

## Solid phase extraction using silica gel modified with murexide for preconcentration of uranium (VI) ions from water samples

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### ABSTRACT

Murexide was chemically bonded to silica gel surface immobilized 3-aminopropyl trimethoxysilane (APMS) to produce the new sorbent. A solid phase extraction method using the new sorbent has been developed to separate and concentrate trace amount of uranium (VI) from aqueous samples for the measurement by spectrophotometry method using Arsenazo III reagent. The influences of some analytical parameters on the quantitative recoveries of the analyte were investigated both in batch and column methods. Quantitative recovery of U(VI) was achieved by stripping with  $0.1 \text{ mol L}^{-1}$  HCl. The maximum sorption capacity of the modified silica gel was  $1.13 \text{ mmol g}^{-1}$  U(VI). A high preconcentration factor value of 400 with a lower limit of detection of  $1 \mu\text{g L}^{-1}$  was obtained for U(VI). The practical applicability of the developed sorbent was examined using synthetic and real samples such as sea/ground water samples.

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### 1. Introduction

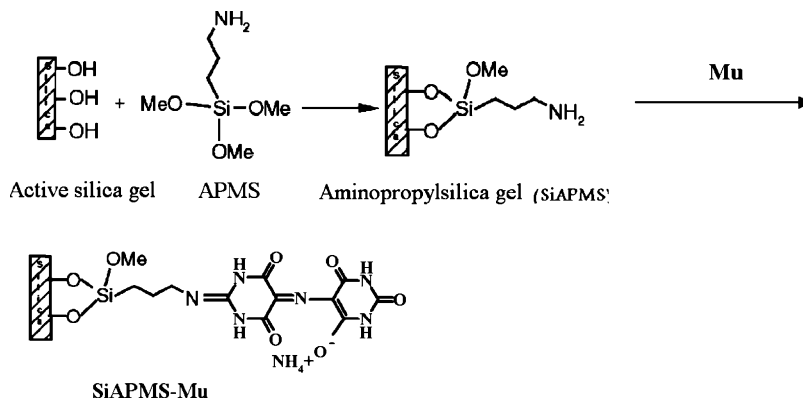
There is high interest for new separation techniques which selectively extract metal ions from dilute water and waste water samples. Although a variety of methods such as precipitation, solvent extraction, electrolysis and ion exchange can be used to remove dissolved metals from aqueous samples, most of them have disadvantages of non economic, poor removal efficiency, high cost, generation of secondary pollution and ineffectiveness for low metal concentrations [1].

Solid phase extraction (SPE) has commonly been used as a technique for preconcentration/ separation of various inorganic and organic species. SPE is used to enhance the selectivity and sensitivity of the method as it allows for discriminatory binding of analyte to a solid support where it will be accumulated and subsequently eluted with a small volume of solvent. This technique has advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, environment friendly, flexibility and easier incorporation into automated analytical techniques [2–5]. Selectivity of the solid phase sorbent towards an analyte depends on the structure of the immobilized organic ligands.

Uranium is extensively used in the nuclear industry and is highly radioactive. It is present in low quantities in wash streams

coming out of nuclear reactors both in aqueous as well as non aqueous medium and monitoring of these streams for the presence of uranium in high activity content is essential. The maximum uranium concentration in drinking water and seawater also is reported less than  $9 \mu\text{g L}^{-1}$  and  $1\text{--}3 \text{ ng mL}^{-1}$ , respectively [6]. This extreme dilution in the presence of relatively high concentration of other ions makes it difficult to determine directly uranium ions and refined analytical methods must be employed to detect small concentrations. For this purpose, new sorbent materials such as polymeric resins, activated carbon, naphthalene and silica gel have been developed for more effective extraction. However, some of the sorbents suffer from a number of drawbacks such as long preconcentration time, low mechanical stability of the sorbent, slow kinetics, irreversible adsorption of target and swelling [7–17]. So, there is still a need for developing good sorbent for U(VI) ions. Silica gels modified with both inorganic and organic functionalities have been most commonly used in various areas, notably in separation and preconcentration of trace metal ions from aqueous systems since immobilization reactions on silica are relatively simple and show fast kinetics in metal ions uptake [18–24]. Recently, a number of silica gel sorbents functionalized with a variety of chelating ligands have been synthesized for preconcentration of U(VI) from aqueous solutions [25–29]. Some of the reported chemically modified sorbents are those containing ligands with oxygen and nitrogen donors involved in U(VI) chelation forming for selective extraction of U(VI) from various matrix components. Murexide (Mu, the ammonium salt of purpuric acid) is a dark red reagent, and soluble in water which is used as an indicator in

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**Scheme 1.** Proposed route for preparation of SiAPMS–Mu adsorbent.

complexometric titrations. Complexation of Mu with the alkaline, alkaline earth and transition cations had been studied [30–32]. To the best of our knowledge, there is no report on complexation of Mu with U(VI) ions or immobilization on the surface of silica gel. Therefore, this work is devoted to the preparation and the evaluation of the sorption properties of silica gel modified with murexide (SiAPMS–Mu) as a new solid phase extractor for preconcentration of U(VI) from aqueous samples.

## 2. Experimental

### 2.1. Chemicals and reagents

Reagent grade of uranyl acetate,  $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , was obtained from Fluka. Extra pure silica gel with particle size 70–230 mesh and 60 Å pore diameter purchased from Merck. All reagents and solvents used were of analytical reagent grade and were provided from Merck. Buffer solutions were prepared by using 0.01 mol L<sup>-1</sup> sodium acetate–acetic acid (pH 3–6) or ammonium acetate (pH 7–8) and the pH of the resulting solutions was adjusted by the use of pH meter. Stock solution of U(VI) was prepared by dissolving an appropriate amount of uranyl acetate in buffer. All aqueous solutions were prepared in doubly distilled water.

### 2.2. Apparatus

The pH measurements were conducted by a corning 125 pH-meter. The UV–vis spectra were recorded using Shimadzu 2501 PC spectrophotometer. The IR spectra were obtained using KBr pellets by PerkinElmer 781 IR-spectrophotometer. A Shimadzu flame atomic absorption spectrophotometer (FAAS) model 6300 was used for determination of some transition metals as interfering ions.

### 2.3. Preparation of the murexide modified silica gel

The procedure for preparation of the new sorbent includes three steps as follows: In the first step, activation of 50.0 g silica gel surface was accomplished by reflux in 6.0 mol L<sup>-1</sup> hydrochloric acid for 24 h, filtered and repeatedly washed with doubly distilled water till acid free filtrate and finally dried in an oven at 160 °C for 8 h.

In the second step, 40.0 g of the activated silica gel was suspended in 400 mL of dry toluene containing 45 mL of 3-aminopropyltrimethoxy silane (APMS) as silylating reagent and refluxed for 12 h. At the end of this period, the modified silica gel (SiAPMS) was filtered off, washed with toluene, ethanol and diethyl ether, respectively, to eliminate possible trace amounts of the reagent and dried at 70 °C for 6 h.

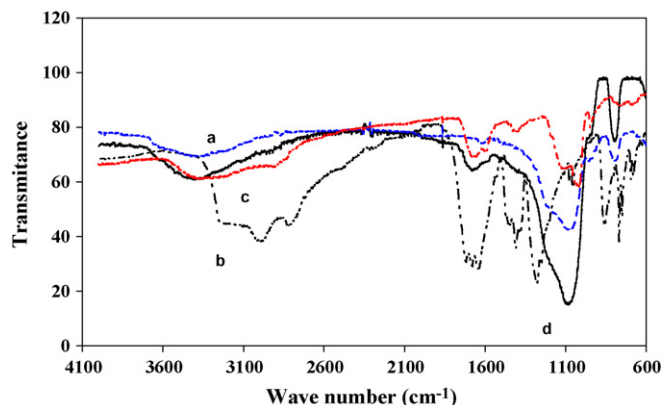
In the last step, silica gel bounded murexide was prepared by mixing 30 g of dry SiAPMS with 30 mmol of Mu already dissolved in 300 mL of dimethyl sulfoxide (DMSO) and the reaction mixture was refluxed for 24 h. The resulting product was filtered, washed with DMSO and water several times until the filtrate showed no trace color of adsorbed Mu. The resulting brown sorbent (SiAPMS–Mu) was then dried at 80 °C for 6 h. The preparation route to SiAPMS–Mu can be proposed in Scheme 1.

### 2.4. Analytical procedure

#### 2.4.1. Batch method

The stability of the SiAPMS–Mu in different buffer solutions (pH 2–8) was investigated by the batch equilibrium technique in order to identify the degree of hydrolysis or possible leaching of the sorbent. In this procedure, 500 mg of the SiAPMS–Mu was mixed with 100 ml of the selected buffer solution (pH 2–8) and automatically shaken for 2 h. The mixture was filtered off, washed with the same buffer and doubly distilled water, respectively, and dried in an oven at 70 °C. To determine the uptake of U(VI), 100 mg of the treated SiAPMS–Mu was added to a solution of 100 ml of 135 μg mL<sup>-1</sup> of U(VI) at pH 5.5. The percentage of hydrolysis of SiAPMS–Mu at various pH was calculated from μmol g<sup>-1</sup> value of treated sorbent.

For sorption study, a sample solution containing 2.7 μg mL<sup>-1</sup> of U(VI) in a volume of 10–100 mL was taken and its pH was adjusted to 5.5 by acetate buffer. Then, 100 mg of the SiAPMS–Mu was added to the above solution in a polyethylene bottle and was shaken mechanically for 15 min. The amount of U(VI) adsorbed was estimated by the difference between the initial concentration in aqueous solution and that found in the supernatant spectrophotometer.



**Fig. 1.** IR spectra of silica gel (a), Mu (b), APMS–Mu (c) and SiAPMS–Mu (d).

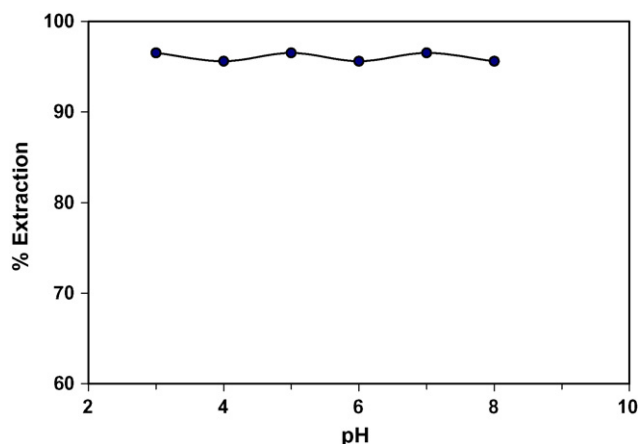


Fig. 2. Stability of SiAPMS–Mu in different buffer solutions determined by  $\mu\text{mol g}^{-1}$  value of the sorbent.

metrically using Arsenazo III reagent after the addition of 4.0 mL of 1:1 HCl, 0.3 g Zn powder and then 0.5 mL of 0.01% Arsenazo III in a total volume of 10.0 mL. The absorbance of Arsenazo III complex of U(IV) was measured at 664 nm against the reagent blank solution.

#### 2.4.2. Column method

The polyethylene syringe ( $25.0 \times 9.0$  mm) was packed with 100 mg of SiAPMS–Mu and washed with 5 mL of acetate buffer at pH 5.5. A sample solution containing 135  $\mu\text{g}$  of U(VI) in a volume of 100–1000 mL was taken and its pH was adjusted to 5.5. The sample was passed through the column at a flow rate of  $10 \text{ mL min}^{-1}$  by means of a peristaltic pump. The adsorbed U(VI) ions were stripped from the minicolumn by using 2.5 mL of  $0.1 \text{ mol L}^{-1}$  HCl at a flow rate of  $0.5 \text{ mL min}^{-1}$  and were subjected to spectrophotometric determination by Arsenazo III reagent as described in Section 2.4.1. The procedure was repeated with untreated silica gel and no selectivity in sorption of U(VI) ions was detected.

The influence of the sample loading flow rate on the preconcentration of U(VI) was studied in order to examine whether the interaction of the analyte with 100 mg of SiAPMS–Mu was fast enough in column method. When the concentration of U(VI) ion

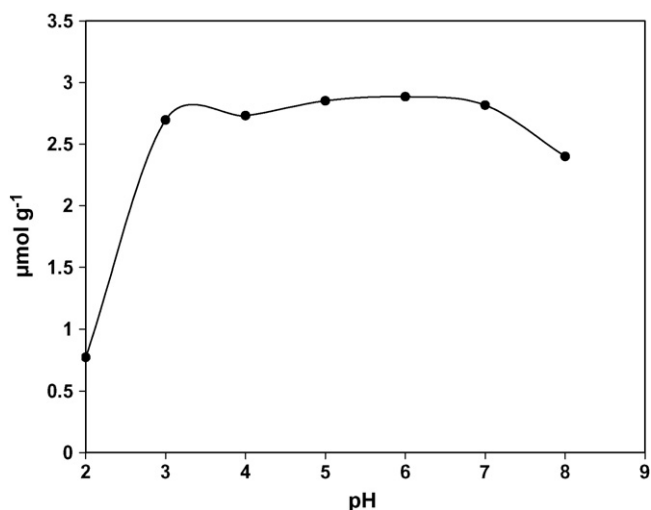


Fig. 3. Influence of pH of sample solution on uptake capacity of sorbent (experimental conditions; batch method: 100 mL of  $1.35 \mu\text{g mL}^{-1}$  U(VI) ion, 100 mg sorbent, 15 min).

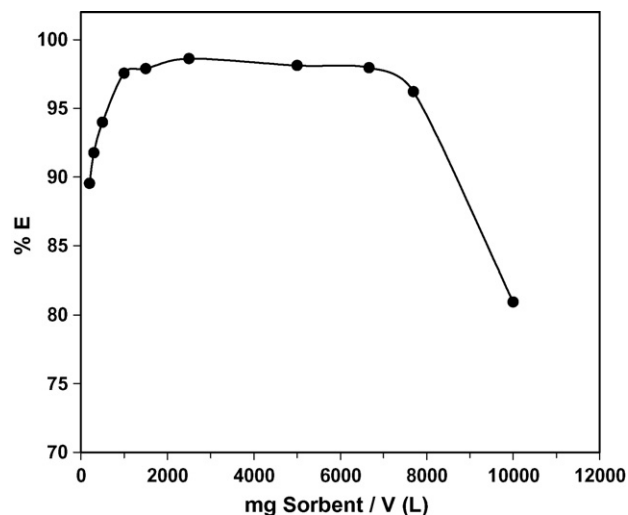


Fig. 4. Effect of amount of sorbent to volume of sample ratio on extraction of U(VI) ions in batch method ( $1.35 \mu\text{g mL}^{-1}$  U(VI) ion; 15 min).

solution ( $2.7 \mu\text{g mL}^{-1}$  at pH 5.5) and the minicolumn containing 100 mg of the sorbent were kept constant, flow rate of sample loading was changed from 2.0 to  $15.0 \text{ mL min}^{-1}$ . The sorbed ions were then eluted with 5.0 mL of  $0.1 \text{ mol L}^{-1}$  HCl at a flow rate of  $0.5 \text{ mL min}^{-1}$ .

For quantitative desorption of U(VI) from the column, the effect of HCl concentration was also studied. HCl was selected as stripping agent because most of the analytical procedures for preconcentration and separation of metal ions from environmental samples are performed in this medium. For this study, different acid concentrations were examined in the range of  $0.05$ – $2.0 \text{ mol L}^{-1}$ . Similarly, the dependence of desorption of U(VI) at varying volume of the eluent was studied in the range of 2.5–10.0 mL at optimum acid concentration.

### 3. Results and discussion

#### 3.1. Spectral study

The modification of silica gel surface with Mu is suggested based on the elimination of a  $\text{H}_2\text{O}$  molecule from the SiAPMS and Mu to form the C=N bond which was confirmed from the IR analysis. Comparing the IR spectrum of Mu–APMS with that of Mu (Fig. 1) showed the absence of a band due to amino group which should be appeared at  $3300 \text{ cm}^{-1}$ . Furthermore, the formation of C=N band due to azomethane group as a weak peak appeared at  $1435 \text{ cm}^{-1}$  which overlaps with vibration frequency of C=O group. The band corresponding to the asymmetric N=N vibration of stretching mode near  $1600 \text{ cm}^{-1}$  was not detected as it merged with strong C=C ring vibration. Also, Mu presented bands in the range of  $1650$ – $1700 \text{ cm}^{-1}$  indicating the C=O asymmetric stretching vibration modes that after reaction with U(VI) ions shifted to  $1796 \text{ cm}^{-1}$  [33,34]. Consequently, the bonding of Mu to aminopropyl group is suggested to occur via the displacement of nitrogen in propylamine substrate for oxygen in Mu.

Interaction of U(VI) ion with Mu in aqueous solution was also investigated by UV–vis spectrophotometry. On complexation of U(VI) with Mu, the strong specific absorption of Mu ( $\lambda_{\text{max}}$  538 nm) shifts toward shorter wavelength ( $\lambda_{\text{max}}$  490 nm). Moreover, the existence of a well defined isosbestic point in the spectrum of Mu upon addition of U(VI) ions at 520 nm is an indication for a simple complexation equilibrium.

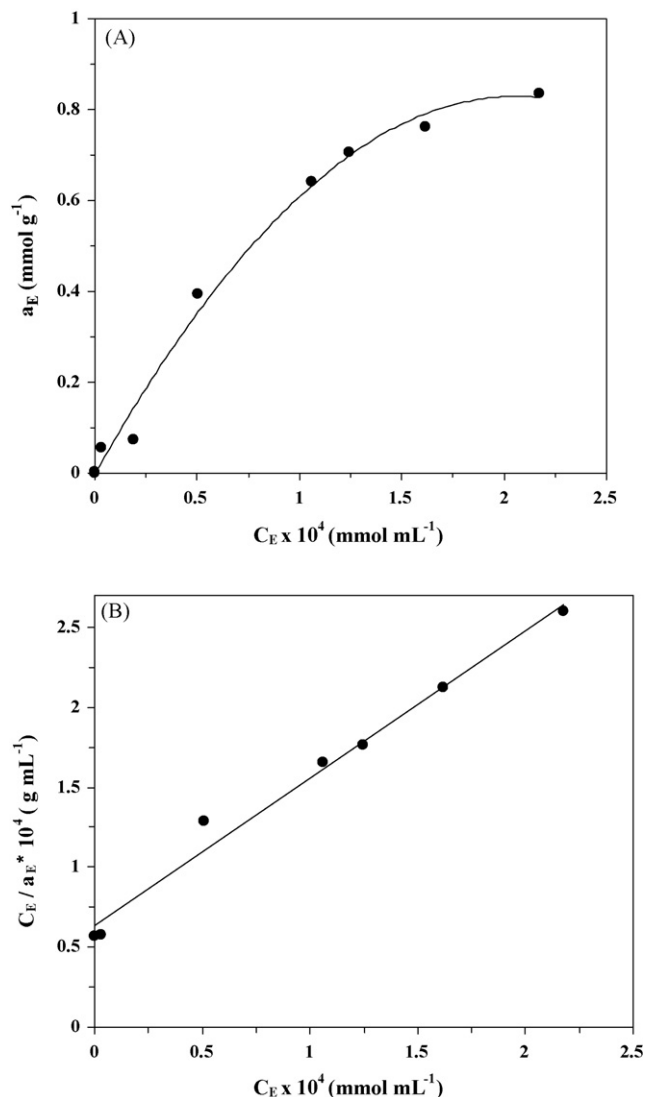


Fig. 5. (A) Adsorption isotherm of U(VI) ions from aqueous solution on the surface of SiAPMS-Mu at pH 5.5 and (B) the linearized form of the Langmuir adsorption isotherm.

SiAPMS and SiAPMS-Mu are white and pale brownish in color, respectively. Upon addition of the U(VI) ions solution to the SiAPMS-Mu, the color of sorbent changed drastically from pale to dark brownish. The interaction of U(VI) ions with the Mu is mainly based on direct complex formation according to the presence of oxygen donor atoms as well as nitrogen bridge atom in Mu. The above points evidenced the functionalization of silica gel with Mu.

### 3.2. U(VI) extraction studies by batch method

#### 3.2.1. Effect of pH

The stability of modified silica gel was performed in different buffer solutions in order to assess the possible leaching or hydrolysis process. The results of this study are shown in Fig. 2 indicating at the pH range of 3–8, only 0–2% hydrolysis of SiAPMS-Mu was occurred which proved that the chemically immobilized silica gel is resistant to the studied pH.

In the solid phase extraction for U(VI) ions enrichment based on chelation, the pH value of the sample solution is an effective factor for quantitative adsorption of the analyte due to the competitive reactions with chelate forming groups in sorbent and hydrogen

ions in solution. To find the optimum pH value of sample, 100 mg of the sorbent was equilibrated with U(VI) ion solutions (100 mL, 2.7  $\mu\text{g mL}^{-1}$ ) with various pH 2–8 for 2 h. U(VI) ion concentration was estimated from the amount of the left U(VI) ions in the supernatant which was analyzed spectrophotometrically by Arsenazo III. The results in Fig. 3 showed that the most uptake of U(VI) ion occurred in the pH range of 5.0–6.0. Lowering the pH value of the U(VI) solution decreased the uptake capacity of the sorbent due to the electrostatic repulsion of the protonated active sites on the sorbent with the positively charged uranyl species. At higher pH values, the uranyl ion may hydrolyze to form species such as  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  [35].

#### 3.2.2. Effect of time

The rate of adsorption of U(VI) by SiAPMS-Mu was studied (100 mL, 2.7  $\mu\text{g mL}^{-1}$ ) with 100 mg of the sorbent over a series of varying shaking time (5–120 min). The results showed that the percentage extraction of U(VI) at any shaking time was higher than 98%, but 15 min was used in all subsequent experiments for quantitative sorption of U(VI) at higher concentrations.

#### 3.2.3. Effect of amount of sorbent and sample volume

Effects of the amount of SiAPMS-Mu (20–150 mg) and the sample volume (10–500 mL) on the uptake of uranyl ion were investigated. The results were expressed in terms of ratio of the weight of the sorbent to the sample volume. It is evident from Fig. 4 that 100 mg of SiAPMS-Mu was necessary for quantitative sorption of U(VI) in 100 mL solution.

#### 3.2.4. Capacity of sorbent

For investigation of adsorption of U(VI) ions in solution, the same volume (100 mL) of U(VI) ion solution with different concentrations of U(VI) ions (1.35–217  $\mu\text{g mL}^{-1}$ ) at pH 5.5 was equilibrated for 2 h. The sorption capacity ( $a_E$ , mmol g<sup>-1</sup>) was calculated as:

$$a_E = (C_0 - C_E) V m^{-1} \quad (1)$$

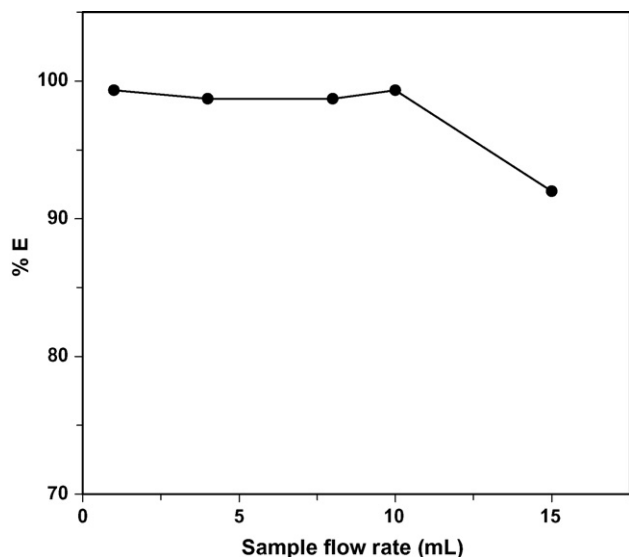
where  $C_0$  and  $C_E$  are the initial and equilibrium concentrations (mmol mL<sup>-1</sup>) of U(VI) in the solution, respectively;  $m$  is the weight of the sorbent in g and  $V$  is the volume of the aqueous solution in cm<sup>-3</sup>. The mmol of U(VI) sorbed per gram of sorbent,  $a_E$ , vs. equilibrium concentration as adsorption isotherm is shown in Fig. 5 A. As seen, the sorption capacity increases with increase in initial U(VI) concentration and reaches to a constant and maximum value. The equilibrium adsorption isotherm is important for understanding the mechanism of the adsorption. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of homogeneous sites [36]. The Langmuir expression is represented by the equation:

$$a_E = \frac{A_s K C_E}{1 + K C_E} \quad (2)$$

where  $K$  and  $A_s$  are the binding constant and maximum uranyl ion sorption capacity, respectively. The linear form of the Langmuir isotherm equation is shown as

$$\frac{C_E}{a_E} = \frac{1}{A_s K} + \frac{C_E}{A_s} \quad (3)$$

The plot of  $C_E/a_E$  versus  $C_E$  gives a straight line with slope of  $1/A_s$  and the intercept of  $1/KA_s$  which confirms the validity of the Langmuir model for this process (Fig. 5B). The maximum sorption capacity ( $A_s$ ) and binding constant ( $K$ ) calculated from the intercept and slope were 1.13 mmol g<sup>-1</sup> (0.07 mmol g<sup>-1</sup> for unmodified silica gel) and  $1.47 \times 10^5 \text{ mL g}^{-1}$ , respectively. The numerical value of distribution coefficient ( $\log K_d$ ) for U(VI) ions can be determined



**Fig. 6.** Effect of sample flow rate on recovery of U(VI) ion (experimental conditions: 100 mL  $1.35 \mu\text{g mL}^{-1}$  U(VI) ion solution at pH 5.5, 100 mg sorbent, 2.5 mL of eluent at  $0.5 \text{ mL min}^{-1}$ ).

by  $K_d = a_E/C_E$  which was found as 4.67 in this study. The high binding constant and distribution coefficient values are due to strong binding of U(VI) to O donor sites on SiAPMS–Mu in comparison with unmodified silica gel at this pH ( $\log K_d = 1.98$ ). It seems the complex formation plays a key role for uptake of U(VI) by this new sorbent.

### 3.3. Extraction studies by column method

#### 3.3.1. Elution studies

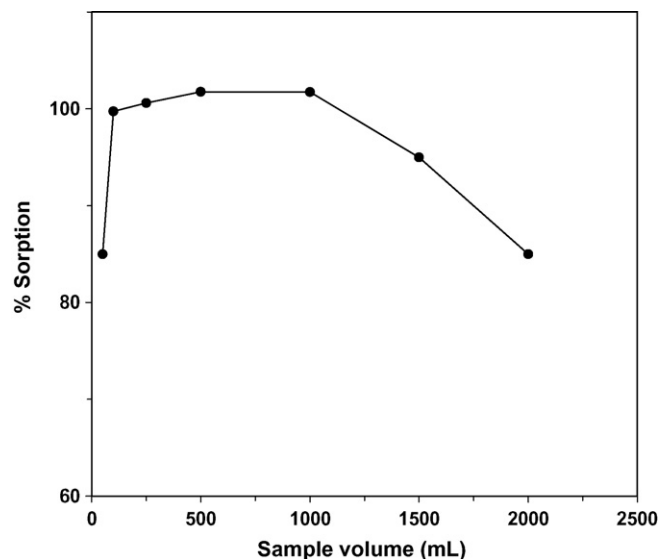
The percent sorption of 100 mL of  $2.7 \mu\text{g mL}^{-1}$  U(IV) ions on the sorbent surface as a function of sample flow rate was examined in the range of  $2.0\text{--}15 \text{ mL min}^{-1}$  (Fig. 6). The flow rates slower than  $2.5 \text{ mL min}^{-1}$  were not studied to avoid extended analysis time. The results showed that even at high flow rate of  $10 \text{ mL min}^{-1}$ , quantitative recovery of U(VI) ions was possible, indicating the fast U(VI) sorption ability of the sorbent. At flow rates greater than  $10.0 \text{ mL min}^{-1}$ , there was a decrease in the percentage of recovery. This might be due to the insufficient contact time of analyte with the sorbent. All further studies were performed at the sample flow rate of  $10.0 \text{ mL min}^{-1}$ . Similarly, the variation of elution flow rate from  $0.2$  to  $2.5 \text{ mL min}^{-1}$  showed that the elution of the sorbed U(VI) was quantitative over the range of  $0.2\text{--}1.0 \text{ mL min}^{-1}$ .

The desorption of the analyte from the sorbent was studied using HCl solution as stripping agent at various concentrations ( $0.05\text{--}1.0 \text{ mol L}^{-1}$ ) and volumes ( $2.0\text{--}10.0 \text{ mL}$ ). The results show that  $2.5 \text{ mL}$  of  $0.10 \text{ mol L}^{-1}$  of HCl is favorable to quantitative elution of U(VI). Consequently,  $2.5 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  of HCl at flow rate of  $0.5 \text{ mL min}^{-1}$  was used for quantitative elution of sorbed U(VI) (Table 1).

**Table 1**

Influences of elution parameters on pre-concentration of U(VI) ions in column method based on triplicate analysis

Parameter				
Concentration ( $\text{mol L}^{-1}$ ); % recovery	0.05; 97	0.1; >99	0.5; >99	1.0; >99
Volume (mL); % recovery	2.5; >99	5.0; >99	7.0; >99	10.0; >99
Flow rate ( $\text{mL min}^{-1}$ ); % recovery	0.2; >98	0.5; >99	1.0; >98	2.5; 95



**Fig. 7.** Sample breakthrough volume curve for U(VI) ion sorption (experimental conditions:  $135 \mu\text{g}$  U(VI) ion solutions at different volumes, 100 mg sorbent, 2.5 mL of eluent at  $0.5 \text{ mL min}^{-1}$ ).

#### 3.3.2. Sample breakthrough volume

Maximum sample volume up to which quantitative U(VI) sorption occurred was determined by varying the sample volume over a range of  $100\text{--}15000 \text{ mL}$  each containing  $135 \mu\text{g}$  U(VI) and passing through the column at flow rate of  $10 \text{ mL min}^{-1}$ . The sorbed U(VI) ions were eluted with  $2.5 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  HCl at flow rate of  $0.5 \text{ mL min}^{-1}$ . The plot of percentage of sorption against sample volume is shown in Fig. 7. As can be seen, at volumes higher than  $1000 \text{ mL}$ , the sorption of U(VI) was not quantitative, so a pre-concentration of 400 was obtained for U(VI) ions with a recovery more than 98%, reflecting enhanced chelating site accessibility of the sorbent.

#### 3.4. Effect of foreign ions

As NaCl, KCl and  $\text{KNO}_3$  are the main electrolytes present in nuclear fuel waters and environmental samples [37], their influences on the quantitative extraction of U(VI) were studied in the concentration range of  $0.001\text{--}0.1 \text{ mol L}^{-1}$ . The results showed that the alkaline ions had no significant effect on sorption of U(VI) at the studied concentrations.

The influence of foreign ions that might be adsorbed on SiAPMS–Mu was investigated in order to identify potential interferences. Effect of alkaline, alkaline earth and transition metal ions and some anions on sorption of U(VI) ions was investigated in binary solution of U(VI) accompanying interfering ions. The tolerance limit for a foreign ion was taken as the largest amount of the ions that could be present with the U(VI) and gives the adsorption within 5%

**Table 2**

Tolerance limits of some cations and anions on the sorption of U(VI) on SiAPMS–Mu at optimum condition

Foreign ion	Tolerance limit <sup>a</sup>
$\text{K}^+, \text{Cl}^-, \text{Na}^+, \text{NO}_3^-, \text{CH}_3\text{CO}_2^-$	>1000
$\text{I}^-, \text{SO}_4^{2-}, \text{Cd}^{2+}, \text{Tl}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Zn}^{2+}$	1000
$\text{La}^{3+}, \text{Ce}^{3+}, \text{Al}^{3+}, \text{MoO}_4^{2-}, \text{Cs}^+$	100
$\text{Fe}^{3+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cr}^{3+}$	70
$\text{VO}_3^-, \text{PO}_4^{3-}, \text{C}_2\text{O}_4^{2-}$	7
$\text{Th}^{4+}, \text{Zr}^{4+}$	2

<sup>a</sup> The concentration ratio of the foreign ions to the U(VI) ions.

**Table 3**  
Comparison of important characteristics of various sorbents used for the separation and preconcentration of the U(VI) ions

Matrix	Capacity, (mmol g <sup>-1</sup> )	LOD, (ng mL <sup>-1</sup> )	Eluent	Preconcentration factor	Analyzed sample
Support: Silica gel					
N-tripropionate-substituted tetraazamacrocyclic [29]	0.032	0.0985	2N HNO <sub>3</sub>	50	Nuclear center effluents
Quinoline-8-ol [28]	–	0.001	0.7 M HCl	–	Sea water
Benzoylthiourea [26]	0.85	2.0	0.1 M HCl	250	Synthetic sample and soil sample
Calixarene Semicarbazone [27]	0.0127	–	0.25 M HCl	108	Geological samples
Catechol [41]	0.059	–	1.0 M HCl	–	Marine sediment and soil
Murexide [this study]	1.13	1.0	0.1 M HCl	400	Synthetic seawater and ground water
Support: Octadecyl silica membrane disc					
Tri-n-octyl phosphineoxide [14]	0.019	–	0.5 M HNO <sub>3</sub>	–	Natural water
Support: Amberlite XAD-4					
O-vanillin semicarbazone [9]	0.01	100	0.25 M HCl	143	Simulated river water
Succinic acid [7]	0.046	2.0	1.0 M HCl	200	Soil and sediments
Quinoline-8-ol [39]	0.01	2.0	1.0 M HCl	200	Sediment and soil
Support: Amberlite XAD-2					
Pyrogallol [40]	0.025	1.0	4 M HCl	70	River and well water
Support: Amberlite XAD-16					
[1,2-Dihydroxy arsinoyl phenyl amino)methyl]phosphonic acid [45]	0.25	23	1 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	365	Nuclear spent fuel and seawater mixtures, natural water, and geological samples.
Support: Polystyrene-DVB					
4-(2-thiazolylazo) resorcinol [10]	0.62	880	2 M HNO <sub>3</sub>	–	Seawater
Support: Molecularly imprinted polymers					
5,7-dichloroquinoline-8-ol [13]	0.11	4.0	2.0N HCl	100	Sea water and sediment
5,7-dichloroquinoline-8-ol [46]	0.13	2.0	1 M HCl	–	–
Piroxicam [42]	0.14	0.8	2 M HCl	150	Synthetic sea water and natural water
Support: Merifield resins					
Calix[4]arene-O-vanillin semi-carbazone [44]	0.18	6.14	0.25 M HCl	143	Natural water and geological materials
Thenoyltrifluoroacetone [38]	0.38	–	1 M HCl	–	Synthetic solution
Octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide [37]	0.984	20	4 M HNO <sub>3</sub>	400	Nuclear spent fuel
Support: Crosslinked chitosan					
3,4-dihydroxy benzoic acid [43]	1.22	0.93	1.0 M HNO <sub>3</sub>	20.2	Tap water, sea water and river water
Support: Naphthalene/ Benzophenone					
5,7-dichloroquinoline-8-ol [16]	0.007	2.0	Acetone	200	Soil and sediment
1-(2-pyridylazo)2-naphthol [15]	0.009	2.0	Acetone	500	River and marine sediment and soil
Support: activated carbon					
Diarylazobisphenol [8]	0.068	5.0	1.0 M HCl	100	Soil and sediments

of that of the U(VI) ions alone. Concentration of transition metal ions in the solutions was determined by FAAS. The degree of tolerance for some alkaline, alkaline earth and transition metal ions are presented in Table 2. From the tolerance data, it can be seen that except thorium and zirconium, other ions have no significant effects on preconcentration of U (VI).

### 3.5. Analytical performance

The calibration curve for the preconcentration of U(VI) by the SiAPMS–Mu was found to be linear over the concentration range of 1.35–217 µg mL<sup>-1</sup> with recovery of >98%. The relative standard deviation of 10 replicates was found to be less than ±1.6% at 1.35 µg mL<sup>-1</sup> of U (VI). To test the sorbent ability to extract trace

quantity of U(VI) ions, studies were performed by passing 1000 mL of sample solution containing U(VI) ion over the concentration of 0.1–10 µg L<sup>-1</sup>. The sorbed U(VI) ions were eluted with 2.5 mL of 0.1 mol L<sup>-1</sup> of HCl and estimated. The limit of detection was found to be 1 µg L<sup>-1</sup> U(VI). The SiAPMS–Mu was subjected to several loading with the sample solution and eluting with the eluent and could be used over ten sorption–desorption cycles. The sorption capacity of the SiAPMS–Mu stored at ambient conditions did not change for 6 months.

The sorption characteristics of SiAPMS–Mu is compared with those of other sorbents in Table 3 [7–16,26–29,38–46]. The new synthesized sorbent in the present study shows highest preconcentration factor for U(VI) among other modified silica gel with N-tripropionate-substituted tetraazamacrocyclic [29], Quinoline-8-

**Table 4**  
Determination of U(VI) in water samples by the proposed sorbent

Real sample <sup>a</sup>	Added (µg mL <sup>-1</sup> )	Found (µg mL <sup>-1</sup> )	% Extraction (batch method)	Added (µg mL <sup>-1</sup> )	Found (µg mL <sup>-1</sup> )	% Recovery (column method)
Synthetic seawater <sup>b</sup>	1.35	1.24 ± 0.01	92.2	1.35	1.27 ± 0.02	94.2
	2.70	2.49 ± 0.10	92.2	2.70	2.58 ± 0.10	95.6
Ground water	1.35	1.31 ± 0.04	97.4	1.35	1.38 ± 0.02	102.5
	2.70	2.55 ± 0.10	94.5	2.70	2.66 ± 0.10	98.7

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

<sup>b</sup> Composition in w/w%; Na<sup>+</sup> = 1.18; Cl<sup>-</sup> = 2.2; Ca<sup>2+</sup> = 0.005; K<sup>+</sup> = 0.04; Mg<sup>2+</sup> = 0.15.

ol [28], benzoylthiourea [26], calixarene semicarbazone [27] and catechol [41]. Similarly, SiAPMS–Mu offers better retention capacity compared to those reported for various chelate or impregnated SPE sorbent. The low acid concentration required for desorption of U(VI) ion in this study avoids any further dilution step for FAAS measurements of co-existing cations.

### 3.6. Application

The applicability of the sorbent for preconcentration of trace level of U(VI) was tested using ground water (Bojd Ganat, Birjand, Iran) and synthetic seawater samples. Synthetic seawater was prepared according to the reference [47]. Before the analysis, the samples were filtered through a 0.45  $\mu\text{m}$  membrane filter. For the preconcentration procedure, pH of the 1000 mL of water samples was adjusted to 5.5 and spiked with uranyl ions and was subjected to the sorbent in batch and column methods. The sorbed U(VI) ions were estimated based on triplicate analysis (Table 4). It was found that the sorbent was successful in quantitative extraction of the U(VI) ions even in the presence of various diverse ions.

### 4. Conclusion

Modification of silica gel surface with Mu resulted in producing of U(VI) ion extractor which needs only few minutes to complete the U(VI) ion extraction process, so that 92% of U(VI) ions were adsorbed within first 5 min of equilibration. The sorbent exhibits a much higher preconcentration factor for the enrichment of traces of U(VI) from large sample volumes. The obtained results clearly demonstrated the high potential of SiAPMS–Mu for U(VI) ions separation from co-existing alkaline, alkaline earth, transition and heavy metal ions. The selective extraction of U(VI) could be extended to the recovery of U(VI) ions from water samples.

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