

## *p*-tert-Butylcalix[8]arene loaded silica gel for preconcentration of uranium(VI) via solid phase extraction

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**Abstract** This paper reports silica gel loaded with *p*-tert-butylcalix[8]arene as a new solid phase extractor for determination of trace level of uranium. Effective extraction conditions were optimized in column methods prior to determination by spectrophotometry using arsenazo(III). The results showed that U(VI) ions can be sorbed at pH 6 in a mini-column and quantitative recovery of U(VI) (>95–98%) was achieved by stripping 0.4 mol L<sup>-1</sup> HCl. The sorption capacity of the functionalized sorbent is 0.072 mmol uranium(VI) g<sup>-1</sup> modified silica gel. The relative standard deviation and detection limit were 1.2% (*n* = 10) for 1 μg uranium(VI) mL<sup>-1</sup> solution and 0.038 μg L<sup>-1</sup>, respectively. The method was employed to the preconcentration of U(VI) ions from spiked ground water samples.

**Keywords** *p*-tert-Butylcalix[8]arene · Preconcentration · Uranium(VI) · Solid phase extraction

### Introduction

Adsorption of metals from water onto a chelating adsorbent is a powerful means of selective concentration of traces of the metals with a high concentration factor [1]. By passing a water sample through a column packed with an appropriate adsorbent, the desired metals are effectively collected on the column. The collected metals are subsequently desorbed

with a small volume of eluent for determination by instrumental analytical methods. For this purpose, a wide variety of chelating adsorbents have been prepared by loading or chemically modifying solid supports with selective chelating agents [2–7]. Uranium is extensively used in the nuclear industry and is highly radioactive. The maximum uranium concentration in drinking water and seawater also is reported less than 9 μg L<sup>-1</sup> and 1–3 ng mL<sup>-1</sup>, respectively [8]. Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of metalion in water samples [9, 10] along with that in plants, soils and rocks. There has been many methods to determine uranium U(VI) with different types of chelating resins, activated carbon, silica gel and textile [11–19]. Silica gels loaded or immobilized with organic functionalities have been mostly used in separation and preconcentration of trace metal ions from aqueous solutions. In recent times, various silica gel sorbents modified with many kinds of chelating agents have been used for enrichment of uranium(VI) from aqueous systems [8, 17–22].

Calixarenes because of their well-defined frame and chemically stable intermolecular cavity of tunable size and coordination selectivity are frequently selected as host molecules in separation sciences [23]. For solid phase extraction of U(VI), polymeric calixarenes can play a dominant role [14, 24–27]. Also, calixarenes have been used for extraction of uranium, cesium and technetium from various matrices by liquid–liquid extraction [28, 29]. There is no report using *p*-tert-butylcalix[8]arene for preconcentration of U(VI).

This work is dealt with preparation and evaluation of sorption properties of *p*-tert-butylcalix[8]arene loaded silica gel as a new solid phase sorbent for preconcentration of uranium(VI) from water samples.

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## Experimental

### Materials and methods

#### Chemicals and reagents

The stock metal ion solutions were prepared by dissolving analytical reagent-grade metal nitrates, chlorides, carbonates or sulfates in doubly deionized water. Stock solution of U(VI) was prepared by dissolving an appropriate amount of  $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in water. A 0.1% Arsenazo III solution was prepared in deionized water. Potassium bromide (Merck, for spectroscopy) was used for the preparation of pressed discs for the Fourier Transform Infrared (FT-IR) spectrometer. All other reagents and solvents used were of analytical reagent grade. The water used throughout the study had been deionized by means of a Millipore Milli-Q system. The silica sorbent (styrene–divinylbenzene copolymer, surface area:  $800 \text{ m}^2 \text{ g}^{-1}$ , pore diameter: 10 nm and bead size: 20–60 mesh) was supplied by Sigma. For purification, silica gel was washed with  $4 \text{ mol L}^{-1}$  HCl solution, and filtered, then for elimination of chlorides washed with distilled water, with an ethanol–water (1:1) solution and finally with water again. Then, the silica gel was dried in vacuum oven at  $60 \text{ }^\circ\text{C}$  and stored in a polyethylene bottle.

#### Apparatus

FT-IR spectra of silica gel, *p*-tert-butylcalix[8]arene and *p*-tert-butylcalix[8]arene impregnated silica gel were recorded with a Perkin Elmer Spectrum BX Fourier Transform IR spectrometer using KBr discs in the range of  $4000\text{--}700 \text{ cm}^{-1}$ , 30 co-added interferograms were scanned at  $2 \text{ cm}^{-1}$  resolution. Shimadzu UV-1601 model UV spectrometer was used for the determination of uranium(VI) contents of all the solutions. pH measurements were made on a Lab WTW model digital pH-meter. For solid phase experiments a Varian cartridge (plastic container,  $0.8 \text{ cm} \times 6.2 \text{ cm}$ ) equipped with polypropylene frits were used.

#### Preparation of sorbent and column

Hundred milligram of *p*-tert-butylcalix[8]arene was dissolved in 20 mL of tetrahydrofuran–toluene (1:9) in a 50 mL of reaction flask. Then, 2 g of dry silica gel was added to solution and stirred for 24 h at room temperature. The solid was separated by filtration through a sintered glass funnel and washed with a water to remove the solvent. The sorbent was used as an air-dried product. The amount of *p*-tert-butylcalix[8]arene loaded silica gel was found to be  $0.077 \text{ mmol g}^{-1}$ .

This prepared sorbent was transferred to the polyethylene column and 10 mL of methanol and then 10 mL of

water was passed through the column. Before passing metal solution, column was washed with 5 mL of suitable working pH solution. Tygon<sup>®</sup> tubing was used to connect the outlet tip of the syringe barrel to a Watson Marlow peristaltic pump. This conditioning was repeated for each column before the application.

#### Column process

A 50–250 mL solutions containing uranium(IV) in the range of  $0.5\text{--}2.5 \text{ } \mu\text{g mL}^{-1}$  was passed through a mini-column packed with 100 mg of the sorbent at a flow rate of  $1.5 \text{ mL min}^{-1}$ . The U(VI) ion was eluted from the column by 5 mL of  $0.4 \text{ mol L}^{-1}$  HCl at a flow rate of  $1 \text{ mL min}^{-1}$ . After sorption and desorption steps, U(VI) ion concentrations in the filtrates were determined by spectrophotometer using Arsenazo III. The absorbance of arsenazo III complex of U(VI) was measured at 652 nm against the reagent blank solution.

## Results and discussion

### Characterization of sorbent

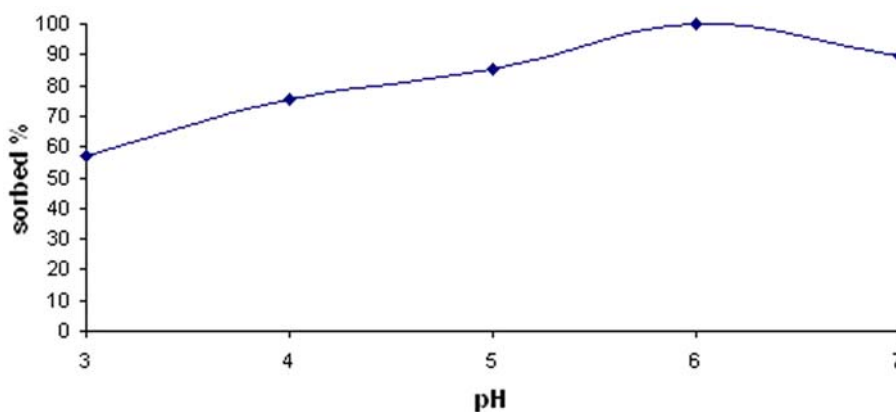
Infrared spectrum of *p*-tert-butylcalix[8]arene, silica gel and *p*-tert-butylcalix[8]arene impregnated silica gel have been recorded. The IR absorption frequencies assignments for calix[8]arene/silica gel sorbent show small modifications on the characteristic normal modes compared with the spectrum of the silica gel. The OH stretching vibration at  $3225 \text{ cm}^{-1}$  for calixarene and  $3444 \text{ cm}^{-1}$  for silica gel shifts to  $3450 \text{ cm}^{-1}$  in impregnated silica gel. The C–H stretching vibrations at  $2956 \text{ cm}^{-1}$  and  $2869 \text{ cm}^{-1}$  were observed in the calixarene loaded sorbent.

### Effect of pH and flow rate on metal sorption

Extraction experiments were carried out to determine the optimum pH for quantitative recovery of uranium(VI). The effect of pH on the extraction of U(VI) was studied in the range of 3–7 (Fig. 1). The pH of the solution was adjusted to the desired pH by addition of  $0.1\text{--}1.0 \text{ mol L}^{-1}$  sodium hydroxide and/or nitric acid. The sorption experiments were carried out in triplicate. Sorption was quantitative ( $\geq 95\text{--}98\%$ ) around pH 6. In lower pH medium ( $\leq 3$ ), the sorption of uranium(VI) was low because of the competing of hydronium ions with the uranyl ions for the adsorption sites. At higher pH, uranium becomes increasingly hydrolyzed and forms oligomeric species [30]. For further studies, U(VI) solutions at pH 6 were mostly preferred.

The contact between the metal ion in sample solution and the sorbent is depended on the flow rate of sample

**Fig. 1** Effect of pH on the sorption of U(VI) on *p*-tert-butylcalix[8]arene/silica gel



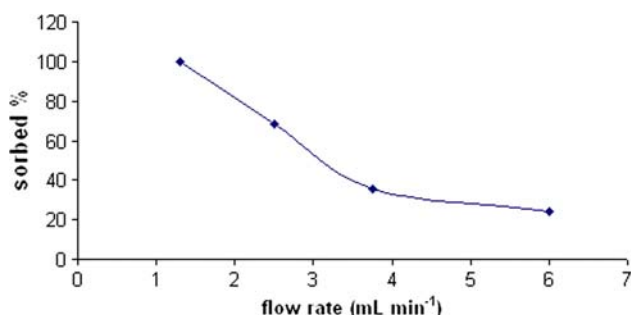
solution. Aliquots of 50 mL of  $1 \mu\text{g U(VI) mL}^{-1}$  solutions at pH 6 were separately passed at different flow rates ( $1\text{--}6 \text{ mL min}^{-1}$ ) through the column having 0.1 g of *p*-tert-butylcalix[8]arene/silica gel (Fig. 2). A U(VI) ion was sorbed completely at a flow rate of  $1.5 \text{ mL min}^{-1}$  with a good precision.

#### Sorption capacity of modified silica gel

In order to show the applicability of *p*-tert-butylcalix[8]arene physically bound to silica gel for the preconcentration of U(VI) ion, the sorption of U(VI) was investigated using the batch method. A 25 mL of  $100 \mu\text{g mL}^{-1}$  of U(VI) solution was stirred with 100 mg of sorbent at room temperature for 2 h to determine the sorption capacity of immobilized silica gel. Maximum uranium(VI) sorption capacity was found as  $0.072 \text{ mmol U(VI) g}^{-1}$  modified silica gel which is 10 times higher than calix[6]arene modified textile [16]. This indicates that *p*-tert-butylcalix[8]arene/silica gel could be used as a sorbent for preconcentration of U(VI) in the trace concentration range.

#### Elution studies

The experiments were carried out to choose the proper eluent for the elution of sorbed uranium(VI) ion from



**Fig. 2** Effect of sorption flow rate on the sorption of U(VI) on *p*-tert-butylcalix[8]arene/silica gel

loaded silica gel. The U(VI) ions were desorbed using various concentrations ( $0.1\text{--}2 \text{ mol L}^{-1}$ ) of HCl and  $\text{HNO}_3$ . From the data given in Figs. 3 and 4, it is clearly seen that  $0.4 \text{ mol L}^{-1}$  HCl could accomplish the quantitative elution of U(VI) from the modified silica gel. Also, the volume of eluent was controlled and 5 mL of  $0.4 \text{ mol L}^{-1}$  HCl was completely desorbed uranyl ions from the column.

#### Tolerance of diverse ions

The effect of some electrolytes of NaCl,  $\text{NaNO}_3$ , KCl and  $\text{KNO}_3$  on quantitative extraction of  $1.0 \mu\text{g mL}^{-1}$  U(VI) using the recommended column method under optimum conditions were studied in the concentration range of  $0.001\text{--}1.0 \text{ mol L}^{-1}$ . The results show that no significant effect on sorption of U(VI) ions at studied concentrations. Effect of some transition ions and some anions on sorption of U(VI) in binary solution of uranyl ion with interfering ions were also investigated. Each ion was considered to be an interferent when it caused an error greater than  $\pm 5\%$  in the determination of uranyl ion. The relevant data is presented in Table 1.

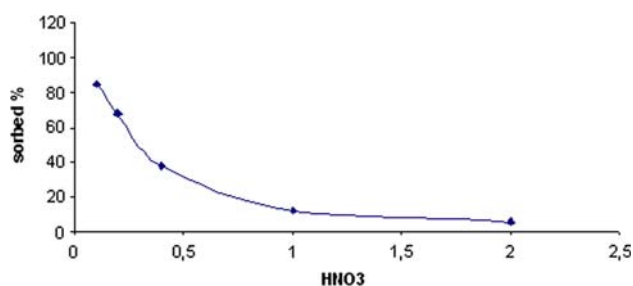
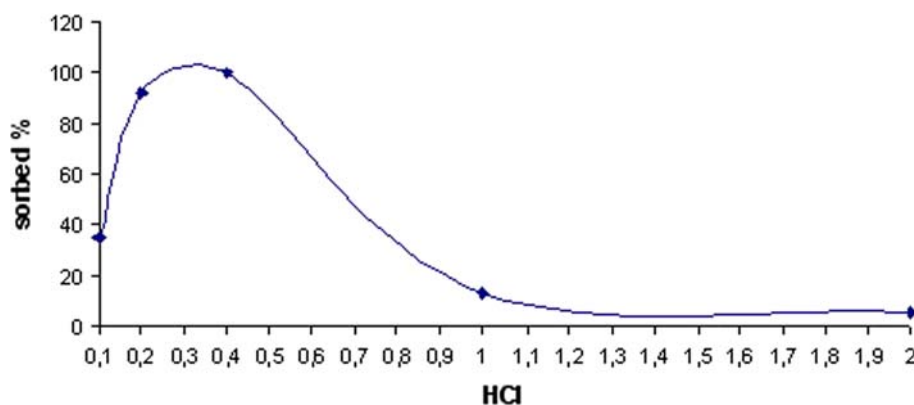
#### Reusability and stability of the modified sorbent

The reproducibility and reliability in analytical data on subsequent reusage was investigated by equilibrating 100 mg loaded silica gel with U(VI) solution ( $50 \text{ mL}$ ,  $1 \mu\text{g mL}^{-1}$ ) under optimized sorption conditions. After desorption, the sorbent was washed with distilled water to remove acid and condition the sorbent. The results obtained on subsequent reusage of the same sorbent were reproducible up to 15 cycles, reflecting on its high mechanical stability and reusability nature.

#### Analytical performance

In order to study the adsorptive capacity of *p*-tert-butylcalix[8]arene loaded silica gel, batch method was used. A

**Fig. 3** Elution with different concentration of HCl. Conditions: U(VI): 1 mg L<sup>-1</sup>; sample volume: 100 mL (pH 6); eluent: 5 mL; flow rate: 1.5 mL min<sup>-1</sup>



**Fig. 4** Elution with different concentration of HNO<sub>3</sub>. Conditions: U(VI): 1 mg L<sup>-1</sup>; sample volume: 100 mL (pH 6); eluent: 5 mL; flow rate: 1.5 mL min<sup>-1</sup>

**Table 1** Tolerance limits for anions and cations on the sorption of U(VI) (1 μg mL<sup>-1</sup>) on the *p-tert*-butylcalix[8]arene/silica gel

| Interfering ion               | Tolerance limit (mol L <sup>-1</sup> /μg mL <sup>-1</sup> ) <sup>a</sup> |
|-------------------------------|--|
| NO <sub>3</sub> <sup>-</sup>  | 0.1  |
| Cl <sup>-</sup>               | 1  |
| PO <sub>4</sub> <sup>3-</sup> | 0.01   |
| SO <sub>4</sub> <sup>2-</sup> | 0.1  |
| CO <sub>3</sub> <sup>2-</sup> | 0.001  |
| Cu <sup>2+</sup>              | 20   |
| Pb <sup>2+</sup>              | 5  |
| Mn <sup>2+</sup>              | 20   |
| Co <sup>2+</sup>              | 20   |
| Th <sup>4+</sup>              | 5  |

<sup>a</sup> Unit for anion (mol L<sup>-1</sup>), for cations (μg mL<sup>-1</sup>)

0.1 g sorbent was added to 50 mL of solution containing 1.0 μg of uranium(VI) ion at pH 6.0. The capacity of sorbent for U(VI) ion was found as 0.072 mmol g<sup>-1</sup>. The relative standard deviations for spectrometric determination of U(VI) was 1.2%. The limits of detection (LOD) of the proposed method for the determination of U(VI) was studied by passing 100 mL of blank solutions from the column under the optimal experimental conditions. The limit of detection (LOD) calculated based on 3 s/slope of 10 measurements of the blank sample, respectively, where s is the standard

**Table 2** Determination of U(VI) in ground water samples

| Real samples <sup>a</sup> | Added (μg 100 mL <sup>-1</sup> ) | Found (μg 100 mL <sup>-1</sup> ) | Recovery (%) |
|---------------------------|----------------------------------|----------------------------------|--------------|
| Ground water 1            | 0                                | ND                               | 96.8         |
|                           | 100                              | 96.8 ± 1.7                       |              |
| Ground water 2            | 0                                | ND                               | 98.7         |
|                           | 100                              | 98.7 ± 2.4                       |              |
| Ground water 3            | 0                                | ND                               | 94.9         |
|                           | 100                              | 94.9 ± 1.6                       |              |

ND not detected

<sup>a</sup> Based on values obtained on triplicate analysis

deviation of the blank solution was 0.038 μg U(VI) mL<sup>-1</sup>. In order to check the accuracy of the proposed method, the recovery for 1.0 μg U(VI) mL<sup>-1</sup> added to 100 mL of ground water was measured (Table 2). Good agreement was obtained between the added and found analyte content. The recovery was found as ≥95–98%.

### Applications

To check the ability of the proposed method for preconcentration and determination of uranium(IV), the sorbent was subjected to ground water samples from Eagean region, Turkey. The amount of sample used was always 100 mL. The results in Table 2, indicate that an agreement between the amounts of spiked and detected by the proposed method.

### Conclusion

This study investigated the use of *p-tert*-butylcalix[8]arene loaded on silica gel for the sorption of uranium(VI) from aqueous solutions. The reusability of immobilized silica gel was more than 15 cycles without any loss in its sorption behavior. The SPE method has a good potential for the

separation of uranium(VI) ion from co-existing electrolytes and some of transition metal ions. By this proposed sorbent, separation and preconcentration of uranium(VI) from large sample volume could be possible. The method was applied for the determination uranyl ion in spiked ground water samples and found accurate and precise.

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