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Preconcentration and Separation of Uranium from Thorium by Solid Phase Extraction with XAD-4 Modified with Organic Reagents

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ABSTRACT

Uranyl ion can be separated from aqueous solution and preconcentrated on XAD-4 modified with organic reagents. Dibenzoyl methane (DBM), 8-hydroxy quinoline (oxine), and tri-*n*-octyl phosphine oxide (TOPO) were impregnated on the adsorber resin and treated with aqueous solutions containing microgram quantity of uranium. The preconcentrated uranium could be eluted out with dilute acid from the column modified with DBM or oxine, while ammonium bicarbonate was necessary for the elution of uranium from the column modified with TOPO. Uranium in the eluate was determined spectrophotometrically using Arsenazo(III). Adding EDTA to the sample solution could separate uranium from transition metal ions and thorium. The method of preconcentration has

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been successfully applied to the recovery of uranium from synthetic seawater.

Key Words: Solid phase extraction; Peconcentration; Uranium; Arsenazo(III); Oxine; TOPO.

INTRODUCTION

Determination of metal ions at low concentrations often requires initial preconcentration in order to meet the detection limit of the prescribed method and it usually helps to eliminate the interference of the matrix elements. There are several methods for carrying out the preconcentration. These include liquid–liquid extraction, carrier facilitated transport of the species, and solid phase extraction (SPE). SPE offers several advantages over the other preconcentration methods. The waste generation is minimal, matrix effect is reduced to a greater extent, and the metal ions are collected on the solid support in a well-defined chemical form making the further processing of the collected species simpler.

There are several variations in the absorbing solid support on which the metal ions are collected. Polyurethane foam,[1,2] filter papers,[3] cellulose,[4] ion exchange resins,[5] and silica gel,[6] etc., have been used as support materials for the preconcentration of metal ions but octadecyl silane (ODS) bonded to silica gel are more commonly used,[7] probably due to their higher efficiency and availability in the form of commercial disks and cartridges. The technique could also be useful for the recovery and preconcentration of strategically important metals from their sources containing the metal ion at low concentration level. In the absence of rich sources, such studies are of paramont importance. The development of efficient methods for the recovery of uranium from its low-grade source, like seawater, have attracted the attention of scientists primarily due to the application of uranium in the nuclear industry. Determination of traces of uranium in environmental sites and in the facilities of the nuclear industry is also important from environmental safety considerations and such analytical studies need preconcentration methods.

Metal chelating resins (adsorbed or chemically bonded chelates) have, recently, been found to be of great utility for the preconcentration and separation of trace metals from different matrices.[8–10] We previously reported selective transport of uranium through Nafion membrane[11] and facilitated uphill transport of uranyl ion across bulk liquid membrane containing suitable carriers.[12–14] In the present study, we modified the adsorber resin Amberlite XAD-4 with different organic reagents known to form stable complexes with UO_2^{2+} and examined the retention of uranium in the modified resin bed. Dibenzoyl methane (DBM), 8-hydroxy quinoline (oxine), and tri-*n*-octyl phosphine oxide (TOPO) were chosen for the modification of the resin and uranium(VI) from aqueous solutions was preconcentrated on it. The method has been applied to the recovery of traces of uranium from synthetic seawater. The resin modified with TOPO has been successfully applied to the separation of U(VI) from Th(IV). Uranium retained on XAD was eluted out using a minimum volume of a suitable eluent and the eluted uranium was determined spectrophotometrically with arsenazo(III).[15]

EXPERIMENTAL

Reagents

Adsorber resin Amberlite XAD-4 was obtained from E. Merck (Germany). Oxine, DBM, TOPO, and EDTA were also obtained from E. Merck. All other reagents were of analytical grade.

Procedure

Approximately 5 mL of XAD-4 was treated with 50 mL of 2 M HCl for 30 min and repeatedly washed with deionized water till the washing was free of acid. The washed resin was dried in an oven at 100°C and then equilibrated for 2 hr with excess of 10^{-1} M solution of the desired organic reagent dissolved in methanol. The reagent penetrated inside the resin by this treatment and held up strongly. The resin was filtered and washed with deionized water. The treated resin was packed in a glass column (10 cm long and 1 cm i.d) to a height of 2 cm. Aqueous solution (100 mL) of UO_2^{2+} adjusted to pH $\approx$ 5 (acetate buffer) was passed through the column at the rate of 3–4 mL per minute and the column was washed with water after the uranium was loaded. The effluent was collected and evaporated to a small volume and the concentration of the residual uranium in the effluent was determined spectrophotometrically using Arsenazo(III). The uranium retained in the column was eluted out with dilute nitric acid (for DBM) or ammonium bicarbonate (for TOPO). When ammonium bicarbonate was used for elution, the eluted solution was evaporated to dryness on water bath. The residue was dissolved in water and 1 mL of 0.05% Arsenazo(III) and 2 mL of 2 M HCl were added. The solution was thoroughly mixed and the volume was made up to 25 mL in a standard volumetric flask. The absorbance of the solution was measured at 650 nm against a corresponding reagent blank. A Shimadzu

120 UV/VIS spectrophotometer (Shimadzu, Kyoto, Japan) was used for the measurement of the absorbance.

The retention of transition metal ions, thorium, and other metal ions in the presence of EDTA was studied by measuring the concentration of free EDTA after the elution. EDTA (5 mL of 0.1 M) at pH 5 was added to the binary mixture of UO_2^{2+} and the other metal ion and the mixture was allowed to pass through the column. Since UO_2^{2+}–EDTA complex has a lower stability than the uranyl TOPO complex, uranium is held up in the column modified with TOPO. The transitional metal ions, on the other hand, form very stable anionic complexes with EDTA and elute out of the column. Thus, in the presence of transition metal ions, a part of EDTA initially added is fixed as metal EDTA complex and the rest remains free. The concentration of free EDTA was determined in the mixture before passing it through the column. If any metal ion is retained in the column, there will be an increase in the free EDTA concentration in the treated solution. The free EDTA in the eluent was determined by back titration with a standard solution of Zn^{2+} using Eriochrome Black T (EBT) or Xylenol Orange (XO) indicator. The difference between the amount of free EDTA in the solution before and after passing through the column corresponds to the amount of metal ion retained by the resin.

RESULTS AND DISCUSSION

Fritz[16] has described, in detail, the development and applications of SPE. He has discussed the applications of XAD of different porosity in the removal of organic pollutants from various matrices. In the present study, XAD-4 has been chosen as a support material for some selective organic reagents capable of forming stable complexes with UO_2^{2+}. DBM is a β-diketone with two phenyl groups attached to the carbonyl carbon atoms of the diketone. The reagent is bulky and highly hydrophobic in nature. It forms a stable complex with UO_2^{2+} and remains adsorbed on XAD. The TOPO is also a common organic reagent used for the selective extraction of UO_2^{2+} from the acid solution. The reagent Oxine is a versatile chelating agent used as an analytical reagent for the extraction or gravimetric determination of many metal ions. The reagent has a nitrogen atom in the heterocyclic ring and a phenolic –OH group adjacent to it. This makes it a good chelating agent for various metal ions.

The modification of the adsorber resin with the reagents was simple and straightforward. Equilibration of the resin with excess of the desired reagent solution (50 mL of 10^{-1} M) for 2 hr was sufficient for the saturation of the active sites of the resin. The resin loaded with the reagent developed light color characteristic of the reagent. Preliminary studies suggested that there was no uptake of uranium by XAD prior to its modification, but quantitative uptake of uranium was evidenced after the modification of the resin with the complexing agents. Table 1 shows the adsorption of UO_2^{2+} from aqueous solution at pH 5.5 by the XAD modified with different reagents. The adsorption of uranium was determined by measuring the concentration of UO_2^{2+} in the effluent. The amount of uranium retained in the column was also determined by measuring its concentration after eluting out with ammonium bicarbonate. It is seen in Table 1 that the modified resin columns are capable of retaining uranium quantitatively, which results in a very high preconcentration of uranium from the aqueous solution.

As the retention of uranium was pH dependent, the uptake of the metal ion by the modified resin was studied as a function of pH. For the resin modified with DBM or Oxine, the retention of the metal ion was highest at pH between 5 and 6. This is due to the favorable conditions for the complex formation of uranium with these ligands in this pH region. However, the resin modified with TOPO showed high adsorption of UO_2^{2+} even at a lower pH. The effect of pH variation on the absorption of uranium on XAD column modified with TOPO is shown in Fig. 1. It is seen from the Fig. 1 that a pH of 5.5 ± 0.5 is the optimum for the absorption of uranium. Uranium taken up by the modified resin from different volumes of aqueous solutions is shown in Table 2. The values listed in Table 2 are the average of at least three experimental results and are subjected to an error of $\pm 5\%$. It is also seen from Table 2 that the resin modified with TOPO has the highest efficiency of adsorption of uranium followed by Oxine and DBM. However, it was interesting to note that the adsorption of UO_2^{2+} on the column modified with TOPO was not quantitative in the absence of nitrate. The variation in the absorption of uranium with the change in the nitrate concentration in the feed solution is shown in Table 3. Thus, all the adsorption experiments with uranium were carried in the presence of 0.02 M nitrate. It was, therefore, necessary to add nitrate in sufficient

Table 1. Retention of UO_2^{2+} in modified XAD columns.

Modifying agent	Uranium recovered from the column (μg)	Absorption of UO_2^{2+} (%)
Nil	nd	<0.05
DBM	18.0	90
Oxine	19.6	98
TOPO[a]	19.8	99

Note: Total uranium in the solution was 20 μg.
[a] In the presence of 0.02 M NO_3^-.

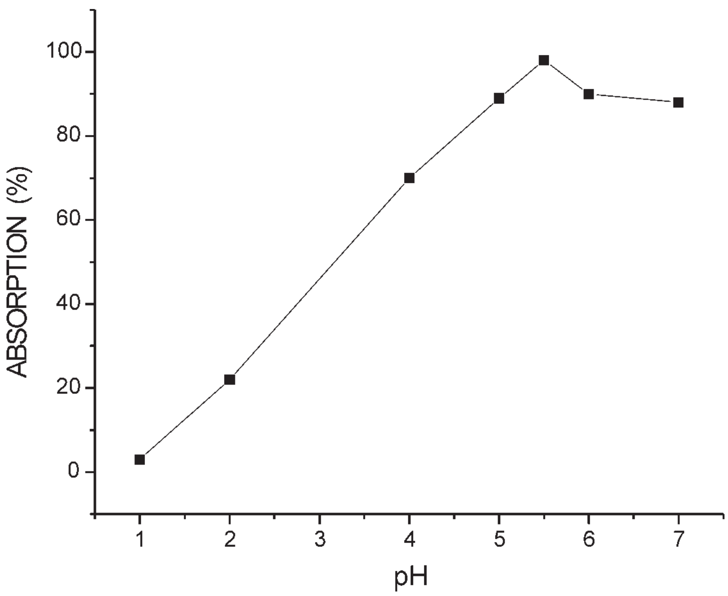

Figure 1. Effect of pH on the absorption of uranium on XAD-4 modified with TOPO. Total amount of uranium is 20 μg; concentration of nitrate is 0.02 M.

excess (≈0.02 M) to the feed solution for quantitative retention of uranium by the resin modified with TOPO.

Elution of uranium from the resin was tried with various eluting agents. A small amount (10 mL) of 2 M HNO_3 was sufficient for the quantitative recovery of the metal ion (20 μg) from the resin bed modified with DBM or oxine. The recovery of uranium from the column modified with DBM was 18 μg, while 19.4 μg of uranium could be recovered from the column modified

Table 2. Recovery of 10 μg of uranium from aqueous solutions of different volumes.

Column modified with	Volume of solution passed (mL)			
	10	100	300	500
DBM	9.5	9.0	9.0	9.0
Oxine	9.8	9.5	9.1	9.0
TOPO	10	9.7	9.7	9.6

Note: Concentration of $NO_3^- = 0.02\,M$.

Table 3. Effect of NO_3^- concentration on the absorption of uranium on an XAD column modified with TOPO.

Conc. NO_3^- (m/L)	Uptake of UO_2^{2+} (%)
0	50
5×10^{-4}	72
1×10^{-3}	100
2×10^{-2}	100

with oxine. Although, the retention of uranium was quantitative from the column modified with oxine, the elution was complicated due to the simultaneous elution of the regent along with uranium. The difficulty was due to the presence of both nitrogen and –OH in the reagent. At lower pH, nitrogen gets protonated and the phenolic –OH dissociates at higher pH. For this reason, the reagent has considerable solubility in water both in acid and alkaline regions and elutes out along with the metal ion. Hence, the uranium eluted out from the column modified with oxine was not chemically pure and no further study was made on the recovery from the oxine-modified column. Dojozan et al.[17] reported the preconcentration of UO_2^{2+} from seawater by oxine adsorbed on ODS column, where the reagent and the uranium complex were eluted out in chloroform and determined by differential pulse polarography. Uranium was held up very strongly in the column modified with TOPO. Quantitative elution of uranium from the column was not possible even with 6 M HCl. Since, carbonate forms a very strong complex with uranium,[18] ammonium bicarbonate was used for the elution of UO_2^{2+} from the column. However, the volume and the concentration of the eluent influence the elution of the uranyl ion. It was observed that 50 mL of 1 M NH_4HCO_3 could elute out only 76% of uranium held up in the column, while 100 mL of 0.5 M solution of the reagent was needed for the elution of 99% of uranium from the column modified either with DBM or TOPO.

Metal–EDTA complexes were not retained on the modified columns. Since UO_2^{2+} forms a very weak complex with EDTA, selective separation of uranium from its binary mixture with various metal ions was studied on these columns using EDTA as a masking agent for the interfering metal ions. The UO_2^{2+} was strongly retained on the column modified with TOPO, so this column was chosen for further retention studies. EDTA (2 mL of 0.1 M) was added to the mixtures and the solutions were passed through the column. The quantitative removal of interfering metal ions and the retention of uranium on the column was ascertained by the measurement of UO_2^{2+}

concentration and the concentration of free EDTA in the effluent coming out of the column. Any increase in the free EDTA concentration in the effluent would be a measure of the retention of the interfering ion on the column. The separation of uranium from its binary mixtures with other ions including Th(IV) in milligram quantities is shown in Table 4. It is clear from Table 4 that uranium in the mixture is almost quantitatively retained on the resin, while the other ion is eluted out as its EDTA complex.

In order to investigate the separation of uranium from thorium, the recovery of uranium was studied at different ratios of uranium to thorium (Table 5). In the absence of EDTA, both UO_2^{2+} and Th^{4+} were quantitatively retained on the modified columns. However, the elution of uranium from the DBM modified column with ammonium bicarbonate resulted in the partial elution of thorium along with uranium. In the presence of EDTA, there was no retention for thorium in the column but the retention of uranium was partial. About 65% uranium eluted out along with thorium. The partial retention of UO_2^{2+} is presumably due to the lowering of the conditional stability of UO_2^{2+}–DBM complex in the presence of EDTA. For the column modified with TOPO on the other hand, the retention of uranium was quantitative even in the presence of EDTA; only thorium came out quantitatively as its EDTA complex. The XAD column modified with TOPO has the added advantage that in the presence of EDTA, both thorium and transition metal ions are rejected out making the separation selective for uranium. Hence, the XAD column modified with TOPO was chosen for the separation of thorium from uranium and it was possible to separate microgram amount of uranium from milligram quantity of Th(IV) and other metal ions by selectively complexing the later with EDTA (Table 4).

The applicability of the preconcentration method was further assessed by the recovery of known amount of uranium added to synthetic seawater

Table 4. Separation of 20 μg of U(VI) from binary mixtures.

Name of the ion	Added as	Amount added (mg)	U(VI) recovered (%)
Ca^{2+}	$CaCl_2$	8.0	98.6
Mg^{2+}	$MgCl_2$	4.8	97.2
Cu^{2+}	$CuSO_4$	12.6	98.7
Zn^{2+}	$ZnCl_2$	13.0	100.0
Mn^{2+}	$MnSO_4$	10.8	98.6
Al^{3+}	Al_2 (SO4)$_3$	5.4	97.2
Fe^{3+}	Fe_3 $(SO_4)_3$	11.2	97.3
Th^{4+}	Th $(NO_3)_4$	46.4	98.2

Table 5. Separation of uranium from thorium.

Th(IV) added (μg)	U(VI)/ Th(IV) ratio	In the eluent U(VI) (%)	In the eluent Th(IV) (%)
20	1 : 1	1.2	99
30	2 : 3	1.2	100
40	1 : 2	1.3	98
50	2 : 5	2.0	98

Note: Uranium content = 20 μg.

samples. The seawater samples were prepared according to the composition given in the literature.[19] A known amount (10 μg) of uranium was added to the water samples of different volumes, namely 100, 300, and 500 mL. The solutions were allowed to pass through the XAD columns modified with TOPO and the uranium retained in the columns was eluted out with ammonium bicarbonate and determined spectrophotometrically. The results are shown in Table 6. The results suggest a near quantitative recovery of uranium and compare well within the experimental error from those obtained for the recovery of the metal ion from the aqueous solutions (Table 2). The marginally low recovery of uranium from seawater may be attributed to various factors involved in handling large volumes of samples.

CONCLUSION

Adsorber resin XAD-4 could be modified with organic reagents like DBM, oxine, or TOPO, and the modified resin could be used for the separation and preconcentration of uranium from aqueous solution. In the presence of

Table 6. Preconcentration and recovery of 10 μg uranium from synthetic seawater.

Vol. of sample (mL)	Uranium recovered (%)
100	98.7
300	97.8
500	95.4

EDTA, uranium could be separated from thorium and transition metal ions, and preconcentrated on an XAD column modified with TOPO. The retained uranium was quantitatively eluted out from the column with ammonium bicarbonate and determined.

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