efficiency of the uranium ions reached a maximum value whenthe adsorption time was 180 min. Fig. 4 shows the dependence of the sorption capacity on the contact time of the uranium ion.
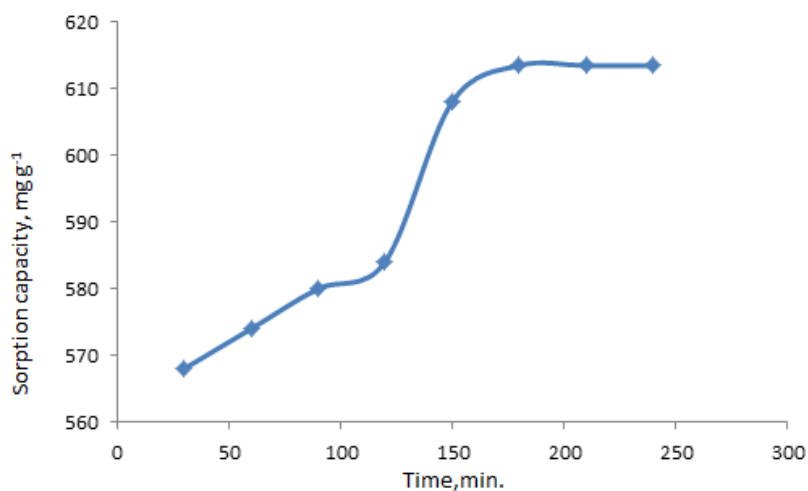

Figure 4. Influence of the contact time to the sorption process.
m_{sorb}= 30 mg, C_{UO2}^{2+}=10^{-2} mol L^{-1}, pH=5

Desorption process

Desorption process was used in order to desorb the sorbed metal ions, regenerate the sorbent and this process is also economical from the point of view of analytical chemistry. In this process a precipitate of uranium (VI) with sorbent was formed, filtered off, washed 2-3 times with distilled water in order to remove the diluents, and then dried. As desorbing agents used the 0.5M;1M;1.5M;2 M solutions of $HClO_4$, HCl, H_2SO_4 and HNO_3. The results of analysis showed, that the maximum sorption properties toward uranium (VI) ions had the 1 M solution of HCl.

Applications of the developed method to the water samples taken during oil extraction.

Influence of matrix components

The influence of matrix components on uranium concentration applied to the water samples taken during oil extraction has been studied. For this aim macro and microcomponents such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, Cl^-, SO_4^{2-} were added separately to 50 ml of uranium(VI) solution. Then, the uranium was concentrated and determined spectrophotometrically. The results of experiment have been shown in Table 2.

Table 2. The influence of matrix components to sorption process

Ion	Concentration, mkg mL^{-1}	R,%
Na^+	19 000	93,1
K^+	29500	97,35
Mg^{2+}	6 000	95
Ca^{2+}	4 500	85,5
Cu^{2+}	9	86,4
Mn^{2+}	10	96
Fe^{3+}	9	85,5
Al^{3+}	9	86,4

According to the results Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, Cl^-, SO_4^{2-} ions do not significantly affect the extraction of uranium. The present method has been applied to the determination of trace uranium in the water taken during oil extraction.

Determination of trace uranium (VI) ions in the water samples taken during oil extraction.

The water samples used for this method are derived from the oil extracted during the production at the State Oil Company of Azerbaijan Republic. In the first step, in order to clean out the microprimes was taken 1000 mL of water sample from the oil extracted and filtered. Then 100 mg of sorbent is added to the minicolumn. The acidity of the filtered water sample was achieved to pH 5 by using the HNO_3 and hold through a minicolumn at the optimal speed. The sorbed metal ions are eluted with 2 ml of 1 M HCl at a rate of 1.0 ml/min. The concentration of uranium, containing in the eluate was determined by the photometric method. The correctness of the procedure was checked by the method "introduced - found". The results of experiments are shown in Table 3.

Table 3. Results of the analysis of water taken during oil extraction (volume of the sample 100 ml, volume of the eluent 2 ml, m_{sorb}= 100 mg, P = 0.92, n = 5.5).

Introduced, mkg L^{-1}	Found: $\overline{x} \pm \dfrac{t_P s}{\sqrt{n}}$, mkq L^{-1}
-	8,5100±0,101
10	17,9200±0,205
20	29,04±0,410
30	37,77±0,504

3.   Conclusion

Study of sorption behavior of U(VI) on chelating sorbent modified with acetilacetone show that the highest sorption achieved at value of pH 5. Sorption capacity of U(VI) onto the polymer modified sorbent was studied and found to be 613.5 mg g^{-1}.Uranium (VI)removal efficiency (%) increased with increasing initial U(VI)concentration to 1.0 mol L^{-1} and then decreased.By the results of analysis period of 3 hours was selected as time to reaching the sorption equilibrium or contact time.

Table 4. Comparative study of adsorption capacity of uranium

Sorbent	Sorption capacity	References
Acetilacetone	613.5 mg g^{-1}	Present work
Bentonite	31.35 mg g^{-1}	(Krajnak, 2014).
Bacteriogenic iron oxides	9.25 mg g^{-1}	(Bakatula, 2015)

Acknowledgment

References

Bakatula, E., Mosai, A., Tutu, H. (2015). Removal of Uranium from Aqueous Solutions using Ammonium-modified Zeolite.*South African Journal of Chemistry,* 68, 165–171. Retrieved from: http://hdl.handle.net/10539/21466

Basargin, N., Magerramov, A., Hajiyeva, S., Bahmanova, F., Gamidov, S., Alieva, T., Chyragov, F. (2013). Determination of uranium(VI) in natural waters after preconcentration on adsorbent containing *m*-aminophenol fragments. *Journal of Analytical Chemistry*, 68, 123-126. doi: 10.1134/S1061934813020032

Cutter, L., Nunn, R. Making styrene/maleic anhydride copolymers by suspension polymerization, US4145375 A.

Handley-Sidhu,S.,Mullan, T., Grail, Q., Albadarneh, M., Ohnuki, T., Macaskie. L. (2016). Influence of pH, competing ions, and salinity on the sorption of strontium and cobalt onto biogenic hydroxyapatite. *Scientific Reports,*6, 2-8. doi: 10.1038/srep23361

Katsoyiannis, I. (2007). Carbonate effects and pH-dependence of uranium sorption onto bacteriogenic iron oxides: Kinetic and equilibrium studies. *Journal of Hazardous Materials*, 139, 1, 31-37. doi:10.1016/j.jhazmat.2006.05.102

Krajnak, A., Viglasova, E., Galambos, M., Rosskopfová, O. (2014). Sorption of uranium anionic species from aqueous solutions on HDTMA-bentoniteJelšovýpotok. *Chémia,* 989-994. Retrieved from: https://inis.iaea.org/search/search.aspx?orig_q=RN:45114851

Kulyukhin, S., Krasavina, E. (2016). Sorption of U(VI) onto layered double hydroxides and oxides of Mg and Al, prepared using microwave radiation. *Radiochemistry*, 58, 350-353. doi: 10.1134/S1066362216040093

Magerramov, A., Hajiyeva, S., Bahmanova, F., Gamidov, S., Chyragov F. (2011). Preconcentration of uranium(VI) on a chelating adsorbent followed by photometric determination with 2,3,4-trihydroxy-3′-nitro-4′-sulfoazobenzene. *Journal of Analytical Chemistry*, 66, 480-483. doi: 10.1134/S1061934811050108

Rashed, M. (2013). Adsorption Technique for the Removal of organic pollutants from water and wastewater. M.N. Rashed (Ed.), *Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater* (pp. 167-194).

Zeng, Z., Yang, S., Zhang, L., Hua, D. (2016). Phosphonate-functionalized polystyrene microspheres with controlled zeta potential for efficient uranium sorption. *RSC Advances,* 6, 74110-74116. doi: 10.1039/C6RA16219C

Zhou, K., Liu, Y., Yang, Z., Liu, H., Xie, T. (2016). High-capacity sorption of U(VI) from aqueous solution using a bio-based oxidized polymeric material. *Journal of the Taiwan Institute of Chemical Engineers*, 63, 453-462. doi: 10.1016/j.jtice.2016.02.031