

Use of *o*-phenylene dioxydiacetic acid impregnated in Amberlite XAD resin for separation and preconcentration of uranium(VI) and thorium(IV)

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Abstract

The impregnation of *o*-phenylene dioxydiacetic acid (OPDA) into a polymeric matrix, Amberlite XAD-2000, is reported and was characterized by infrared spectroscopy. The amount of attached OPDA to the polymer resin was found to be 1.77 mmol g⁻¹ resin. The resin was used for the sorption of U(VI) and Th(IV) from aqueous solution. This sorbent was capable of preconcentrating U(VI) and Th(IV) from weakly acidic or neutral solution. The retained metals were eluted sequentially using 0.25 mol L⁻¹ HCl for U(VI) and 1 mol L⁻¹ HCl for Th(IV) and determined spectrophotometrically using arsenazo-(III). The capacity of the resin for U(VI) and Th(IV) was found to be 0.121 and 0.113 mmol g⁻¹, respectively. The impregnated resin exhibits a high chemical stability, reusability and fast equilibration. The method was used for the determination of U(VI) and Th(IV) in synthetic samples and rock samples.

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1. Introduction

Uranium and thorium are very essential elements in nuclear and atomic energy program. Their recovery is essential to minimize their discharge into the environment from the point of view of safety and economy. Their selective extraction simultaneously in presence of each other and closely associated metal ions has drawn much attention of the chemists world over because of their importance in energy related applications [1]. The separation of these economically important metal ions is also a matter of concern as the nuclear waste coming out of reactors cause serious and irreversible environmental and biological damage [2]. Both the metal ions are known to cause acute toxicological effects in mammals and their compounds are potential occupational carcinogens [3]. Thus, there remains a need of pre-organized complexing agents that discriminates U(VI) and Th(IV) from associated metal ions present in great excess in solid or aqueous media. Solvent extraction technique has been serving this purpose for many decades.

Solid phase extraction (SPE) technique is thus recognized as the fast and reliable approach for quantitative metal ion extraction and preconcentration [4–6]. The impregnated resins which are designed by physically loading the successful organic extractants on a solid inert support material also found effective for this process [7].

Amberlite XAD series resins have shown promise for designing chelating resins. Several previous studies have been reported for the XAD series resins in which an inert support is impregnated or functionalized with a selective organic extractant, e.g. 4-(2-thiazolylazo)resorcinol [8], bicine [9], quinoline-8-ol [10], octacarboxymethyl-C-methylcalix[4]resorcinarene [11], 3-hydroxyphosphinoyl-2-oxo-propyl phosphonic acid dibenzyl ester [12], succinic acid [13], 8-hydroxy quinoline [14], tiron [15], *o*-vanilinthiosemicarbazone [16], *p*-tert-butylcalix[8]arene [17], pyrogallol [18], *o*-vanilinsemicarbazone [19] and humic acid [20] to produce a solid sorbent for the isolation of U(VI) and/or Th(IV) from various analytical matrices.

In this work, Amberlite XAD-2000 resin was impregnated with *o*-phenylene dioxydiacetic acid to investigate the separation and preconcentration of U(VI) and Th(IV) by column and batch experiments.

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2. Experimental

2.1. Instrumentation

FTIR spectra of impregnated resins were recorded with Perkin-Elmer Spectrum BX Fourier Transform IR spectrometer using KBr discs in the range 4000–700 cm^{-1} , 30 co-added interferograms were scanned at 2 cm^{-1} resolution. UV-1601 model Shimadzu UV-vis spectrophotometer was used to determine U(VI) as U(VI)-arsenazo(III) complex at 653 nm and Th(IV) as Th(IV)-arsenazo(III) at 667 nm. Batch experiments were carried out in an isothermal water-bath circulator (Lindberg Blue, USA) at 200 rpm. The pH measurements were made Ino Lab WTW model digital pH-meter. For solid phase experiments, Varian cartridge (plastic container, 1.0 cm \times 10.0 cm) equipped with 20 μm polypropylene frits were used.

2.2. Reagents and chemicals

All chemicals used were of analytical grade from Merck or Fluka unless otherwise stated. Standard and stock solutions were prepared using double distilled water: arsenazo III (0.1%), $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1000 mg L^{-1} in 0.1 mol L^{-1} HNO_3), $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (1000 mg L^{-1} in 1 mol L^{-1} HNO_3) and OPDA (1% in methanol). Amberlite XAD-2000 (styrene-divinylbenzene copolymer, surface area: 588 $\text{m}^2 \text{g}^{-1}$, pore diameter: 4.2 nm and bead size 20–60 mesh) was supplied by Sigma. To remove inorganic and organic contaminants, it was washed with methanol, water, 1 mol L^{-1} HNO_3 , water, 1 mol L^{-1} NaOH and water, respectively. For pH adjustment, 0.01–1 M HCl and NaOH solutions were used.

2.3. Impregnation process

0.5 g of dry Amberlite XAD-2000 resin was placed in 25 mL of methanol containing 1% OPDA (Fig. 1) and stirred for 24 h. The resin was separated by filtration through a sintered glass funnel and was washed with double distilled water to remove

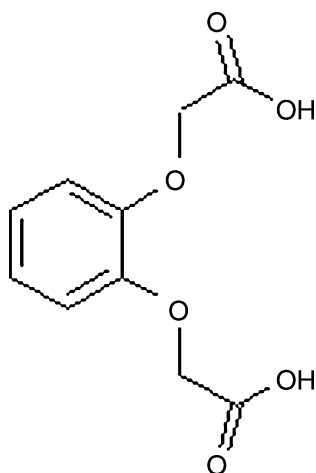


Fig. 1. Chemical structure of *o*-phenylene dioxydiacetic acid.

the solvent. The resin was used as an air-dried product. The ligand content in the impregnated solution was determined gravimetrically by weighing the dry ligand residue after removing the resin and evaporation of the solution. The amount of impregnated resin was calculated from the material balance. The maximum sorption of OPDA in the XAD-2000 was found as 1.77 mmol g^{-1} .

2.4. Column “dynamic” method

0.1 g of impregnated resin was wetted with 5 mL methanol and stirred for 10 min, then 5 mL of doubly distilled water was added and stirred for 10 min again. Lastly, the mixture was transferred to the polyethylene column and 25 mL of methanol:water (10:90) was passed through the column. A sample solution (50 mL) containing 50 μg of U(VI) or Th(IV) was taken at optimum pH and passed through the column. After this step, stripping was carried out by suitable eluting agents: 0.25 mol L^{-1} HCl for U(VI) and 1.0 mol L^{-1} HCl for Th(IV). The stripping solutions were analyzed spectrophotometrically. All runs were carried out at ambient temperature (23–25 $^\circ\text{C}$).

2.5. Batch “static” method

One hundred milligrams of impregnated resin was equilibrated with a sample solution containing 50 μg metal ion in a volume of 50 mL in a 100 mL well-stopped reagent bottles at 200 rpm for 15 min using a mechanical shaker, under optimized conditions. The impregnated resin containing metal ions were filtered and then metal ions were desorbed as given in dynamic method and were determined spectrophotometrically.

2.6. Spectrophotometric arsenazo III method for the determination of U(VI) and Th(IV)

KCl/HCl solution having pH 2 was prepared by mixing 8.1 mL of 0.2 mol L^{-1} HCl and 41.9 mL of 0.2 mol L^{-1} KCl solutions and diluting to 100 mL with doubly distilled water. Reagent blank solution containing arsenazo III (1% (w/v)) and buffer solution was freshly prepared at each measurement.

Calibration solutions and sample solutions containing 2.0 mL of standard/sample solution +0.2 mL of arsenazo III solution +1 mL of buffer solution were diluted to 5.0 mL with distilled water and measured at 653.5 nm for U(VI). For Th(IV) at 667 nm, instead of adding buffer, solution was completed by 1.0 mol L^{-1} HNO_3 .

2.7. Procedure for the analysis of rock sample

About of 0.10–0.50 g of the rock sample (Dasite and Andesite from Kula region on a place nearby Izmir, Turkey) was treated with 5.0 mL of HF and 1.0 mL of conc. H_2SO_4 at 150 $^\circ\text{C}$ on a hot plate. The process was repeated thrice. The residue is cooled and fused with 2.0 g of KHSO_4 at 800 $^\circ\text{C}$ in a muffle furnace for 45 min. The melt is then cooled, dissolved in 50 mL of double

distilled water and diluted to 100 mL. Then, the sorption and the desorption of U(VI) and Th(IV) in the soil sample solution was done as given in dynamic procedure. After passing of sample solution through the column, the sorbed and desorbed metal ions were determined spectrophotometrically.

3. Results and discussion

3.1. Characterization studies

The FTIR spectra of XAD-2000 and OPDA impregnated XAD-2000 have been recorded (Fig. 2). The spectrum associated with the polymeric matrix of styrene/divinyl benzene exhibits two strong bands at 3020 and 2925 cm^{-1} attributed to the stretching modes of the aromatic and aliphatic C–H groups. In addition, the three absorption bands between 1610 and 1440 cm^{-1} are due to ring vibration of benzene rings, which also contain bending bands at 895, 830, 794 and 709 cm^{-1} ascribed to out of plane ring C–H bending vibrations. The IR absorption frequencies assignments for OPDA impregnated XAD-2000 show small modifications on the characteristic normal modes compared with the spectrum of the pure Amberlite XAD-2000. Also, the IR absorption frequencies assignments for OPDA on loaded XAD-2000 show some modifications of the characteristic normal modes of these extractant compared with the spectrum of the free reagent. The C=O stretching vibration at 1725 and 1730 cm^{-1} and the OH stretching vibration at 3480 and 3495 cm^{-1} were observed sharply in the OPDA loaded Amberlite XAD-2000. The FTIR spectra of OPDA loaded XAD-2000/U(VI) and Th(IV) complexes have been characterized. It is seen that the characteristic frequency of –C=O and –OH stretching bands of OPDA and have been shifted in the interval of 2–8 cm^{-1} for both ions.

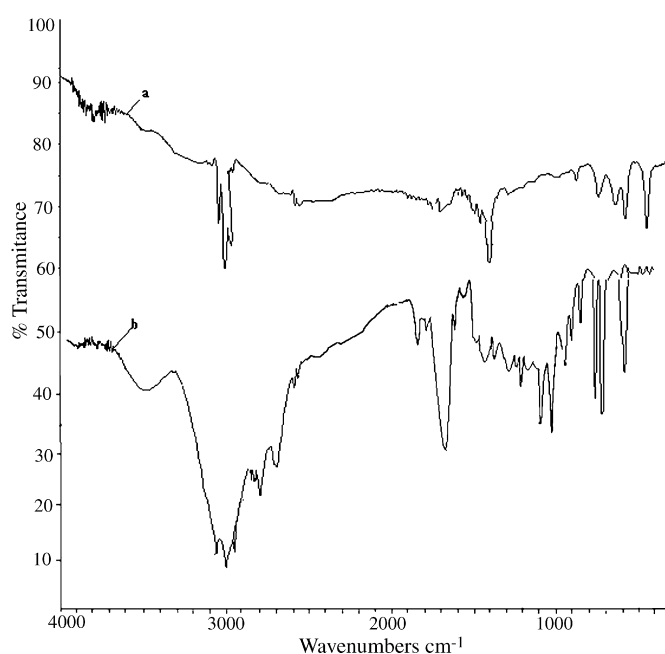


Fig. 2. FT-IR spectra of (a) XAD-2000 and (b) OPDA impregnated XAD-2000.

3.2. Effect of pH

The effect of pH on the sorption of metal ions was determined by column method. A 50 mL metal solution containing 1 $\mu\text{g mL}^{-1}$ of metal ion was passed at varying pH from 2 to 7. The percentage of metal sorption was measured by desorbing the resin with suitable eluent and then determined spectrophotometrically. Sorption of U(VI) was decreased severely by decreasing pH. In Th(IV) sorption, moderate acidic pH range was effective, above pH 5 sorption was decreased gradually. The optimum pH for maximum sorption as 100% was found to be between pH 5.5–7.0 for U(VI) and pH 3–5 for Th(IV).

3.3. Effect of concentration of eluting agents

After trace of U(VI) and Th(IV) was enriched on the resin column, 10 mL of 0.1–1.0 M of HNO_3 and HCl solutions were tested for quantitative desorption. The recoveries of both ions with all HNO_3 solutions were found lower than 80%. However, the quantitative elution was achieved for U(VI) with 5 mL 0.25 mol L^{-1} HCl and for Th(IV) with 4 mL 1.0 mol L^{-1} HCl.

3.4. Kinetic studies

In general, uranium species varies over the pH range. Uranium becomes increasingly hydrolyzed and forms oligomeric species with the increasing pH. Many researcher reported [21,22] and [23] that at $\text{pH} \leq 4.3$, uranium exist predominantly as monomeric species, UO_2^{2+} , and small amount as $\text{UO}_2(\text{OH})^+$. When the $\text{pH} \geq 5$, the formation of colloidal or oligomeric species, i.e. $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, $(\text{UO}_2)_3(\text{OH})_7^-$, are formed. In this experiment, in strong acidic solutions ($\text{pH} < 3$) hydroxonium ions H_3O^+ compete with the UO_2^{2+} ions for the adsorption sites and, thus, decrease uranium adsorption. On the other hand, above $\text{pH} > 5$, uranium adsorption reaches the maximum level. The reason may be the interaction between carboxylate ions in OPDA and various hydroxo complexes of U(VI). The different chemical forms of Th(IV) can be possible in solution of different pH [24]. Th^{4+} is the least hydrolyzed tetravalent ion, the uncomplexed cation is stable at pH 3 or less. $\text{Th}(\text{OH})^{3+}$ around pH 3–5, $\text{Th}(\text{OH})^{2+}$ around pH 4.5–5.5, $\text{Th}(\text{OH})^{3+}$ around pH 5 and $\text{Th}(\text{OH})_4$ above pH 6 are formed [25]. In this work, $\text{Th}(\text{OH})^{3+}$ and $\text{Th}(\text{OH})^{2+}$ species may be dominant in the adsorption of thorium by OPDA-impregnated resin.

To determine the rate of transfer of metal ions from aqueous to the resin by batch experiment, 50 μg of 50 mL metal solution with 100 mg of resin over a series of varying time of durations from 10 to 60 min under optimum pH conditions was studied. The amount of metal ion loaded on the resin phase was calculated by difference of the amount of the metal ion in the effluent after passing through the resin to that in the initial concentration of the effluent. The time required for 50% sorption ($t_{1/2}$) for U(VI) and Th(IV) was 12 and 15 min, respectively. This metal ion adsorption time onto impregnated resin is relatively short and feasible for the metal ion adsorption process.

Table 1
The effect of aqueous volume on the recovery of $0.1 \mu\text{g mL}^{-1}$ U(VI) and Th(IV) using batch technique

Sample volume (mL)	Recovery (%)	
	U(VI)	Th(IV)
50	99.2 ± 2.9	99.5 ± 2.2
100	97.8 ± 2.2	99.8 ± 2.4
150	99.4 ± 1.8	98.7 ± 2.1
200	98.3 ± 2.0	99.8 ± 1.8
250	75.6 ± 2.3	70.4 ± 2.2
300	50.7 ± 2.6	51.4 ± 2.0

3.5. Aqueous phase volume

The effect of aqueous volume in batch method was studied in the range 50–300 mL on the individual extraction of $0.1 \mu\text{g mL}^{-1}$ of U(VI) and Th(IV) with 0.1 g of impregnated resin equilibrated at optimum pH for 1 h. It was seen that U(VI) and Th(IV) were sorbed by 100% up to 200 mL in aqueous media (Table 1).

3.6. Sorption capacity of the resin by column method

Metal working solutions at 1 mg L^{-1} were freshly diluted from stock solutions and their pH values adjusted to 4 for Th(IV) and 6 for U(VI) at the time of experiments. These solutions were passed through the column containing 0.1 g of resin at flow rate of 1 mL min^{-1} . As seen Table 2, the sorption capacities of U(VI) and Th(IV) were found as 0.121 and $0.113 \text{ mmol g}^{-1}$ of SPE which are higher than chelate modified or impregnated SPE procedures reported in literature so far, respectively.

3.7. Effect of electrolytes and diverse ions

The tested electrolytes were NaCl, NaNO_3 , Na_2SO_4 and Na_3PO_4 . For 1 mg L^{-1} of metal ions NaCl and NaNO_3 were tolerable up to 0.5 mol L^{-1} . Other studied electrolytes interfere if they are present above 0.25 mol L^{-1} for Na_2SO_4 ,

Table 2
Comparison of sorption capacities of SPE materials prepared by Amberlite resins with chelating or impregnation for U(VI) and Th(IV)

SPE material	Sorption capacity (mmol g^{-1})		Reference
	Th(IV)	U(VI)	
Quinoline-8-ol, Amberlite XAD-4	–	0.012	[10]
<i>o</i> -Vanillinesemicarbazone, Amberlite XAD-4	0.014	0.012	[19]
Succinic acid, Amberlite XAD-4	–	0.052	[13]
<i>o</i> -Vanillinthiosemicarbazone, Amberlite XAD-4	0.007	0.006	[16]
Pyrogallol, Amberlite XAD-2	–	0.019	[18]
Tiron, Amberlite XAD-2	–	0.030	[15]
OPDA, Amberlite XAD 2000	0.113	0.123	Present method

Table 3
Tolerance limits of metal ions for U(VI) and Th(IV)

Metal ion ($\mu\text{g mL}^{-1}$)	U(VI) ($1 \mu\text{g mL}^{-1}$)	Th(IV) ($1 \mu\text{g mL}^{-1}$)
Ni	25	30
Cu	45	45
Pb	30	50
Zn	45	45
Co	25	30
Cd	30	35

Experimental conditions: 0.1 g resin; volume of solution passed: 100 mL; U(VI), pH 6.0; Th(IV), pH 4.0.

0.15 mol L^{-1} for Na_3PO_4 . The diverse ions; Ni, Cu, Co, Pb, Zn and Cd did not show an effect on the U(VI) and Th(IV) retention at a 25–50-fold mg L^{-1} excess of the analyte (Table 3).

3.8. Reusability and stability of the impregnated resin

The reproducibility and reliability in analytical data on subsequent reusage was investigated by passing 100 mL of $2 \mu\text{g mL}^{-1}$ metal ion from column having 0.1 g resin under the dynamic column conditions. After desorption, the results obtained on subsequent reusage of the same resin were reproducible with R.S.D. values of <2.5% up to 18 cycles.

3.9. Preconcentration factor

To find the preconcentration factor of the resin, fixed amount of metal ions as $10 \mu\text{g}$ in varying volumes as 0.5 and 1 L volumes were passed through the resin bed, the retained metals were eluted with 5 mL 0.25 mol L^{-1} HCl for U(VI) and 4 mL 1.0 mol L^{-1} HCl for Th(IV) and then determined spectrophotometrically. The system was successful in preconcentrating both U(VI) and Th(IV) down to 10 ng mL^{-1} (Table 4).

3.10. Analysis of the synthetic metal mixture solutions

The applicability of the proposed method for the determination of U(VI) and Th(IV) from synthetic mixtures was checked. The 0.1 L of synthetic sample solutions containing 2–4 mg of diverse ions and 0.1–0.2 mg of U(VI) and Th(IV) ions were prepared. The results are given in Table 5. The recoveries varied between 96% and 98%.

Table 4
Preconcentration factor and concentration limit of enrichment using column technique

Metal ion	Volume of solution (mL)	Concentration limit (ng mL^{-1})	Preconcentration factor	Recovery (%)
U(VI)	500	20	100	99
	1000	10	200	100
Th(IV)	500	20	125	98
	1000	10	250	102

Table 5
Determination of U(VI) and Th(IV) in synthetic and real samples

Composition of synthetic sample (mg/100 mL)	Concentration ($\mu\text{g mL}^{-1}$)			
	Present method ^a		ICP-MS	
	Added		Found	
	Th(IV)	U(VI)	Th(IV)	U(VI)
Cu(3), Ni(2), Zn(3.5)	1	1	0.98 \pm 0.01	0.97 \pm 0.01
Pb(2.5), Co(2), Cu(3)	2	1	1.97 \pm 0.02	0.98 \pm 0.01
Ni(2), Zn(2), Cd(2.5), Pb(2.5)	1	2	0.97 \pm 0.02	1.96 \pm 0.02
Co(2), Cd(2), Ni(2), Cu(4)	2	2	1.98 \pm 0.01	1.97 \pm 0.02

Rock sample	U(VI) ($\mu\text{g mL}^{-1}$)		Th(IV) ($\mu\text{g mL}^{-1}$)	
	Present method ^a	ICP-MS	Present method ^a	ICP-MS
Dasite	5.25 \pm 0.01	5.60	17.18 \pm 0.02	17.40
Andesite	5.18 \pm 0.02	5.40	15.01 \pm 0.03	15.80

^a Average of three determinations.

3.11. Analysis of rock sample

In the analysis of andesite and dacite rock samples, no significant difference between our results and reported values with ICP-MS from ACME laboratory in Canada was found (*t*-test, 95% confidence level) (Table 5). Thus, the SPE method developed in the present paper enables simple and low cost instrument to analyze rock, soil and sediment samples containing trace and ultra trace amounts of U(VI) and Th(IV).

4. Conclusions

o-Phenylene dioxydiacetic acid loaded Amberlite XAD-2000 resin has good potential for enrichment of traces of U(VI) and Th(IV). The capacity of the resin is sufficiently high to preconcentrate more than one metal ion simultaneously. The impregnated resin was recycled more than 18 times without affecting its sorption capacity. The selective extraction of U(VI) and Th(IV) could be extended to the recovery of these ions from various analytical matrices such as geological, biological and radioactive waste samples.

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