International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 974-979, 2017

Separation of Uranium (VI) from associated elements using poly-(dibenzo-18-crown-6) resin from nitrate medium

S. H. Burungale*

PG Department of Chemistry, Laboratory of Analytical Chemistry, Yashwantrao Chavan College of Science Karad -415124, India

Abstract : A simple column chromatographic method has been developed for the separation of uranium from associated elements using poly-(dibenzo-18-crown-6). The separations are carried out from sodium nitrate medium. The adsorption of uranium was quantitative from 0.5M sodium nitrate. Amongst the various eluents tested, 1.0 8.0M HCl was found to be uranium was found to be 1.034 mmole/g of crown polymer. Uranium was separated from number of elements in binary mixtures in which most of the elements showed a very high tolerance limit. It was possible to separate Uranium from a number of elements in Multicomponent mixtures. Method is very simple, rapid, and selective and has good reproducibility.
Keywords : Uranium (VI),poly-(dibenzo-18-crown-6) resin, Sorption capacity.

Introduction

This is unique because the only element that goes into making nuclear reactor fuel is uranium; the other elements are created during the actual fission process. While the chemistry is quite complex, the only thing that needs to be extracted with this proposed method is the uranyl ion [UO^{2+}].1-4 Solvent extraction is certainly a very good method for selectively separating metal ions from complex aqueous solutions because of great number of ligands are available which can be used as metal extractants. However, these ligands are quite expensive and their application on a large scale remains limited. In solvent extraction it is difficult to avoid loss of ligand in the aqueous phase due to its distribution. The synergistic extraction of uranyl ion from dilute nitric acid medium employing HIT All-phenyl-3-methyl-4-benzoyl-S-pyrazolone(HPMBP) in toluene and their mixture with several structurally modified monoamides viz. di-2-ethylhexylacetamide (D_2EHAA), di-2-ethylhexy lpropanamide (D_2EHPrA), di -2-ethylhexy lisobutyramide(D_2EHiBA), di-2-ethylhexylpivalamide (D_2EHPvA) has been investigated. The nature of the extracted species for the binary and ternary extraction systems were reported as UO_2A_2 and $U0_2A_2$.B, respectively, where A = TTA or PMBP and B = D_2EHAA, A linear correlation was observed between the basicity of the amide and the corresponding adduct formation constants.5-8The fonner criterion requires some understanding of the coordination chemistry and particularly, knowledge of the solution speciation of the cation and the extractants. However, remarkably few studies of synergistic extraction have probed the cation coordination environment 9-11

Use of polymericlig and material appears to be a good alternative to eliminate this difficulty. Use of crown ethers for solvent extraction separation of uranium is very limited. Polymeric crown ethers possess special features such as high resistance to chemicals, to temperature, to radiolysis and also to polar solvents such as acetone and alcohol's, their regeneration is very easy, and repeated use of the material can be made for the next operation. Polymeric crown ethers such as poly-(dibenzo-18-crown-6) has been used in this laboratory

for column chromatographic separation studies of various metalions from associated elements.[12-14]There are no reports on the use of polymeric crown ethers for the column chromatographic separation of uranium. This paper describes in detail the separation of Uranium (VI) from a number of other elements using poly(dibenzo-18-crown-6) in sodium nitrate medium.

2. Experimental

2.1 Apparatus

Spectrophotometer, a digital pH meter, with glass and Calomel electrodes, els was used.

A stock solution of Uranium (VI) was prepared by dissolving 2.166 g of uranyl nitrate hexahydrate (BDH) in 1000 ml of distilled deionized water and standardized gravimetrically. The solution was found to contain 1.0 mg /ml of Uranium (VI). A solution containing 100 µg /ml of Uranium (VI) was prepared by appropriate dilution of the standard stock solution. Poly-(dibenzo-18-crown-6) polymeric resin was purchased from Merck without further purification. All other chemicals were of guaranteed grade and were used without further purification.

2.2. General procedure

To an aliquot of solution containing 100µg of Uranium (VI) sodium nitrate was added in the concentration range of 0.1-4.0M in a total volume of 10 ml. The solution was then passed through as poly-(dibenzo-18-crown-6) polymeric resin columnr econditioned with the same concentration of sodium nitrate as that of the sample solution, at a flow rate of0.5 ml/minute. The column was then washed with the same concentration of sodium nitrate. The adsorbed Uranium (VI) was eluted with different eluting agents at aflow rate of 0.5 ml/minute. 5 ml fractions were collected and the thorium content was determined spectrophotometrically with Arsenazo-III at 655 nm.

3. Results and Discussion

3.1. Adsorption of Uranium as a Function of sodium nitrate concentration on poly-(dibenzo-18-crown-6)

Adsorption of U (VI) on PDB18C6 polymeric resin as a function of sodium nitrate concentration. A sorption study of U (VI) was carried out from sodium nitrate medium. The concentration of sodium nitrate varied from 0.05 M to 2.0 M. After sorption, U (VI) was eluted with 2.0 M sodium nitrate. It was found that there is quantitative (100%) sorption of U (VI) from 0.5 M to 2M sodium nitrate concentration. Further decrease in sodium nitrate concentration there is decrease in sorption of U (VI) shown in Table 1, Figure 1. The subsequent sorption studies of U (VI) were carried out with 1.4M sodium nitrate.

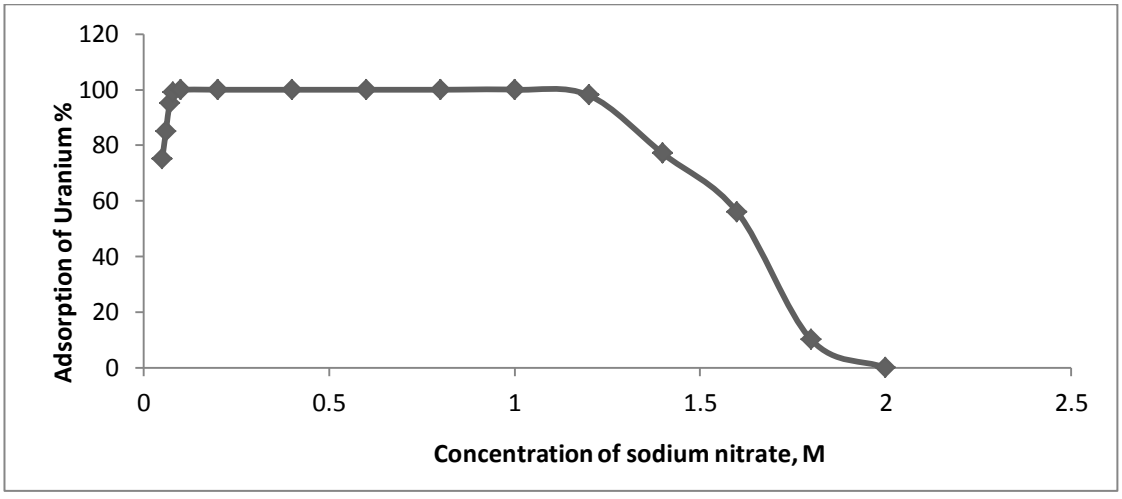

Fig.1: Adsorption of Uranium as a Function of sodium nitrate concentration on poly-(dibenzo-18-crown-6)

Table.1: Adsorption of Uranium as a Function of sodium nitrate concentration on poly-(dibenzo-18-crown-6)

sodium nitrate Concentration M	Adsorption of U(VI) %
0.05	75
0.06	85
0.07	95
0.08	99
0.1	100
0.2	100
0.4	100
0.6	100
0.8	100
1.0	100
1.2	98
1.4	77
1.6	56
1.8	10
2.00	00

3.2. Effect of varying concentration of U(VI)

The capacity of the poly-(dibenzo-18-crown-6) polymeric resin for U(VI) was evaluated using 4.0 g of poly-(dibenzo-18-crown-6) polymeric resin and sorption studies were carried out in 0.1M sodium nitrate. The concentration of U(VI) was varied from 100-2000 µg of U(VI). Per10 mL of solution. The result shows that sorption of U(VI) is quantitative up to 1500 µg/10 mL. Further increase in concentration of U(VI) there is decrease in percentage sorption as shown in Table 2, Figure 2. The capacity of poly-(dibenzo-18-crown-6) polymeric resin for U(VI) was found to be 0.87 ±0.01 mmol/g

Table:2 Effect of varying concentration of U(VI)

Concentration of U(VI) µg	Adsorption of U(VI)
100	100
200	100
400	100
600	100
800	100
1000	100
1200	80
1400	65
1600	45
1800	30
2000	20

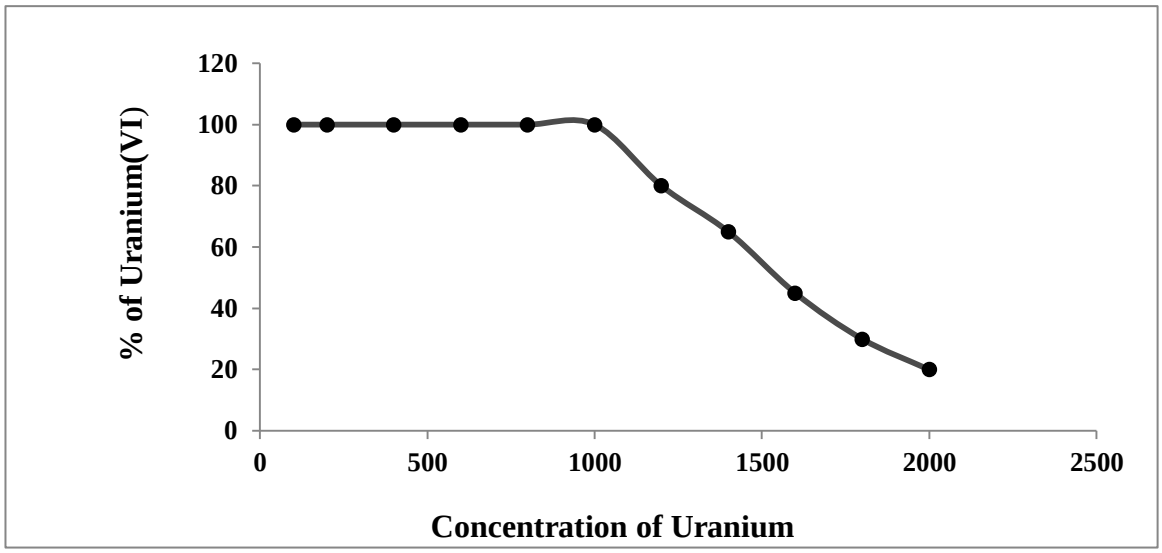

Fig:2 Effect of varying concentration of U(VI)

The amount of lead adsorbed on one gram of dibenzo-18-crown-6) polymeric resin and percentage removal calculated using the following equations

$$qe = \frac{C_o - C_e}{m} X\ V \quad \text{----------(1)}$$

$$\%\ \text{removal} = \frac{C_o - C_e}{C_o}\ 100 \text{----------(2)}$$

Where, (mg/L) is concentration of lead before adsorption, (mg/L) is equilibrium concentration, m (g) adsorbent weight and V solution volume in liter.

3.4. Column reuse

To test the long-term stability of the column containing the modified resin, successive sorption and elution cycles were carried out by passing U(VI) solution through the column at the optimum flow rate, then eluted. The procedure was carried out several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed U(VI) .The results of 100 sorption/desorption cycles indicate that, the recovery decreases by ≤ 3 % reflecting good stability of the modified resin

3.5. Separation of Uranium (VI) from binary mixtures

An aliquot of solution containing 100 µg Uranium (VI) and the foreign ions to be tested was taken and sodium nitrate was added so that its concentration was 0.1M in a total volume of 10.0 ml. The tolerance limit was set as the amount of foreign ions required to cause +2% error in the recovery of thorium. The solution was passed through a poly-(dibenzo-18-crown- 6) column pre-conditioned with 0.1M sodium nitrate, at a flow rate of 0.5 ml/minute. Subsequently, the column was washed with 15 ml of 0.1M sodium nitrate. Various foreign ions were not adsorbed and so passed through the column. Effluent as collected and was analyzed for foreign ion content. The tolerance limit of various foreign ions is shown in Table 4. Most of the alkali and alkaline earth elements were not adsorbed and showed very high tolerance limits. Amongst p-block elements, lead(II) was adsorbed quantitatively whereas other p-block elements were not adsorbed and showed high tolerance limit.

Table-7 Separation of Uranium (VI) from Binary Mixtures

Ions	Added as	Tolerance Limit(mg)	Ions	Added as	Tolerance Limit (mg)
Na^{+}	NaCl	25	Cr^{3+}	$Cr(NO_3)_3.9\ H_2O$	25
Be^{2+}	$BeSO_4.4H_2O$	05	Ce^{3+}	$CeCl_3.6H_2O$	1
Mg^{2+}	$MgCl_2.6H_2O$	35	Zr^{4+}	$Zr(NO_3)_4.4H_2O$	3
Ca^{2+}	$CaCl_2$	20	V^{4+}	$VOSO_4.4H_2O$	5
Sr^{2+}	$Sr(NO_3)_2$	25	Cr^{6+}	$K_2Cr_2O_7$	7
Ba^{2+}	$Ba(NO_3)_2$	15	Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	4
Cu^{2+}	$CuCl_2.2H_2O$	0.5	W^{6+}	$Na_2WO_4.4H2O$	30
Ni^{2+}	$NiCl_2.6H_2O$	2	La^{3+}	$LaCl_3$	6
Mn^{2+}	$MnCl_2.4H_2O$	1.5	Al^{3+}	$Al(NO_3)_3.9\ H2O$	3
Zn^{2+}	$ZnCl_2$	30	SCN^{-}	NaSCN	75
Pb^{2+}	$Pb(NO_3)_2$	20	ClO_4^{-}	ClO_4	10
Fe^{3+}	$FeCl_3.6H_2O$	25	CH_3COO-	CH_3COOH	35

3.6. Separation Uranium (VI) from Multicomponent mixtures

The different adsorption and elution behavior of uranium (VI) thorium (IV), Mg(II) and other elements were exploited for the separation of Uranium(VI) from various multicomponent mixtures. When a mixture containing Mg(II), thorium(IV)and uranium(VI) was passed through poly-(dibenzo-18-crown-6) column at 0.1M sodium nitrate concentration, Mg(II)was not adsorbed hence passed through the column, whereas thorium and uranium were adsorbed. The adsorbed thorium (IV) was first eluted with 6.0Mhydrochloric acid, under this condition uranium (VI) was not eluted because of formation of adsorbable chloro species.

Table .8 Separation of Uranium (VI) from multicomponent Mixtures

Sr.No	Mixture	Taken µg	Found µg	Recovery %	Eluents
1	Th(IV)	100	100	100	6M HC1
	U(VI)	100	100	100	1M HNO_3
	Mg (II)	100	100	100	NAPC
2	Th(IV)	100	100	100	6M HC1
	U(VI)	100	100	100	1M HNO_3
	Mg (II)	100	100	100	NAPC
3	Th(IV)	100	100	100	6M HC1
	U(VI)	100	100	100	1M HNO_3
	Sr (II)	100	100	100	NAPC
4	Th(IV)	100	100	100	6M HC1
	U(VI)	100	100	100	1M HNO_3
	Ba(II)	100	100	100	NAPC

3.7. Determination of Uranium in real sample

The proposed method was applied for the determination of uranium in geological samples such as syenite rock sample (SY-II) and monazite sample. The samples were brought in to solution by adsorbed with poly-(dibenzo-18-crown-6) polymeric resin from 0.1M $NaNO_3$. Under these conditions only uranium was adsorbed which was then eluted with 1M HNO_3 and determined Spectrophotometrically. The amount of uranium found in SY-II sample was 278 ppm as against the reported value of 280 ppm. In monazite sand it was 0.31% as against the standard value of 0.30%.

4. Conclusion

A simple, rapid and selective column chromatographic method for the separation and determination of U(VI) from other metal ions by using poly-(dibenzo-18-crown-6) polymeric resin in sodium nitrate medium has been developed. In addition to adopting a simple method for the determination of U(VI) from real samples. The experiment was repeated 5 times and the results obtained as 0.2 % to the certified values.

References:

1. Burungale, S.H. Mohite, B.S. "Liquid-liquid extraction separation of uranium (VI) from associated elements using dibenzo-24-crown-8 from hydrobromic acid medium". Journal of Radio analytical and Nuclear Chemistry, 1999. 241, 3.*5 589-593.*
2. "Energy Sources". U.S. Department of Energy. 2007.
3. Garrett, Major. "Bush Backs Nevada Site for Nuclear Waste". February 15, 2002.
4. Hunt, Dr. Ian. "Crown Ethers". Organic Chemistry Online Learning Center. McGraw Hill. 2006
5. Banerjee, S., Bhattacharya, A., Mohapatra, P.K., Basu, S., and Manchanda,V.K., Extraction of the uranyl ion with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and neutral donors from dilute nitric acidmedium," Radiochim. Acta,2003,91, 729-736.
6. Bhattacharya, A., Banerjee, S., Mohapatra, P.K., Basu, S., and Manchanda, V.K., "Extraction of ternary p-diketonates of uranyl ion usingsome substituted monoamides," Solv. Extr. Ion Exch.,2003,21, 687-705.
7. Bhattacharya, A., Mohapatra, P.K., Banerjee, S., Basu, S., and Manchanda,V.K., "Role of ligand structure and basicity on the extraction ofuranyl isoxazolonate adducts," So Iv. Extr. Ion Exch., 2004,22, 13-29.
8. Bond, W.D., "Science and Technology of Tributyl Phosphate",Vol.III, Applications of Tributyl Phosphate in Nuclear FuelReprocessing, Schulz, W.W., Burger, L.L., and Navratil, J.D., CRCPress, Inc., Florida,1990,225.
9. Bond, A.H., Dietz, M.L., and Chiarizia, R., "Incorporating sizeselectivity into synergistic solvent extraction: a review of crown ethercontainingsystems," Ind. Eng. Chem. Res., 2000,39, 3442-3464.
10. Caceci, M., Choppin, G.R., and Liu, Q., "Calorimetric studies of thesynergistic effect. The reaction $U0_2^{2+,}$ $Th^{4+,}$ and Nd^{3+}-TTA complexeswith TBP and TOPO in benzene," Solv. Extr. Ion Exch.,1985 3,605-621.
11. Choppin, G.R., and Morgenstem, A., "Thermodynamics of solvent extraction," Solv. Extr. Ion Exch., 2000,18, 1029-1049.
12. B.S. Mohite,J.M. Patil, D.N. Zambare, Talanta, 1993,40,1511.
13. B.S. Mohite,J.M. Patil, D.N. Zambare, U. G. MaliBull.Chem. Soc. Japan, 1993,66, 3639.
14. B.S. Mohite, D.N. Zambare B. E. Mahadik, Analyst,1994)119, 2033.

*****