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Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium(VI)

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Abstract

Amberlite XAD-4 resin has been functionalized with succinic acid by coupling it with dibromosuccinic acid after acetylation. The resulting resin has been characterized by FT-IR, elemental analysis and TGA and has been used for preconcentrative separation of uranium(VI) from host of other inorganic species prior to its determination by spectrophotometry. The optimum pH value for quantitative sorption of uranium(VI) in both batch and column modes is 4.5–8.0 and desorption can be achieved by using 5.0 ml of 1.0 mol l^{-1} HCl. The sorption capacity of functionalized resin is 12.3 mg g^{-1}. Calibration graphs were rectilinear over the uranium(VI) concentrations in the range 5–200 μg l^{-1}. Five replicate determinations of 50 μg of uranium(VI) present in 1000 ml of solution gave a mean absorbance of 0.10 with a relative standard deviation of 2.56%. The detection limit corresponding to three times the standard deviation of the blank was found to be 2 μg l^{-1}. Various cationic and anionic species at 200-fold amounts do not interfere during the preconcentration of 5.0 μg of uranium(VI) present in 1000 ml (batch) or 100 ml (column) of sample solution. Further, adsorption kinetic and isotherm studies were also carried out by a batch method to understand the nature of sorption of uranium(VI) with the succinic acid functionalized resin. The accuracy of the developed solid phase extractive preconcentration method in conjunction with Arsenazo III procedure was tested by analyzing marine sediment (MESS-3) and soil (IAEA soil-7) reference material. Further, the above procedure has been successfully employed for the analysis of soil and sediment samples.

Keywords: Succinic acid; Amberlite XAD-4; Synthesis; Preconcentration; Uranium(VI); Soils and sediments

1. Introduction

Solid phase extraction (SPE) has been increasingly used for preconcentration/separation of trace and ultra trace amounts inorganic and organic species from complex matrices as seen from recent reviews [1–4]. Various researchers [3–5] have highlighted the advantages of SPE over other preconcentration techniques and in particular over liquid–liquid extraction. Chelating resins have been frequently used SPE's as they provide good stability, high sorption capacity for metal ions and good flexibility in working conditions. Iminodiacetate resins such as chelex 100 [6] Amberlite IRC-718 [7] are widely used for this purpose but lacks selectivity [8,9]. Other chelating resins that are employed include Amberlite XAD series resins, 4-vinyl pyridine-divinylbenzene/acrylonitrile-divinylbenzene copolymers, Amberlite IRA-400, Biorad AGMP-1, silica based C_{18} support, Amberlyst A-26, Dowex-2 and Merrifield chloromethylated resins. Of these, Amberlite-XAD resins have superior physical properties like durability and chemical stability towards harsh environments [10]. Two methodologies are frequently adopted for designing such chelate functionalized Amberlite XAD resins. First involves physical sorption of ligands onto a matrix. The other is based on covalent coupling of a ligand with polymer backbone through a spacer arm, generally –N=N– or $–CH_2$ group. The latter strategy renders rugged systems, free from ligand leaching problems but sorption capacities are low. One way of achieving high sorption capacity is by the use of ligands of small size which can extensively functionalize an appropriate crosslinked polymer. Recently, Amberlite XAD-4 functionalized with quinoline-8-ol [11] has shown reasonably good adsorption capacity. It was therefore thought worthwhile to couple succinic acid molecule

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Table 1
Summary of SPE preconcentration procedures developed for uranium(VI) since 1990

S. no.	Chelating agent	Solid sorbent	Analytical technique	pH	Detection limit ($\mu g\,l^{-1}$)	Application
1	Quinoline-8-ol	Silica [15]	ICP-AES	5.0	1.0	Sea water
2	Tri-*n*-octyl phosphine oxide	Octadecyl silica membrane discs [16]	Spectrophotometry	$0.5\,mol\,l^{-1}$ HNO_3	–	Soil samples
3	Tri-*n*-octyl phosphine oxide	Octadecyl silica membrane discs [17]	Spectrophotometry	–	0.1	Natural waters
4	–	Activated silica gel [18]	–	9.3	0.1–0.2 μg	Wastes and natural waters
5	Iminodiacetate	Controlled pore glass [19]	ICP-MS	–	–	Coastal sea water
6	Phosphonic acid	Polyurethane foam [20]	–	5.5–8.5	–	–
7	4-(2-Thiazolylazo) resorcinol	Chelating resin [21]	NAA	4.3–4.5	–	Wastes
8	4-(2-Thiazolylazo) resorcinol	Resins [22]	Spectrophotometry	5.4–5.5	–	Geological materials
9	Alizarin red S	Anion exchange resin [23]	Spectrophotometry	2.8–5.0	–	Natural waters and ores
10	Phosphonic acid	Polystyrene–DVB resin [24]	–	0–4.0	–	–
11	Vinyl benzoate	Molecularlyimprinted resins [25]	Spectrophotometry and ICP-AES	3.0–3.5	–	Sea water
12	5,7-Dichloroquinoline-8-ol	Naphthalene [32]	Spectrophotometry	4.5–7.0	5.0	Soil and sediments
13	1,2-(Pyridylazo)2-naphthol	Benzophenone [26]	Spectrophotometry	10.5–11.0	5.0	Soils and sediments
14	5,7-Dichloroquinoline-8-ol	Molecularly imprinted polymers [27]	Spectrophotometry	5.0–7.0	5.0	Soils and sediments
15	Diamyl phosphonate	Amberlite XAD-7 [28]	AES	$>1.0\,mol\,l^{-1}$	–	Ground water and soil
16	Pyrogallol	Amberlite XAD 2 [29]	–	5.5–6.2	1.0	–
17	*N*,*N*′-Dibutyl-*N*′-benzoyl thiourea	Amberlite XAD 16 [30]	–	4.5–6.5	–	–
18	Quinoline-8-ol	Amberlite XAD-4 [11]	Spectrophotometry	4.0–6.0	2.0	Soils and sediments
19	Bicine	Amberlite XAD-4 [31]	Spectrophotometry	4.0–8.5	–	–
20	*o*-Vanillin semicarbazone	Amberlite XAD-4 [33]	ICP-AES and GF-AAS	6.0–8.0	100	Simulated river water
21	Succinic acid	Amberlite XAD-4 (present method)	Spectrophotometry	4.5–8.0	5.0	Soils and sediments

with Amberlite XAD-4 through $–CH_2$ linkage and examine the metal ion uptake of the resulting SPE material. This molecule has been widely studied in liquid–liquid extraction as carboxylic acid extractant for the separation of inorganic species [12,13]. Recently, Dogutan et al. [14] synthesized melamine based succinic acid sequestering polymeric resin and was used for the preconcentration of chromium.

Uranium and its compounds like lead are highly toxic which cause acute kidney failure and death. The inhalation of uranium compounds results in deposition of uranium in the lungs and reaches kidneys through blood stream. Table 1 summarizes the salient features of various SPE procedures described in literature for uranium(VI) since 1990. In this paper, Amberlite XAD-4 is functionalized via two steps with succinic acid and has been used for the solid phase extractive preconcentration/separation of uranium(VI) at trace levels using both batch/column operation modes. The accuracy of the developed preconcentration procedure was tested by analysing marine sediment (MESS-3) soil (IAEA soil-7) reference materials and by comparing with the certified values. Further, the results obtained on analysing soil and sediment samples using Arsenazo III spectrophotometric procedure in conjunction with the SPE preconcentration method developed in the present investigation was compared with the standard inductively coupled plasma mass spectrometric (ICPMS) values.

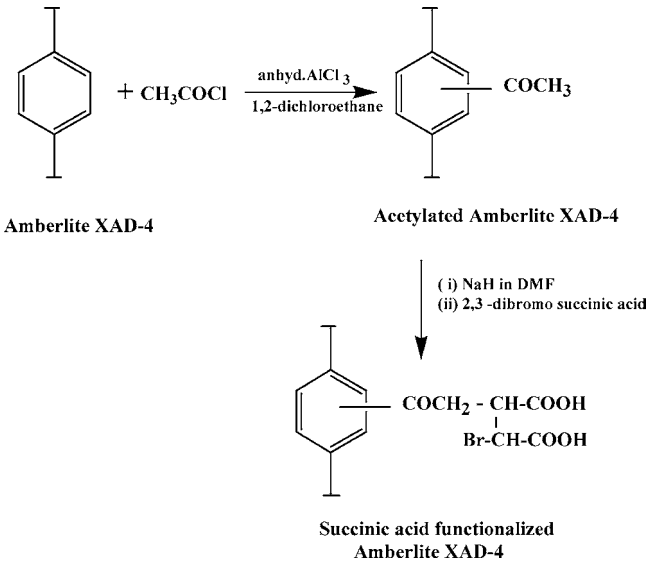
2. Experimental

2.1. Reagents

A stock solution of uranium(VI) was prepared by dissolving appropriate amount of $UO_2(NO_3)_2{\cdot}6H_2O$ (Aldrich, USA) in deionized water. Conc. HNO_3 (5 ml) was added to 100 ml of solution to suppress hydrolysis. 0.1% Arsenazo III (Aldrich, USA) solution was prepared by dissolving 0.1 g of the reagent in 100 ml of deionized water. Hexamine–HCl buffer (1.0 mol l^{-1}) was used to maintain the pH of the aqueous phase. Amberlite XAD-4 (surface area: 725 m^2 g^{-1}, pore diameter 5 mm, and bead size 20–60 mesh) and dibromosuccinic acid were obtained from Aldrich, USA. Acetyl chloride, anhydrous $AlCl_3$, dichloroethane, and methanol were obtained from M/s. E. Merck, India. All other chemicals including electrolytes and other metal ions were of analytical reagent grade. The standard reference materials MESS-3 (marine sediment reference material supplied by National Research Council, Canada) and soil-7 (IAEA, Vienna) were certified for trace elements was used for quality assurance.

2.2. Instrumentation

Absorbances were measured using Computer controlled UV–vis spectrophotometer UV-2401 PC (Shimadzu, Japan). LI-120 digital pH meter (ELICO, India) was used for pH measurements. IR spectra (4000–400 cm^{-1}) was taken by KBr pellet method using MAGNA IR-560 spectrometer (Nicolet, USA). Elemental analyses were carried out on a Perkin-Elmer Elemental analyzer (Rotkrewz, Switzerland). TGA analysis was carried out by using TGA-50H (Shimadzu, Japan).



Scheme 1. Synthesis of succinic acid functionalized Amberlite XAD-4 (SA resin) beads.

2.3. Synthesis of succinic acid functionalized Amberlite XAD-4 resin

2.3.1. Acetylation of Amberlite XAD-4

Amberlite XAD-4 resin (2 g) was taken after drying at 110 °C for 2 h. Anhydrous $AlCl_3$ was dissolved in 10 ml of 1,2-dichloroethane and 4.0 ml of acetyl chloride were added slowly along the sides. Then the sides of the flask were washed with an additional 2.0 ml of 1,2-dichloroethane. Anhydrous $CaCl_2$ drying tube was attached and kept for 8 h with stirring. Thereafter, the reaction mixture was poured into an ice–HCl mixture. The acetylated resin was filtered, washed repeatedly with methanol, water, HCl and dried (see Scheme 1).

2.3.2. Preparation of succinic acid functionalized resin

Sodium hydride (2.0 g) and 15.0 ml of dry dimethyl formamide were added to dried acetylated Amberlite XAD-4 and stirred for 1.0 h. Dibromosuccinic acid (2.0 g) was added to the above solution and stirred for 2 h. The resulting succinic acid functionalized Amberlite XAD-4 (SA resin) beads were filtered, washed with excess of water and air dried (see Scheme 1).

2.4. Characterization studies

2.4.1. IR spectra

The C=O stretching frequency in acetylated Amberlite XAD-4 at 1686 cm^{-1} is overlapping with the carboxylic C=O stretching frequency in SA resin at 1698 cm^{-1}. The

C=O stretching and the C–OH in plane bending frequencies of the carboxyl group are at 1274.14 and 1367.24 cm^{-1}, respectively. The above points evidenced the functionalization of Amberlite XAD-4 with succinic acid after acetylation.

2.4.2. CHN analysis

The theoretical and experimental CHN analysis data of SA resin are given below:

Theoretical (%)	C, 71.5; H, 6.2
Experimental (%)	C, 72.6; H, 7.9

This data confirms the above IR spectral studies.

2.4.3. Thermal analysis

TGA of the SA resin shows weight loss upto 510 °C. The weight loss upto 120 °C was due to the water molecules in the polymer. The major weight loss after 290 °C is due to the dissociation of chemically immobilized succinic acid moiety and the polymeric matrix.

2.5. Recommended procedure for preconcentration and determination of uranium(VI)

Both column and batch methods were used to preconcentrate uranium(VI) from aqueous solutions.

2.5.1. Column "dynamic" method

The glass column (Vensil, size: 7.0 mm diameter and 10 cm length) was packed with 0.10 g of SA resin and washed three to four times with deionized water. A sample solution (100 ml) containing 5–200 μg of uranium(VI) was taken and the pH was adjusted to ∼4.5 after addition of hexamine buffer and passed through the above column at a flow rate of 3.0 ml min^{-1}. The metal ions were stripped from the resin bed by using 5.0 ml of 1.0 mol l^{-1} HCl and determined spectrophotometrically after the addition of 5.0 ml of 1:1 HCl and 0.8 ml of 0.10% Arsenazo III in a total volume of 25 ml. The absorbance of Arsenazo III complex of uranium(VI) was measured at 656 nm [31].

2.5.2. Batch "static" method

A sample solution containing 5–200 μg in a volume of 10–1000 ml was taken and its pH was adjusted to around ∼4.5 after the addition of hexamine buffer. SA resin (0.1 g) was added to above solution and stirred for 10 min. The uranyl ions adsorbed chelating resin was filtered and eluted with 5.0 ml of 1.0 mol l^{-1} HCl and subjected to spectrophotometric determination using Arsenazo III reagent as described in Section 2.5.1.

2.6. Procedure for the analysis of standard reference materials (MESS-3 and IAEA soil-7), soil and sediment samples

About 0.10–0.50 g of the sample was treated with 5.0 ml of HF and 1.0 ml of conc. H_2SO_4 at 150 °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 °C in an electric Bunsen for 45 min. The melt is then cooled, dissolved in 50 ml of deionized water and diluted to 100 ml. Preconcentration of uranium(VI) onto SA resin and determination by Arsenazo III procedure was carried out as described in Section 2.5.1.

3. Results and discussion

3.1. IR spectral studies

By comparing the IR spectra of SA resin (I) and uranium(VI) enriched SA resin (II), it was observed that

(i) C=O streching frequency of I shifts from 1274.14 to 1268.97 cm^{-1} and
(ii) C–OH in plane bending frequency of I shifts from 1367.24 to 1356.9 cm^{-1}.

In addition, a sharp peak at 912 cm^{-1} corresponding to ν_{U-O} of uranyl ion confirm that SA resin enriches uranium(VI) under the present experimental conditions.

3.2. UV–vis spectral studies

The analysis of leachant of II obtained on equilibrating II with 5.0 ml of 1.0 mol l^{-1} HCl for uranium(VI) using UV–vis spectromertry conclusively prove that uranium(VI) was indeed sorbed onto SA resin.

3.3. Optimization of sorption and elution of uranium(VI)

The glass column was packed with 0.1 g of SA resin and was first washed with 25 ml of 1.0 mol l^{-1} HCl and then with deionized water until freed from acid. A set of solutions (volume 100 ml) containing 50 μg of uranium(VI) was taken. The pH of set of solutions was adjusted between 2.0 and 8.0 and the recommended procedure was applied. The sorption of uranium(VI) is quantitative and maximum when the pH is greater than 4.5 (see Table 2). In all subsequent work, the pH was adjusted to ∼4.5 after the addition of 10 ml of 1.0 ml l^{-1} of hexamine–HCl buffer. Other optimal conditions were ascertained in a similar fashion are given in Table 2. For the sorption of uranium(VI) onto SA resin, a flow rate of 1–3 ml min^{-1} was found to be suitable for optimum loading onto resin. The flow rates slower than 1.0 ml min^{-1} were not studied to avoid extended analysis times. At flow rates higher than 3.0 ml min^{-1}, uranium(VI) does not equilibrate adequately with the resin bed. Similarly, the variation of elution flow rate from 1.0 to 4.0 ml min^{-1} show that the elution of sorbed uranium(VI) was quantitative over the entire range. Elution flow rates higher than 4.0ml/min could not be attained under our experimental conditions. Further, as low as 0.1 mol l^{-1} HCl and 2.5 ml of HCl were enough for quantitative elution of sorbed uranium(VI). Therefore, for complete desorption, 5 ml of 1.0 mol l^{-1} of

Table 2
Optimization of experimental parameters for SPE of uranium(VI) [uranium(VI) = 50 μg, pH 4.5, preconcentration and elution flow rates = 3.0 ml min^{-1}, aqueous phase volume = 100 ml]

Parameters					
pH	2.0	4.0	4.5	6.0	8.0
Enrichment (%)	1.30 ± 0.1	90.52 ± 0.2	>99.9	>99.8	>99.8
Preconcentration flow rate (ml min^{-1})	0.5	1.0	2.0	3.0	4.0
Enrichment (%)	>99.8	>99.8	>99.8	>99.8	90.52 ± 0.2
Elution flow rate (ml min^{-1})	0.5	1.0	2.0	3.0	4.0
Enrichment (%)	>99.8	>99.8	>99.8	>99.8	>99.8
Eluent concentration (mol l^{-1})	0.1	0.5	1.0	2.0	–
Enrichment (%)	>99.8	>99.8	>99.8	>99.8	–
Eluent volume (ml) (1.0 mol l^{-1})	2.5	5.0	10.0		
Enrichment (%)	>99.8	>99.8	>99.8		
Aqueous phase volume (ml)	25	50	100	500	1000
Enrichment (%)	>99.8	>99.8	>99.8	>99.8	>99.8

HCl was used for convenience. Under these conditions, the percent enrichment of uranium(VI) onto Amberlite XAD-4 resin (unfunctionalized) was found to be around 30.2%. The sorption and desorption of uranium(VI) was found to be quantitative on changing the volume of sample solution in the range 10–100 ml (column mode) and upto 1000 ml (batch mode) keeping the total amount of loaded uranium(VI) at 50 μg. The enrichment factor and corresponding lowest concentration below which recoveries become non-quantitative are 100 and 5 μg l^{-1}, respectively.

3.4. Stability and reusability of the resin

The uranium(VI) was sorbed and desorbed on 0.10 g of the resin several times. It was found that sorption capacity of succinic acid functionalized resin after 25 cycles of equilibration changes by less than 2.0% indicating the possible reuse of resin for several cycles. The sorption capacity of the resin stored for more than 2 months under ambient conditions has been found to be practically unchanged.

3.5. Statistical and calibration parameters

Under the optimum conditions described above, the calibration curve was linear over the concentration range 5–200 μg of uranium(VI) present in 1000 ml of solution. A sample of 50.0 μg of uranium(VI) gave a mean absorbance of 0.10 with a relative standard deviation of 2.56%. The detection limit corresponding to three times the standard deviation of the blank was found to be 2.0 μg l^{-1}. The linear equation with regression (R^2) is as follows:

$$A = 0.0015C - 0.00128$$

$$R^2 = 0.9997$$

where A is the peak height absorbance and C is the concentration in μg l^{-1}. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

3.6. Adsorption kinetics

The rate of loading of uranium(VI) onto SA resin was determined by shaking 20, 40 and 60 mg (curves A–C in Fig. 1) of uranium(VI) in a refrigerated incubation shaker at 30 °C for 0.5, 1.0, 2.0, 4.0, 6.0, 10.0, 20, 40 and 60 min. The amount of uranium(VI) loaded onto SA resin and in supernatant solution was determined by the recommended procedure, after appropriate dilution. The equilibration time in which SA resin attains 50% saturation with uranium(VI) (i.e. when the amount of metal ion sorbed on the SPE is a half of its maximum sorption capacity) is called loading half time ($t_{1/2}$). From the curves A–C in Fig. 1, it is clear that the loading half time was <30 s.

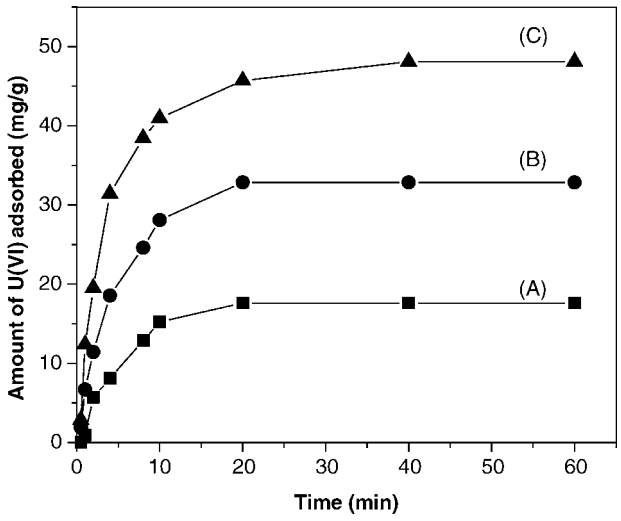


Fig. 1. Effect of shaking time on the adsorption of uranium(VI). Uranium(VI) concentration: (A) 20 mg l^{-1}, (B) 40 mg l^{-1} and (C) 60 mg l^{-1}; pH 6.5; adsorbent dose 2.5 g l^{-1}.

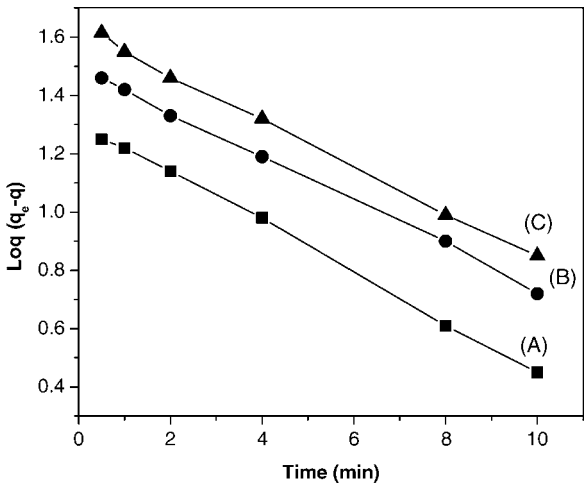


Fig. 2. Lagergren plots for the adsorption of uranium(VI). Uranium(VI) concentration: (A) 20 mg l^{-1}, (B) 40 mg l^{-1}, (C) 60 mg l^{-1}; pH 6.5; adsorbent dose 2.5 g l^{-1}.

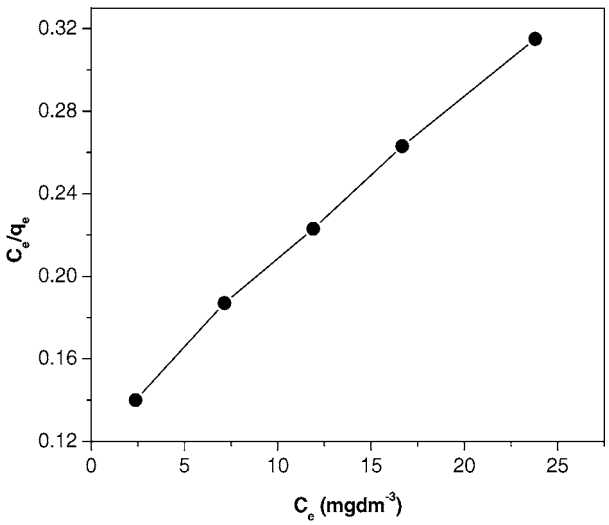


Fig. 3. Langmuir plot for the adsorption of uranium(VI). Uranium(VI) concentration: 20–100 mg l^{-1}; pH 6.5; equilibration time 60 min; adsorbent dose 2.5 g l^{-1}.

The kinetics of uranium(VI) adsorption on SA resin follow the first order rate expression given by Lagergren [34].

$$\log(q_e - q) = \log q_e - K_{ads}\frac{t}{2.303}$$

where q and q_e are the amounts of uranium(VI) adsorbed (mg g^{-1} of functionalized resin) at time, t (min) and equilibrium time (60 min), respectively and K_{ads} the rate constant of adsorption. Linear plots of $\log(q_e - q)$ versus t (Fig. 2) show the applicability of the above equation for SA resin. The correlation coefficients of linear plots obtained for Lagergren plots are 0.9995, 0.9994 and 0.9991, respectively, for 20, 40 and 60 mg l^{-1} of uranium(VI) solution. The K_{ads} calculated from the slopes of Fig. 2 are 0.1974, 0.1757 and 0.1831 l min^{-1} for 20, 40, 60 mg l^{-1} of uranium(VI) solution.

3.7. Adsorption isotherm

The adsorption of uranium(VI) as a function of SA resin was studied by equilibrating for 60 min in a refrigerated incubator shaker. The amount of uranium(VI) loaded SA resin and the supernatant solution were determined by following the recommended procedure described above. The Langmuir treatment [35] is based on the assumption that (i) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate in the plane of the surface

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

where C_e is the equilibrium concentration (mg l^{-1}), q_e the amount adsorbed at equilibrium and q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of C_e/q_e versus C_e shows that adsorption obeys Langmuir adsorption model (Fig. 3). The correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.9982. q_0 and b determined from the Langmuir plot were found to be 123.46 mg g^{-1} of resin and 0.065 l ng^{-1}. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L which is defined by

$$R_L = \frac{1}{1 + bC_0}$$

where b is a Langmuir constant and C_0 is the initial concentration of uranium(VI) [36]. R_L values observed between 0 and 1 indicate favourable adsorption of uranium(VI) onto SA resin (Table 3).

The Freundlich equation was also applied to the adsorption. The Freundlich equation is basically empirical but is often useful as a means of data description. It generally agrees quite well compared to Langmuir equation and experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by the equation [36]

$$\log\left(\frac{x}{m}\right) = \log K_f + \left(\frac{1}{n}\right)\log C_e$$

Table 3
Equilibrium parameter, R_L

Initial uranium(VI) concentration (mg l^{-1})	R_L value
20	0.435
40	0.278
60	0.204
80	0.161
100	0.133

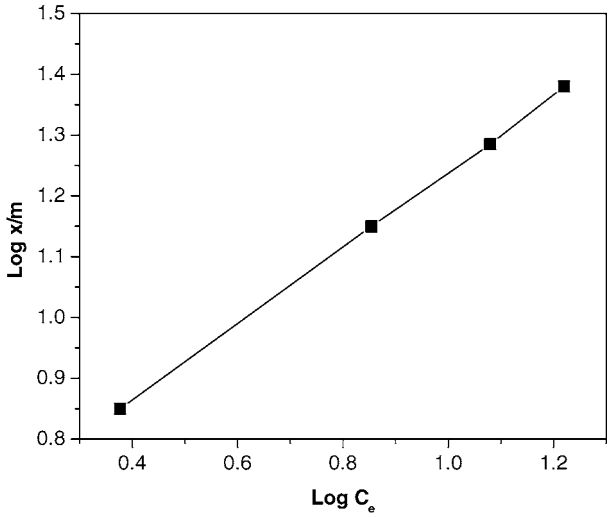


Fig. 4. Freundlich plot for the adsorption of uranium(VI). Uranium(VI) concentration: 20–100 mg l^{-1}; pH 6.5; equilibration time 60 min; adsorbent dose 2.5 g l^{-1}.

where C_e is the equilibrium concentration (mg l^{-1}) and x/m the amount adsorbed per unit mass of SA resin. A plot of $\log(x/m)$ versus $\log C_e$ (see Fig. 4) is linear and the constants K_f and n were found to be 4.24 and 1.595, respectively. The value of $1 < n < 10$ shows a favourable adsorption of uranium(VI) onto SA resin. The correlation coefficient for the Freundlich plot was found to be 0.9999 indicating a better fit of the experimental data compared to Langmuir plot.

3.8. Sorption/retention capacity

The retention capacity of SA resin was determined via batch method by equilibrating 0.05 g of the resin with 2.0 mg of uranium(VI) present in 25 ml of solution under optimum conditions established above. The amount of uranium(VI) ion needed for saturation was determined spectrophotometrically after eluting with 10 ml of 1.0 mol l^{-1} of HCl. As seen from Table 4, the sorption capacity of uranium(VI) was found to 12.3 mg g^{-1} of SPE which is higher than chelate modified SPE procedures reported in literature so far.

Table 5
Analysis of marine sediment (MESS-3) and soil (IAEA soil-7) reference materials

Sample	Weight of sample (g)	Uranium found (μg g^{-1})	
		Present method[a]	Certified value
Marine sediment	0.1	4.15 ± 0.2	4[b]
	0.2	4.10 ± 0.2	
	0.5	4.10 ± 0.2	
Soil	0.1	2.65 ± 0.1	2.60
	0.2	2.60 ± 0.1	
	0.5	2.55 ± 0.2	

[a] Average of three determinations.
[b] Information value.

3.9. Tolerance of electrolytes and diverse ions

The effect of various neutral electrolytes and diverse ions likely to be present in soil and sediment samples on the recovery of 50 μg of uranium(VI) in presence of 1.0 g each of NaF and thiourea was studied. There is no interference from 0.1 mol l^{-1} of NaCl, $NaNO_3$, Na_2SO_4, KCl, $CaCl_2$, $MgCl_2$, NH_4Cl, EDTA, NaSCN and sodium citrate and 1.0 mg amounts of Fe(III), Co(II), Ni(II), Mn(II), Zn(II), Cu(II), Cd(II), Pb(II), Al(III), Sb(III), As(V), V(V) and Mo(VI) cationic species. Further, five-fold amounts of Th(IV) do not interfere during the determination of 5 μg of uranium(VI).

3.10. Analysis of standard reference materials (Supplied by the National Research Council, Canada)

The accuracy of the developed preconcentration procedure was tested by analysing standard marine sediment (MESS-3) and soil (IAEA soil-7) reference materials. The samples were mineralized by using the dissolution procedure described in Section 2.6 and was subjected to preconcentration and determination by adopting the recommended procedure. The uranium(VI) contents established by the present procedure agree well with the certified values (see Table 5).

3.11. Analysis of soil and sediment samples

Soil sample collected from Trivandrum and sediment samples collected from Karamana river, Trivandrum and

Table 4
Comparison of sorption/retention capacities of SPE materials prepared by using various sorbents for uranium(VI)

S. no.	SPE material	Retention/binding capacity (mg g^{-1} of SPE)	Reference
1	Bicine, Amberlite XAD-4	0.90 ± 0.01	[31]
2	5,7-Dichloroquinoline-8-ol, naphthalene	1.88 ± 0.02	[32]
3	1-(2-Pyridylazo)2-naphthol, benzophenone	2.34 ± 0.02	[26]
4	Quinoline-8-ol, Amberlite XAD-4	2.74 ± 0.02	[11]
5	Azooxine ion exchanger	7.14 ± 0.01	[37]
6	*o*-Vanilline semicarbazone, Amberlite XAD-4	2.89 ± 0.02	[33]
7	Succinic acid, Amberlite XAD-4	12.33 ± 0.02	Present method

Table 6
Analysis of soil and sediment samples

S. no.	Description of sample	Uranium(VI) ($\mu g\,g^{-1}$ of sample)			Recovery (%)
		Added	Found		
			Present method[a]	ICP-MS	
1	Soil sample, Trivandrum	–	7.14 ± 0.2	6.96 ± 0.01	–
		7.00	14.14 ± 0.3		101.4
		14.00	21.15 ± 0.5		100.1
2	Karamana river sediment, Trivandrum	–	8.00 ± 0.2	8.22 ± 0.01	–
		8.00	16.05 ± 0.4		100.6
		16.00	24.10 ± 0.5		100.6
3	Marine sediment, Arabian sea, Trivandrum	–	4.76 ± 0.2	4.96 ± 0.01	–
		5.00	9.75 ± 0.2		99.8
		10.00	14.80 ± 0.3		100.4

[a] Average of three determinations.

Arabian sea, Trivandrum was subjected to dissolution, preconcentration and determination using the recommended procedure described in Section 2.6. The results obtained by the present method agree well with standard inductively coupled plasma-mass spectrometric (ICP-MS) values (see Table 6). Thus, the SPE preconcentration method developed in the present paper enables simple and low cost instrument like colorimeter to analyze soil and sediment samples containing trace and ultratrace amounts of uranium(VI).

4. Comparison with other methods

The SA resin exhibits highest preconcentration factor for uranium (∼100) compared to Amberlite XAD-4 bicine (∼50) [31], Amberlite XAD-2 pyrogallol (∼70) [29] and Amberlite XAD-4 quinoline-8-ol (∼40) [11]. Further more, the sorption capacity of SA resin is much higher compared to above two resins and also Amberlite XAD-4 *o*-vanillin semicarbazone [33] (see Table 1). Again, the present procedure finds application to real soil and sediment samples unlike Amberlite XAD-4 *o*-vanillin semicarbazone which has been tested only for simulated river water samples [33]. The impregnated *N*,*N*-dibutyl-*N*′-benzoyl thiourea-Amberlite XAD-16 resin is beset with ligand leaching problems [38]. Two recent papers on chemical immobilization of uranium(VI) concerns with the use of *N*-tripropionate (or *N*-triacetate)-substituted tetraazamacrocycles-silica gel [39] and calixarene-semicarbazone [40] involve tedious synthesis with high cost reagents unlike in the present paper.

5. Conclusions

The SPE procedure developed in this paper using SA resin facilitates a 100-fold enrichment of uranium(VI) from dilute aqueous solutions. This SPE has good potential for its separation of uranium(VI) from host of co-existing alkali, alkaline earth, transition and heavy metal ions. The proposed method is simple and the sorption capacity of the functionalized resin ($12.33\,mg\,g^{-1}$) is much higher than other SPE materials as seen from Table 4. Equilibration is fast as 80–90% of uranium(VI) is sorbed within 5 min of equilibration making the analytical procedure reasonably fast. Again, the SA resin has high mechanical and chemical strength, as it is unaffected even after 25 cycles. In addition, the resin offers reliable analysis of uranium(VI) in soil and sediment samples using simple instrument like colorimeter. The recoveries of uranium(VI) are nearly quantitative (>98%). The R.S.D. is 2.56% which is also a distinct advantage. Flow injection analysis studies are in progress by packing the SA resin beads in home made micro columns.

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