Th(IV)/U(VI) Sorption on Modified SBA–15 Mesoporous Materials in Fixed–Bed Column

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ABSTRACT: *The sorption of thorium and uranium ions by functionalized SBA–15 mesoporous silica materials with Schiff base ligating groups N–propylsalicylaldimine (SBA/SA) and ethylenediaminepropylesalicylaldimine (SBA/EnSA) from aqueous solution was investigated in fixed-bed column method. The effect of pH, sample solution volume, and the column design parameters such as sample and eluent flow rates, and column bed height were studied. These investigations allowed to obtain the experimental breakthrough curves. Regardless to the adsorbent used, application of the columns with 2.5 cm bed height and sample flow rate 0.4 mL/min, resulted in the quantitative removal of 0.5 mg of Th(IV) and U(VI) ions from 200 and 250 mL aqueous solutions, adjusted at pH 4. The quantitative desorption of the loaded ions provided a preconcentration factor of 40 and 50 for Th(IV) and U(VI), respectively. Breakthrough studies showed the higher capacity of the column packed with SBA/EnSA in comparison to that packed with SBA/SA. The breakthrough curves indicated that both of the sorbents presents higher capacity towards uranium than thorium ions. The columns could be used for at least 3 sorption-desorption cycles. The investigated columns were examined for the recovery of Th(IV) and U(VI) from tap water and seawater samples.*

KEYWORDS: *Removal; Recovery; Adsorption; Th(IV); U(VI); Schiff base functionalized SBA–15; Fixed–bed column.*

INTRODUCTION

With the rapid development of nuclear energy and nuclear industry, a large number of radioactive wastes is produced. Radioactive elements contamination can reach the food chain and enter into living bodies, start emitting electromagnetic radiations that can cause progressive and irreversible damage human health. For the work safety in the nuclear industry and human health [1,2], on the one hand, and the increasing need for radionuclides for the production of electricity, on the other, the removal and recovery of long-lived radionuclides such as thorium(IV)

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and uranium(VI) ions from resources such as seawater and industrial wastewater is an important environmental concern [3]. It is noteworthy that sea water contains uranium, more than thousand times more than the quantity available in mines [4]. This source would provide an abundant supply for nuclear power generation. Thorium(IV) is predicted to be able to replace uranium as fuel in nuclear reactors [1]. For these reasons, great efforts are being made to develop the processes for the separation and recovery of uranium and thorium ions [5–15].

Sorption is considered to be the most effective and convenient technique because of its simplicity, reliability, selectivity, high capacity of adsorbents ease of handling and environmental safety [16–21]. In sorption process of radionuclides, both of batch and continuous flow methods have been investigated, although the most of these investigations were restricted to the batch equilibrium studied [16–31]. In a batch system, separation process of adsorbents from aqueous solution is usually complex and time–consuming and the data obtained under batch conditions are generally not applicable to most treatment system where contact time is not sufficiently long for attaining to an equilibrium condition. It has been shown that the fixed–bed column method is easier and more useful for real wastewater treatment from industrial sources [2,31–37].

In our recent reported works [38,39], two SBA–15 mesoporous silica materials functionalized by Schiff base ligands *N*–propylsalicylaldimine and ethylenediaminepropylesalicylaldimine, named respectively as SBA/SA and SBA/EnSA (Fig. 1), have been synthesized and their potentials for removal of thorium and uranium in batch, experiments were investigated. The present work extended these investigations for the removal and recovery of the same species by SBA/SA and SBA/EnSA in a fixed–bed column method. The effect of design parameters, such as bed height, flow rate and volume of the sample was studied and the breakthrough profile for the sorption was obtained. Breakthrough points and breakthrough curves are very important characteristics for process design, dynamic response, and operation of a sorption column because they directly affect the feasibility and economic aspects of the sorption phenomena. In addition, Th(IV) and U(VI) sorption behavior in three consecutive sorption-desorption cycles have been investigated. Finally, the presented procedures were examined for the removal of the studied ions from tap water and seawater samples.

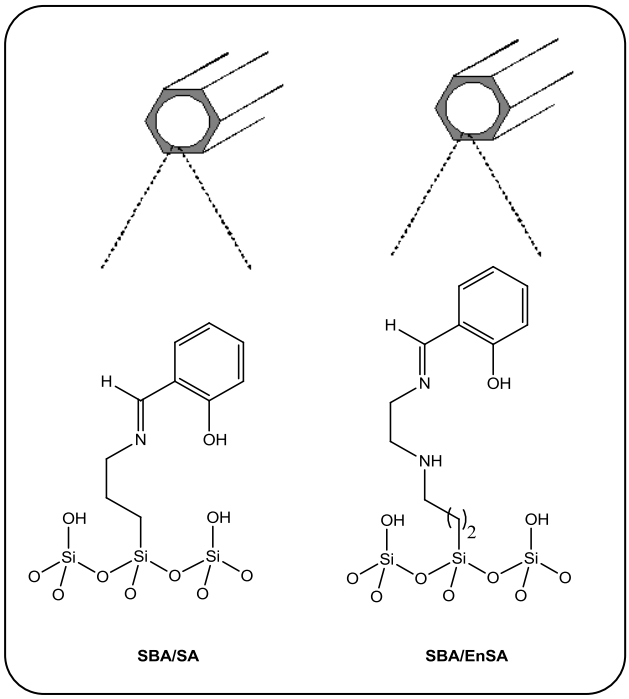

Fig. 1: Structure of the investigated adsorbents.

EXPERIMENTAL SECTION

Reagents and materials

All the chemicals used were analytical grade and were obtained from Merck, Fluka or Acros chemical companies. The SBA–15 mesoporous silica material was synthesized according to the procedure reported in the literature [40,41] and was functionalized by the methods described in the previous studies [38,39,42,43]. In summary, the adsorbents were prepared as follow; calcinated SBA–15 was functionalized by (3–aminopropyl)triethoxysilane to obtained amino functionalized SBA (SBA/NH_2). *N*–propylsalicylaldimine (SBA/SA) was resulted by the reaction of SBA/NH_2 with salicylaldehyde. The SBA/prEn was prepared by adding (2–aminoethyl–aminopropyl)trimethoxysilane to the calcinated SBA–15. The resulted diamino–functionalized SBA–15 type mesoporous was reacted with salicylaldehyde to obtain SBA/EnSA. SBA/SA and SBA/EnSA were characterized by using XRD, SEM, TEM, FT–IR, and TGA. Stock solutions of thorium and uranium ions (1000 mg/L) were prepared by dissolving an appropriate amount of $Th(NO_3)_4$ and $UO_2(NO_3)_2.6H_2O$ salts in deionized water containing 0.01 mol/L HNO_3. The working solutions were prepared by diluting the stock solutions to appropriate volumes, with deionized water.

The pH values of these solutions were adjusted by addition of diluted nitric acid or sodium hydroxide solutions (0.1 mol/L).

Instrumentation

An Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES, Spectro Genesis, Germany), a peristaltic pump, and a cyclonic spray chamber with a concentric nebulizer were used for determination of thorium and uranium ions. The purity of argon gas used in the analysis was 99.999%. A Metrohm digital pH–meter (model 780, Switzerland) was used for pH measurements. A peristaltic pump (pump drive 5101, Heidolph, Germany) was applied for passing the water samples from a container to the bottom of the packed column. Deionized water, with a resistivity of 18.2 MΩ cm, was produced by a M–UV–3^{+} Zolalan (Iran) water purification system.

Fixed-bed column adsorption experiments

The adsorption efficiency of SBA/SA and SBA/EnSA towards Th(IV) and U(VI) ions were investigated by using fixed–bed column apparatus. A 100 mg portion of the adsorbents were filled into a self–made polypropylene columns with inner diameter 0.5 cm and bed height 2.5 cm. Column plugged with a small piece of glass–wool at both ends. For removing all contaminants and preconditioning the bed, the column was washed with 5 mL of absolute ethanol and 20 mL of deionized water. An aqueous solution containing 10 mg/L of the ions pumped at a flow rate of 0.4 mL/min by using the peristaltic pump. The retained ions were eluted with 5 mL of 1 mol/L HNO_3 solution, at a flow rate 0.25 mL/min. To obtain the optimum conditions for the extraction procedure of Th(IV) and U(VI) ions, design parameters including bed height of column and flow rates of sample and eluent, sample solution pH, volume and type of eluent for the desorption of analytes from the adsorbents were assessed. The percent of the adsorption and metal ions eluted were calculated by Eqs. (1) and (2) [44]:

$$\text{Adsorption } \% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$\text{Metal ions eluted } \% = \frac{\text{Amount of metal ions eluted}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (2)$$

Where C_e and C_0 are the metal ions concentration in effluent liquid phase and the inlet metal concentration in the solution in mg/L, respectively.

The performance of packed beds was described by the concept of the breakthrough curve [45,46]. For breakthrough studies, 100 mg of the sorbent was taken in a column. The aqueous solution (10 mg/L at pH 4) was passed through the column, and the effluent was collected periodically. The samples were analyzed for the remaining metal ions concentration by ICP–OES. Operation of the column was stopped when the effluent metal concentration reached a constant value, i.e. the value close to that of the influent concentration. A breakthrough curve was obtained by plotting the ratio C/C_0 against the effluent volume (V_{eff}) or time for a given bed height, where C is the metal ions concentration in effluent liquid phase and C_0 has the same definition given in Eq. (1) [44,47]. The breakthrough time (t_b), the time at which metal concentration in the effluent reached 5% of the influent value (C_t = 0.05 C_0) and exhaustion point (t_e), the time at which metal concentration in the effluent exceeded 95% of the influent value (C_t = 0.95 C_0) were used to evaluate the adsorption performance of the adsorbent bed under specified conditions [45,48,49].

RESULTS AND DISCUSSION

Sample solution pH

Due to the effect of pH on the protonation–deprotonation of the ligating groups anchored on the adsorbents matrix and on the distribution of metal ions, the investigation of the aqueous phase pH forms a key parameter and a basic part of the adsorption studies. To verify this parameter on the sorption of Th(IV) and U(VI) ions by SBA/SA and SBA/EnSA, a series of experiments was performed by passing 50 mL of aqueous solutions containing Th(VI) and U(VI) ions (10 mg/L), adjusted at pH values in the range 2 to 6. The solutions were pumped at a flow rate 0.4 mL/min through the column. After the sample loading, the retained metal ions were eluted with 5 mL nitric acid solution (1 mol/L) with a flow rate 0.25 mL/min. The results (Fig. 2) revealed that the adsorption of both thorium(IV) and uranium(VI) ions onto the studied adsorbents depends profoundly on the sample solution pH. A plateau for the adsorption of the ions as a function of the pH of aqueous solutions was observed beyond pH>4. These results were very close to those obtained in the corresponding batch method studies [38,39].

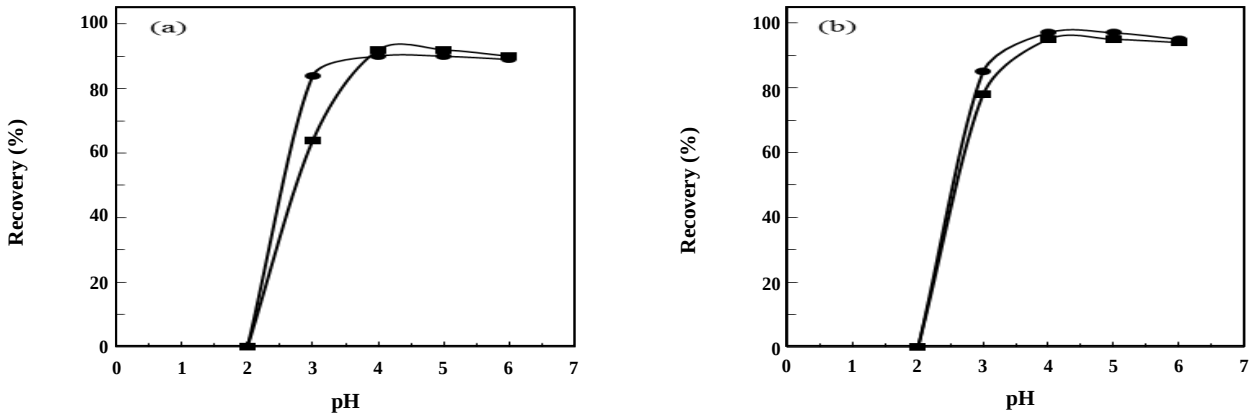

Fig. 2 Effect of pH on the percent recovery of Th(IV) ■ and U(VI) ● ions by SBA/SA (a) and SBA/EnSA (b). Conditions: sample concentration, 10 mg/L; sample volume, 50 mL; eluent, 5 mL of HNO_3 1.0 mol/L; Flow rate of elution, 0.25 mL/min, column bed 2.5 cm.

Elution of the adsorbed ions

An important step in a fixed–bed column studies is the efficient desorption of the adsorbed analyte from the adsorbent. It was confirmed that the desorption of the studied ions from the adsorbents can be quantitatively attained by using a solution of nitric acid [38, 39]. The optimization of the eluent volume was done by passing the different volume of the nitric acid solution (3, 5, 10 and 25 mL) through the column, with a flow rate 0.25 mL/min. The results indicated that 5 mL of the nitric acid the solution was sufficient for quantitative elution of the adsorbed Th(IV) and U(VI) from the column, regardless of the adsorbent used.

Sample flow rate

The sample flow rate through the column is a significant parameter for an efficient fixed–bed column adsorption process. In fact, it is one of the parameters controlling the time of analysis [50, 51]. The effect of sample flow rate on the adsorption of Th(IV) and U(VI) ions by SBA/SA and SBA/EnSA were examined by passing the sample solution (adjusted at pH 4) with flow rates 0.25–0.95 mL/min through the columns containing 100 mg (2.5 cm height) of the adsorbents (Fig. 3). It was found that a nearly quantitative recovery of uranyl ions (> 90%) can be achieved by applying the sample flow rate in the range of 0.25–0.95 mL/min, through the columns containing SBA/SA or SBA/EnSA. The fast kinetics of the adsorption, as that observed in the experiments [38, 52], makes possible the use high sample solution flow rate for the process.

In the case of thorium ions, a quantitative recovery by both of the studied adsorbents was observed by using sample flow rates <0.75 mL/min. Above this flow rates, the recovery of sorption decreases considerably. This can be described by the kinetic control of the process at the higher applied flow rates. These results conduct us to use a flow rate of 0.4 mL/min for continuing the experiments.

Eluent flow rate

The flow rate of eluent must be optimized to ensure an effective desorption of the analytes from the surface of the adsorbent [53]. To this end, the loaded adsorbents were eluted with 5 mL nitric acid solution (1 mol/L), at different flow rates from 0.25 to 0.95 mL/min (Fig. 4). Uranyl and thorium ions were desorbed almost completely from the column packed with SBA/EnSA by applying the eluent flow rates ≤0.83 and ≤0.6 mL/min, respectively. This condition was attained for thorium and uranyl ions from the column packed with SBA/SA by passing the eluent with the flow rates <0.4 mL/min. The results conduct using a flow rate of 0.25 mL/min for desorption of the studied metal ions from the columns packed with the Schiff base functionalized mesoporous silica adsorbents.

Bed height

The effect of bed height on the adsorption efficiency of Th(IV) and U(VI) ions was investigated by using the columns packed with 0.05 g, 0.075 g, 0.1 g and 0.15 g equal to 12, 18, 25 and 49 mm, respectively of the sorbents (Fig. 5). The results show the recovery

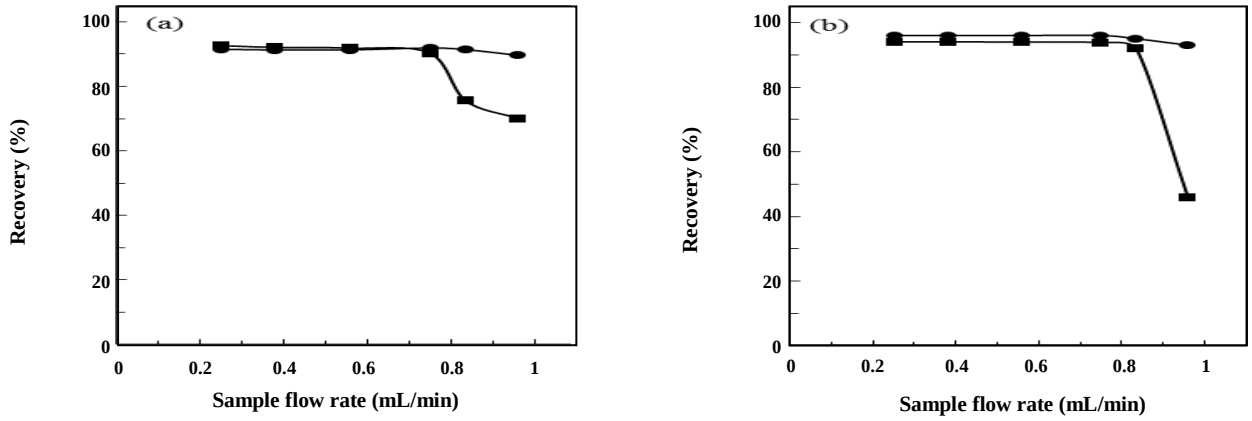

Fig. 3: Effect of the flow rate of the sample on the percent recovery of Th(IV) ■ and U(VI) ● ions by SBA/SA (a) and SBA/EnSA (b). Conditions: sample concentration, 10 mg/L; pH 4; sample volume, 50 mL; eluent, 5 mL of HNO_3 1 mol/L; Flow rate of elution, 0.25 mL/min; column bed, 2.5 cm.

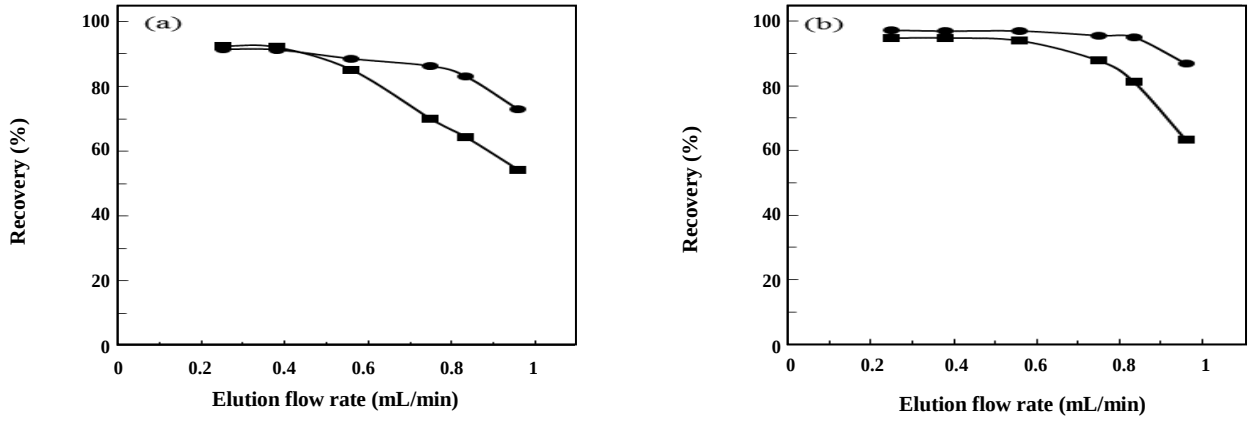

Fig. 4: Effect of flow rate of elution on the percent recovery of Th(IV) ■ and U(VI) ● ions by SBA/SA (a) and SBA/EnSA (b). Conditions: sample concentration, 10 mg/L; pH 4; sample volume, 50 mL; Flow rate of sample, 0.4 mL/min; eluent, 5 mL of HNO_3 1 mol/L; column bed height, 2.5 cm.

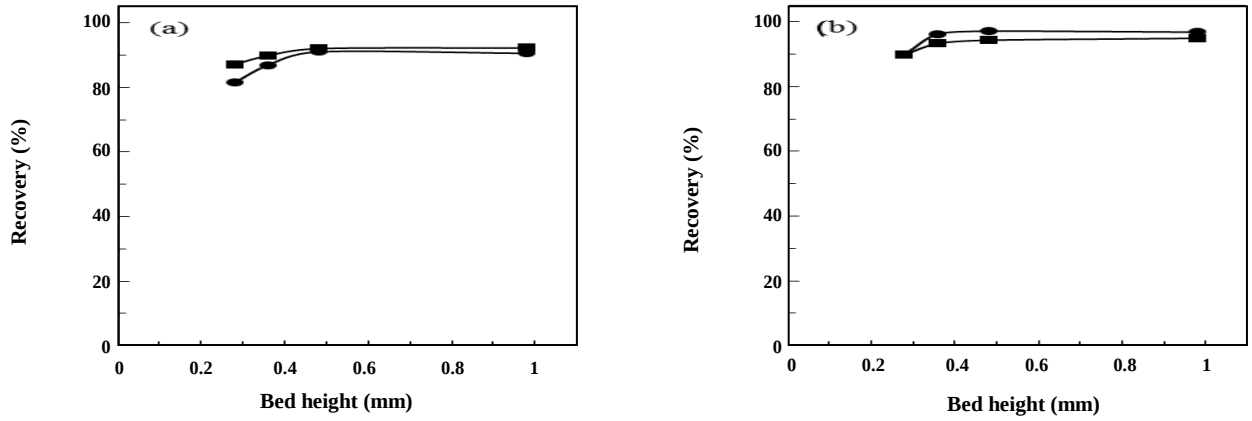

Fig. 5: Effect of bed height on the percent recovery of Th(IV) ■ and U(VI) ● ions by SBA/SA (a) and SBA/EnSA (b). Conditions: sample concentration, 10 mg/L; pH 4; sample volume, 50 mL; Flow rate of sample, 0.4 mL/min; eluent, 5 mL of HNO_3 1 mol/L; Flow rate of eluent, 0.25 mL/min.

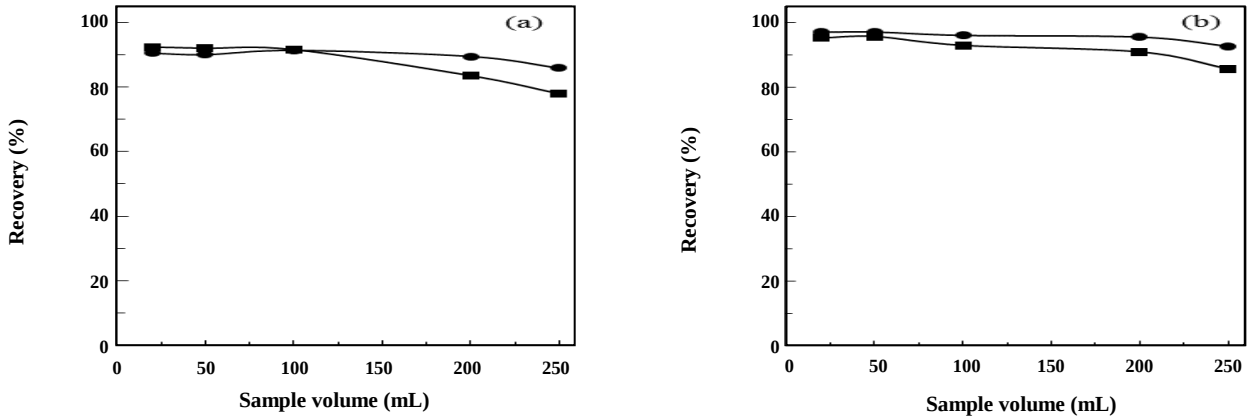

Fig. 6: Effect of sample volume on the recovery of Th(IV) ■ and U(VI) ● ions by SBA/SA (a) and SBA/EnSA (b). Conditions: sample amount, 0.5 mg of each ions; sample flow rate, 0.4 mL/min; eluent, 5 mL of HNO_3 1 mol/L; eluent flow rate, 0.25 mL/min.

percentage increase with increasing the bed height of both adsorbents. This effect was more pronounced for SBA/SA, probably due to the availability of more binding sites on this sorbent.

Sample solution volume

One of the parameters indicating the efficiency of an adsorbent is its potential for removal of a trace amount of an analyte from a solution. To evaluate this potential of the studied mesoporous materials, the recovery of Th(IV) and U(VI) ions (0.5 mg) in different volume of aqueous solution, 20, 50, 100, 200 and 250 mL by SBA/SA and SBA/EnSA sorbents (100 mg) was investigated (Fig. 6). This means that the concentration of the aqueous solutions was in the range 25–2 mg/L. There was no significant change in the efficiency of the recovery of the sorbents towards uranyl and thorium ions up to 250 and 200 mL, respectively. Therefore, a preconcentration factor of 50 and 40 for uranyl and thorium ions can be achieved by the presented method. These results show the excellent potential of SBA/SA and SBA/EnSA for recovery and preconcentration of these ions at trace levels.

Reusability of the column

The possibility of regeneration and reusing of a sorbent gives an economic advantage for its applying for removal process of an analyte from wastewater streams [34]. In this study, Schiff base functionalized SBA–15 were used for 3 adsorption-desorption cycles by using the columns packed with 0.1 g (bed height of 2.5 cm) of sorbent and passing the sample solutions (10 mg/L of metal ions) through the columns with a flow rate 0.4 mL/min. The loaded sorbents were regenerated propelling a solution of 1 mol/L HNO_3 with 0.25 mL/min flow rate through the columns. The columns then, reused for adsorption experiments. It was found that both of the studied sorbents are able to be used at least for three adsorption-desorption cycles. The results are shown in Table 1.

Breakthrough studies

The breakthrough curve for the adsorption of Th(IV) and U(VI) onto the studied sorbents are shown in Fig 7. The corresponding breakthrough time and exhaustion time are presented in Table 2. The breakthrough time and exhaustion time for both of the studied ions onto SBA/EnSA are higher than SBA/SA. The appearance of the breakthrough time for thorium was taken place earlier with respect to that of uranium ions. This indicated that higher capacity of sorbents towards uranium ions. These results agree with those obtained in the batch system studies [38,39]. The breakthrough time for thorium ions started after 265 and 310 mL of the solution passed through the columns packed with SBA/SA and SBA/EnSA, respectively. These values for uranium ions were found to be 280 and 670 mL of the columns filled with SBA/SA and SBA/EnSA, respectively.

Recovery of Th(IV) and U(VI) from real samples

The developed columns were applied to the elimination of injected Th(IV) and U(VI) ions (10 mg/L) in tap water (Zanjan, Iran) and seawater (Anzali region,

Table 1: Results of the recovery percentage of Th(IV) and U(VI) ions in three cycles.

Sorbent	Metal Ion	Recovery (%)		
		Cycle 1	Cycle 2	Cycle 3
SBA/SA	Th(IV)	92.7	91.5	90.6
	U(VI)	91.4	90.9	90.2
SBA/EnSA	Th(IV)	95.6	95.4	93.8
	U(VI)	97.2	96.9	95.5

Table 2: Results of the breakthrough curve study for Th(IV) and U(VI) ions sorption[a].

Sorbent	Metal ion	t_b (min)	t_e (min)	V_e (mL)
SBA/SA	Th(IV)	112	662	265
	U(VI)	275	700	280
SBA/EnSA	Th(IV)	200	775	310
	U(VI)	775	1675	670

[a]Conditions: pH 4, concentration: 10 mg L^{-1}, column bed 2.5 cm, flow rate 0.4 mL min^{-1}

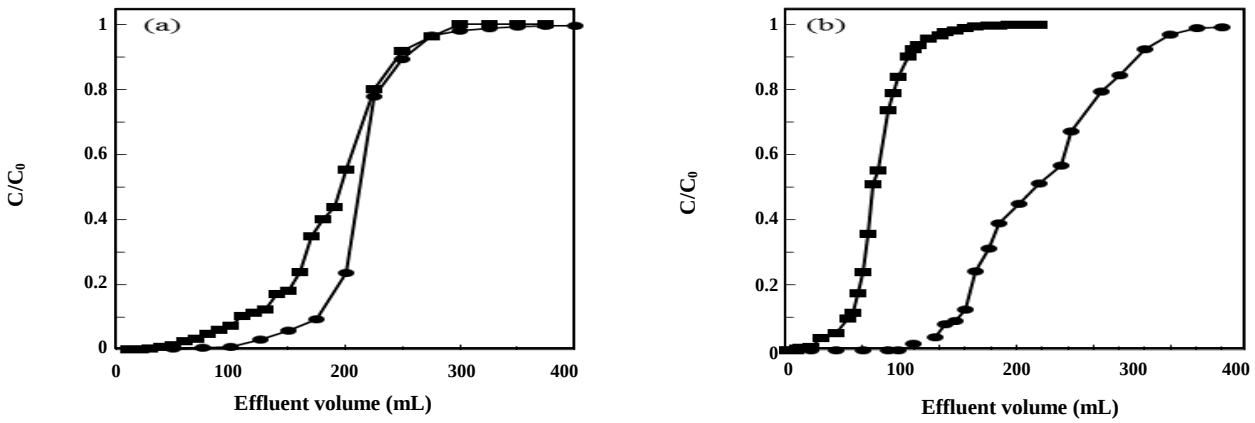

Fig. 7: The breakthrough curve for Th(IV) ■ and U(VI) ● ions onto SBA/SA (a) and SBA/EnSA (b). Conditions: sample concentration, 10 mg L^{-1}; pH 4; Flow rate of sample, 0.4 mL min^{-1}, column bed 2.5 cm.

Caspian sea, Iran) samples. The results of the adsorption of the spiked ions into the samples by using 2.5 cm packed columns and by transferring the samples with a flow rate 0.4 mL/min are given in Table 3. These results confirm the potential of the studied adsorbents for removal of Th(IV) and U(VI) ions from the examined water samples.

CONCLUSIONS

Fixed–bed or column adsorption is a popular option in the practical application of adsorption process. This work demonstrated the adsorption characteristics of Th(IV) and U(VI) ions by the column system packed with two functionalized SBA–15 mesoporous adsorbents with Schiff base ligands *N*–propylsalicylaldimine (SBA/SA) and ethylenediaminepropylesalicylaldimine (SBA/EnSA). Under selected conditions, i.e. sample solution 50 mL containing 10 mg/L of Th(IV) and U(VI) ions adjusted at pH 4, 0.1 g of one of the adsorbents (equals to 2.5 cm bed height) and sample flow rate 0.4 mL/min, the columns packed with each of the adsorbents were able to

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[a]*Conditions: pH 4, concentration: 10 mg/L, column bed 2.5 cm, flow rate 0.4 mL/min.*

remove more than 93 percent of Th(IV) and U(VI) ions. Desorption of the ions from the adsorbents by using 5 mL nitric acid 1 mol/L as eluent, by a flow rate 0.25 mL/min, allows a quantitative desorption of both ions. In addition, the packed columns with both adsorbents permit decontamination of trace amounts of Th(IV) and U(VI) ions from water solutions and are able for a preconcentration of these ions with concentration factors of 40 and 50, respectively. The breakthrough curve profile indicated that adsorption capacity for SBA/EnSA is higher than SBA/SA towards the studied metal ions. Both adsorbents showed a higher affinity towards U(VI) ions with respect to Th(IV) ions. The stability of the adsorbents allowed using the packed columns with the studies adsorbents at least for three adsorption-desorption cycles. It was shown that the proposed method is potentially useful for recovery of thorium and uranium ions from the tap and seawater samples.

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