



Comparison of sorption behavior of Th(IV) and U(VI) on modified impregnated resin containing quinizarin with that conventional prepared impregnated resin

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ABSTRACT

This paper reports the results obtained by studying the ion-exchange properties of a new solvent impregnated resin (SIR), which was prepared by impregnation of quinizarin (1,4-dihydroxyanthraquinone, QNZ) on Amberlite XAD-16 after nitration of the benzene rings present in its structure. The sorption behavior of Th(IV) and U(VI) on/in the modified SIR was compared with that of the SIR prepared via the conventional method. It was observed that sorption capacity and sorption rate of the modified SIR are significantly greater than the conventional one. The modified SIR was then applied to the extraction of Th(IV) and U(VI) ions at the presence of many co-existence metal ions. The results obtained denote on successful application of this new SIR to analysis of natural water samples spiked to Th(IV) and U(VI) ions.

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1. Introduction

Thorium and uranium are important elements in view of nuclear energy production but create some environmental difficulties. It is well known that both the metal ions cause acute toxicological effects in mammals and their compounds are potentially carcinogen [1,2]. Thus, the fact remains that powerful extractant agents need to separate thorium and uranium ions from co-existed metal ions present in great excess in polluted media. The procedures described in the recent literature are mostly on the basis of liquid–liquid extractions for the separation of Th(IV) and U(VI), which are either less effective or time consuming due to high matrix concentration [3–8].

In contrast with the liquid–liquid extraction, which results in huge environmental problem due to toxic organic diluents, solid phase extraction technique using eco friendly materials has been widely used in the preconcentration/separation of trace and ultra trace amounts these ions [9–13]. In treatment with this method, generally, suitable chelating agents can be chemically bonded to a polymeric matrix as a support for the solid phase extraction of metal ions from aqueous solution [14–18]. Frequently, industrial application of these materials is uneconomic in large scale owing to complicated and time-consuming methods for chemical bond-

ing of the chelating agents to polymeric supports. Moreover, these resins are usually suffering from low metal ion loading capacities, expensive chemical regeneration and tedious recycling procedures.

Recently, application of impregnated resins has been proposed as a technological alternative to the other functionalized chelating resins [19,20]. The impregnating technique offers a facile preparation of sorbents for separation/preconcentration of some heavy metal ions [21–26]. This method is free from some difficulties encountered in chemically linking a chelating reagent to a support matrix and combines the advantageous features of both liquid–liquid and solid phase extraction techniques since there is a wide choice of reagents for desired selectivity. The metal binding capacity and the metal binding strength are the other important characteristics of an impregnating resin. A high capacity is usually an advantage, as small amount of impregnated resin is sufficient to concentrate metal ions from a large sample volume. On the other hand, strong metal binding can be disadvantageous in the elution step [27]. The selectivity of an impregnated resin is often relevant to the characteristic properties of the impregnated compound that is used. In spite of these capabilities, the main disadvantage of these extractant materials is their low stability because of the leakage of the extractant from the polymeric support, which results in gradual loss of their capacity and shortening the lifetime [28]. In addition, due to the absence or weak attracting tendency between some reagents and solid support the impregnation process is carried out, inadequately. These drawbacks cause to restrict application of SIRs in hydrometallurgy and other industries. Thus, in economical viewpoint, application of the impregnated resins is unacceptable for

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Nomenclature

b	Langmuir constant related to the free energy of sorption (L mmol^{-1})
C	total concentration of both exchanging species (M)
C_e	the equilibrium concentration of metal ion in the bulk solution (mg L^{-1})
C_r	total concentration of both exchanging species in the ion exchanger (M)
D	diffusion coefficient in solution phase ($\text{m}^2 \text{s}^{-1}$)
D_p	pore diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
E	D–R constant related to mean sorption energy (J mol^{-1})
k	pore diffusion constant (s^{-1})
K_F	Freundlich constant indicative of the relative sorption capacity of the SIR ($\text{mmol}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$)
k_{fi}	rate constant for film diffusion
m	weight of SIR per liter of solution (g L^{-1})
n	Freundlich constant indicative of the intensity of the sorption
q_0	D–R constant (mol g^{-1})
q_t	the amount of metal ion sorbed at any time t (mmol g^{-1})
q_e	the amount of metal ion sorbed per unit weight of SIR at equilibrium (mmol g^{-1} or mol g^{-1})
q_{\max}	Langmuir constant; theoretical maximum sorption capacity (mmol g^{-1})
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
r_0	particle radius (m)
R^2	correlation coefficient
T	temperature (K)
t	time (min or s)
X_t	fractional attainment to equilibrium at time 't'
<i>Greek symbols</i>	
β	D–R constant (g mol^{-1})
δ	liquid film thickness (m)

removal of environmental pollution. Nevertheless, the easy preparation and the extensive spectrum of highly selective available extractants, which can be impregnated on/in polymeric matrices to produce a wide range of impregnating resins with different functionality, are the advantages that cannot be ignored. In such conditions, increasing capacity and improving stabilization of the impregnating resins are solution to these problems. Consequently, any attempt to improve the stability of impregnating resins and prepare high stable materials can be an attractive area of research and substantially stimulates the further development of impregnating concept. However, insufficient efforts have been made in connection with these subjects. For instance, Trochimczuk et al. stabilized the SIRs by coating with water soluble polymers and chemical crosslinking [28]. Jerabek et al. investigated the relationship between polymer support morphology and characteristic properties of the adsorbent [29]; Muraviev et al. examined different techniques of impregnations to study stability characteristics of the SIRs [30]. Up to now, no attempt has been made to improve the structural backbone of the solid support used for the impregnation process.

In our earlier communication, we have reported the synthesis of a solvent impregnated resin containing quinzarin (1,4-dihydroxyanthraquinone, QNZ) and its analytical properties for some heavy metal ions [23,24]. More studies on this synthetic resin denote greater selectivity of the resin on Th(IV) and U(VI) than the other metal ions in moderately pH values. Thus, our studies have

been undertaken to extract these two metal ions with this SIR and overcome some limitations observed generally in treatment with the SIRs by modification of the structure of the solid support used for the impregnation process.

2. Experimental

2.1. Material and apparatus

All the reagents used were of analytical grade and except Th(IV) and U(VI) salts were supplied by E. Merck, Darmstadt, Germany. Stock solutions of Th(IV) and U(VI) were prepared at concentrations of 1.0×10^{-3} M by dissolving the appropriate amounts of its nitrate salts (Fluka, Switzerland) in 50 mL 2 M HNO_3 and diluting to the mark (250 mL) with water. The working solutions were prepared in which the pH and ionic strength were respectively adjusted to 6.00 and 0.01 M using the appropriate buffer solutions and concentration of Th(IV) or U(VI) was exceeding the detection limits. These solutions were prepared daily by using the stock solution. The reagent solutions of 1.0% Arsenazo III and Thoron I were made by dissolving 0.2500 g of these reagents in 25 mL solution of 0.4% sodium acetate and water, respectively. The solutions were protected from light by shielding with a piece of aluminium foil. The following solutions with equal concentrations of 1 M were used to adjust the pH and ionic strength of the working solutions to the desired values: formic acid/sodium formate for pH 2–4; acetic acid/sodium acetate for pH 4–6; hydrochloric acid/imidazole/sodium hydroxide for pH 6–8. To understand the morphology difference between the XAD-16 and nitrated XAD-16 resin beads before and after the impregnation process, the samples beads were gold–palladium sputter coated using a sputter coater instrument, Model SC 7620. Subsequently, the scanning electron microscopic (SEM) micrographs were obtained using a VEGA//TESCAN instrument at an accelerating voltage of 25 kV. The FTIR spectra have been registered using AVATAR 370-FTIR Thermo Nicolet in the $4000\text{--}400 \text{ cm}^{-1}$ range, using KBr discs. A Corning model 130 pH-meter was used for pH measurement. A Gallenkamp automatic shaker model BKS 305-010, UK, was used for the batch experiments. A Shimadzu model UV-1601PC spectrophotometer was used for all absorbance measurements with one pair of 10 mm quartz cells. The flow of liquids through the short column was controlled with an Eyela SMP-23 peristaltic pump and a 6-port valve (V-451, Upchurch). A Sartorius membrane filter of pore size $0.45 \mu\text{m}$ was used for filtration of the natural water samples.

2.2. Modification of the resin structure

In order to remove each type of impurity, which may be found with the fabricated beads, Amberlite XAD-16 beads (10 g) were initially treated with 20 mL of 1:1 methanol–water solution containing 6 M HCl for 12 h. The resin beads were then rinsed with doubly distilled water and dried using a vacuum pump. Afterward, modification of the resin was carried out by nitrating its benzene rings. For this purpose, a portion of 5-g of the resin beads was put into a 50-mL round bottom flask placed in an ice-water bath and a nitrating mixture, containing 10 mL concentrated HNO_3 and 25 mL concentrated H_2SO_4 was added to the flask, very slowly. The cooled mixture was stirred (magnetically) for 3 h at 60°C on an oil bath. The nitrated resin was filtered off and washed repeatedly with distilled water until free from acid content. It was then dried at 50°C and used for preparation of the modified impregnated resin.

2.3. Preparation of the SIRs

2.0 g of QNZ was put into a 50-mL stoppered flask containing 20 mL of dichloromethane and mixed, manually. After that, 1 g of

the cleaned and dried polymer adsorbent was added to the mixture and shaken for 24 h. The resin beads impregnated were then separated using a porous filter, then rinsed with aliquots of distilled water and 4 M HCl, sequentially. To prepare the modified SIR, this procedure was similarly carried out using the modified resin beads. Both types of the SIRs were stored in stoppered dark bottles containing distilled water.

2.4. Sorption equilibrium procedure

The sorption isotherms of Th(IV) and U(VI) ions on/in both types of the SIRs were obtained using the batch technique at the pH of maximum uptake (pH 6.00) and temperature 298 K. For this purpose, aliquots of 100 mL of the buffered solutions containing Th(IV) or U(VI) with various concentration ranges were placed in conical flasks and exact weighed portions of 0.05 g of the SIRs were added to each one. The mixtures were placed in an ambient temperature shaker and were shaken for 30 min. Then, 5 mL of the supernatant was withdrawn and subjected to the determination process of Th(IV) and U(VI) as discussed at the following.

2.5. Sorption rate procedure

Exact weighed portions (0.04 g samples) of both types of the SIRs were immersed into the vessels containing 100 mL buffered solutions (pH 6.00) of Th(IV) and/or U(VI) with concentration of 1.0×10^{-4} M at 25 °C. The mixtures were shaken at ambient temperature (25 ± 2 °C) for different time intervals. Portions of 5-mL of the supernatant were withdrawn from the solutions and subjected to the determination processes to indicate the decreasing of the metal ions concentrations.

2.6. Column-mode extraction

Both conventional and modified SIRs were packed separately into the analogous columns with internal diameter of 0.4 cm. The ends were fitted with glass wool to keep the SIRs inside the columns. The bed length of resin beads in the columns were about 55 mm. Aliquots of 1000-mL of the prepared working solutions were periodically passed through the column at the optimum flow rates. Before the elution process, the columns were washed with 10 mL of distilled water to remove free matrix substances. The metal ion contents sorbed on the columns were then eluted with 5 mL 1.0 M HCl at the prescribed flow rates.

2.7. The determinations procedure

2.7.1. Th(IV)

The eluents obtained from each type of the above treatments were transferred to 10-mL volumetric flasks containing 1.0 mL of Thoron I solution. After 10 min, the solutions were diluted to the marks with water and then subjected to absorbance measurements against a reagent blank prepared by the same manner at 540 nm [31].

2.7.2. U(VI)

Similarly, the eluents were transferred to 10-mL volumetric flasks containing 0.5 mL of Arsenazo III solution and diluted to the marks using 2.0 M HCl. After 20 min, the solutions were subjected to absorbance measurements against a reagent blank prepared by the same manner at 653 nm [32].

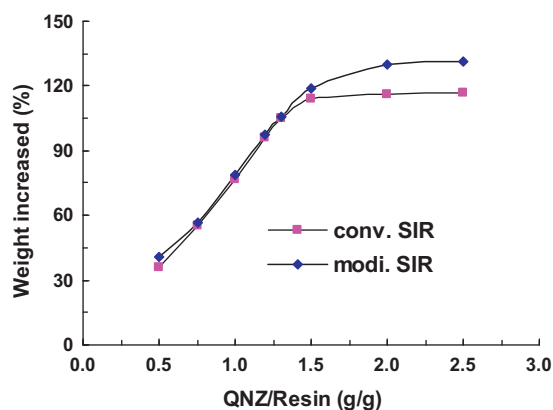


Fig. 1. Plots of weight increasing against impregnation ratio for both conventional and modified SIRs.

3. Results and discussion

3.1. Characterization of the modified SIR

Amberlite XAD-16 is an adsorbent based on polystyrene divinylbenzene-copolymer. It has excellent physical resistance, hydraulic characteristic and thermal stability. In addition, it benefits from high porosity, low polarity, and the largest surface area ($825 \text{ m}^2 \text{ g}^{-1}$) among the XAD series of Amberlite resins. Therefore, it was selected as an appropriate adsorbent for impregnation of low polarity reagents. However, it is not so much suitable for reagents having relatively more polarity. Furthermore, there is not an analogous resin from the other XAD series or similar resins having the proper conditions for such impregnation.

It is clear that substitution of $-\text{NO}_2$ groups on the benzene rings of the polymer backbone gives rise to enhance electron affinity of the resin chain. Consequently, such reagents as QNZ with high electron donor properties show a considerable tendency to impregnate in/on this type resin. The loading of QNZ in/on to the resins was recognized by weight gain of the polymer after impregnating and drying the resins. Fig. 1 depicts the weight change obtained versus the impregnation ratios. As it is shown, the curves reached to plateau at impregnation ratios more than 1.5 and 2.0 g QNZ per g Amberlite XAD-16 and NO_2 -XAD-16, respectively. This observation refers to enhancement of electron affinity of the resin backbone through the nitration process.

To investigate the other benefits of the modified resin, more studies were carried out using both types of the SIRs. Usually, the SEM micrographs are used to observe surface morphological change of the adsorbent materials during the preparation process. Fig. 2 shows the surface morphology of XAD-16 and NO_2 -XAD-16 resin beads before and after the impregnation process. The SEM images clearly show the higher impregnation efficiency of nitrated resin. As observed in Fig. 3, in comparison the infrared spectra of the prepared SIR with that of free Amberlite XAD-16 and nitrated form, there are some additional bands, which are characteristic vibrations bands of QNZ and denote on proper nitration of polymeric beads and impregnation of QNZ in/on them. For example, as observed in Fig. 3(c) and (d), the bands appeared at 1274 and 1237 cm^{-1} are attributed to hydroxyl groups present on aromatic ring of QNZ; the bands of 1629 and 1626 cm^{-1} are the characteristic stretching vibrations of carboxylic functions. Other than Fig. 3(a), the bands related to the presence of $-\text{NO}_2$ group are clearly observed at the 1527–1532 and 1351 cm^{-1} . Furthermore, it is observed that the characteristics bands related to own the polymeric skeleton are present in the impregnated resin spectrum with a slightly red shift ($5\text{--}10 \text{ cm}^{-1}$), which is confirmed that the impreg-

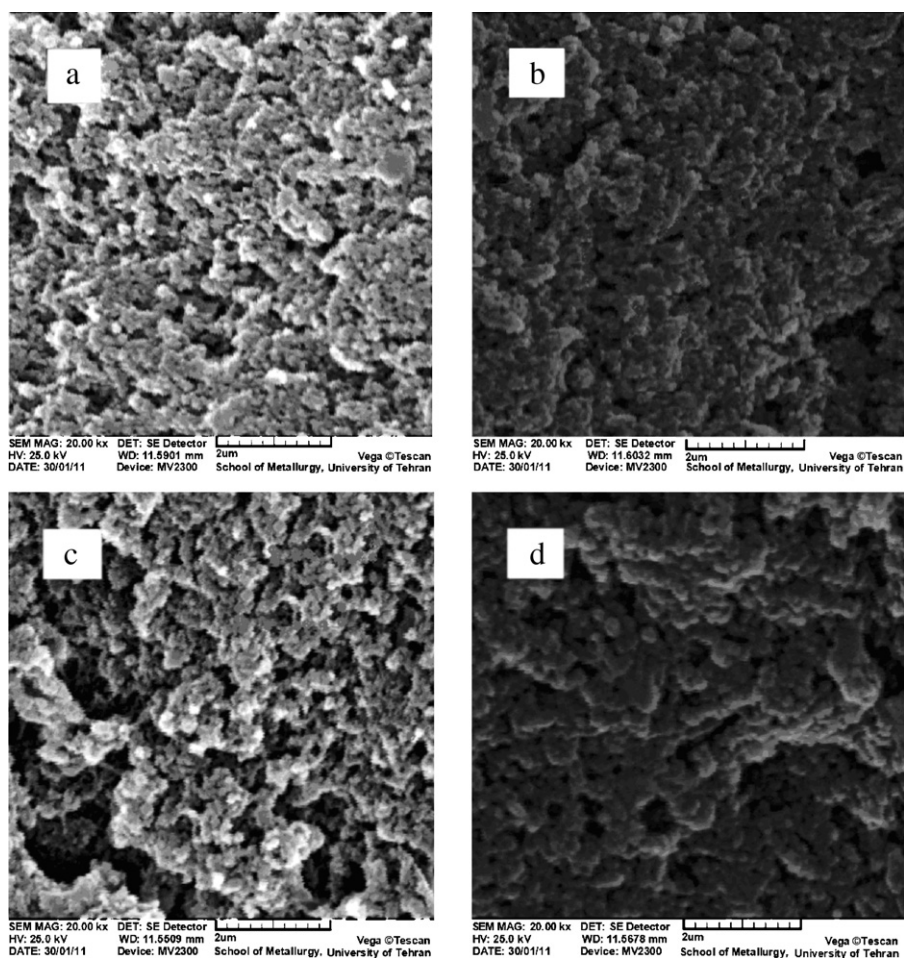


Fig. 2. Scanning electron microscopy (SEM) micrographs (20,000 \times) of polymeric support samples; (a) XAD-16, (b) QNZ-impregnated XAD-16 (conventional SIR), (c) nitrated XAD-16 and (d) nitrated XAD-16 after impregnation with QNZ (modified SIR).

nation process has been performed through a physical sorption pathway.

3.2. Effect of pH and ionic strength on the sorption process

The ability of the resin beads before and after the impregnation process to extract Th(IV) and U(VI) from weakly acidic solutions was investigated within the pH range of 2.0–8.0. Typical experiments were carried out with 0.5 g of the resin beads subjected to aliquots of 100 mL of model solutions containing 5×10^{-6} M Th(IV) or U(VI). After equilibrating (70 min), the resin beads were filtered off and washed with 5 mL 1.0 M HCl. The experiments showed that the extraction with the resin beads before the impregnation process was very weak and negligible, whereas both type of the impregnated resins exhibited a strong ability for adsorbing Th(IV) and U(VI). Fig. 4 indicates the sorption behavior of these ions on both the impregnated resins. It is noted that the modified resin exhibits moderately a better sorption behavior than the conventional impregnated resin and the maximum sorption of Th(IV) and U(VI) contents took place at lower pH values. The low efficiency of the sorption at the pHs less than 4.5 is related to decreasing the dissociated form of QNZ, which is related to its acidic dissociation constants. On the other hand, low efficiencies at the higher pHs are attributed to either precipitation or complexation of the metal ions as hydroxyl compounds. With regard to this interfering process, the subsequent investigations were carried out in buffering media.

The effect of ionic strength on the sorption processes was also studied at the presence of sodium nitrate within the concentration

range 0.01–0.5 M. It was found that the sorption efficiencies diminished at the ionic strength values greater than 0.01 M. Hence, the ionic strength did not exceed this value at subsequent investigations. This behavior is almost predictable since by increasing the ionic strength of the solutions, under the salt effect enhancement, the sorption process encountered some restriction.

3.3. Sorption equilibrium study

Generally, a solute encounters with a finite distribution between both the liquid and solid phases at the sorption equilibrium, which can be described by many isotherms and adsorption models can be used to fit the observed experimental data and determining the model parameters. Sorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of a solute in bulk solution at a given temperature under equilibrium conditions. Also, it is an important physicochemical feature for the evaluation the sorption capacity and sorption energy of an adsorbent [33]. In the current study, equilibrium studies were performed to evaluate the best fit isotherm model for explaining the sorption of Th(IV) and U(VI) onto both the prepared SIRs.

To conduct the equilibrium sorption studies, exact weighed portions of 0.05-g of both types of the SIRs were kept in contact with aliquots of 100-mL of buffered solutions containing Th(IV) or U(VI) over the concentration ranges of 1.0×10^{-5} – 1.0×10^{-3} M at pH 6.0 and temperature 298 K. For sorption of metal ions on solid adsorbents, the Langmuir, Freundlich and Dubinin–Radushkevich (D–R)

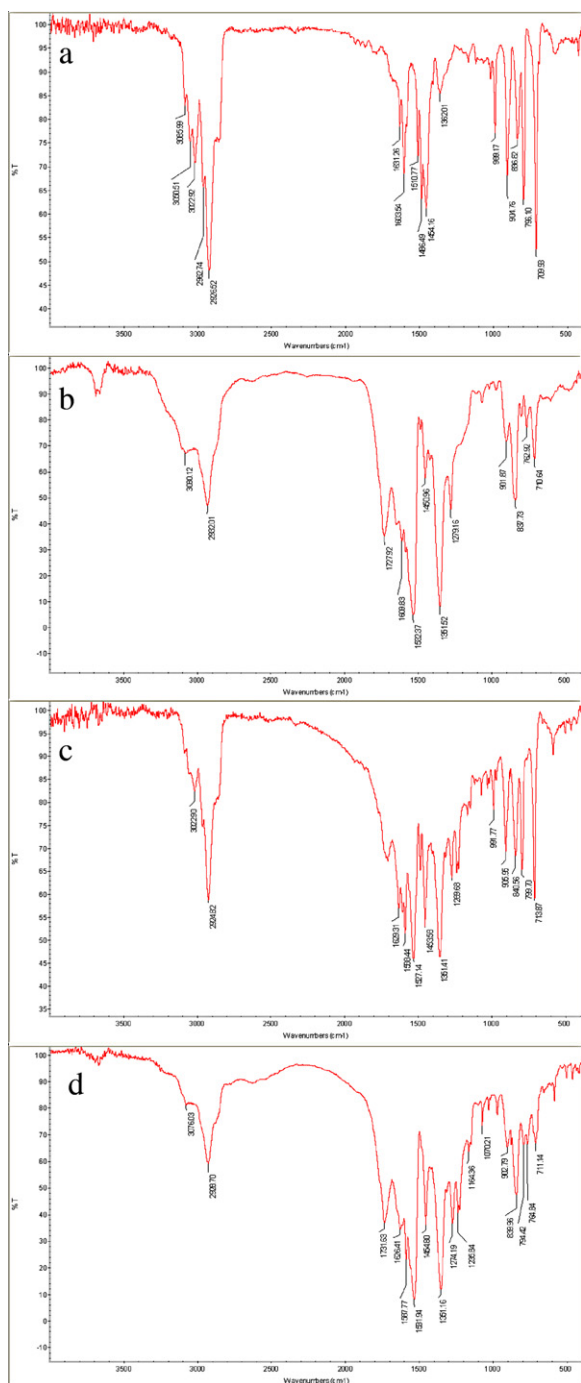


Fig. 3. IR spectra of polymeric support samples (a) Amberlite XAD-16, (b) NO₂-XAD-16, (c) QNZ-impregnated XAD-16 (conventional SIR), and (d) nitrated XAD-16 after impregnation with QNZ (modified SIR).

isotherms are of the most widely used isotherm models. Thus, the equilibrium data were analyzed using the above triple models.

3.3.1. Langmuir isotherm

The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as the following equation [34]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (1)$$

Fig. 5 shows the plots of C_e/q_e versus C_e with a high linearity and regression values for the sorption of Th(IV) and U(VI) ions onto

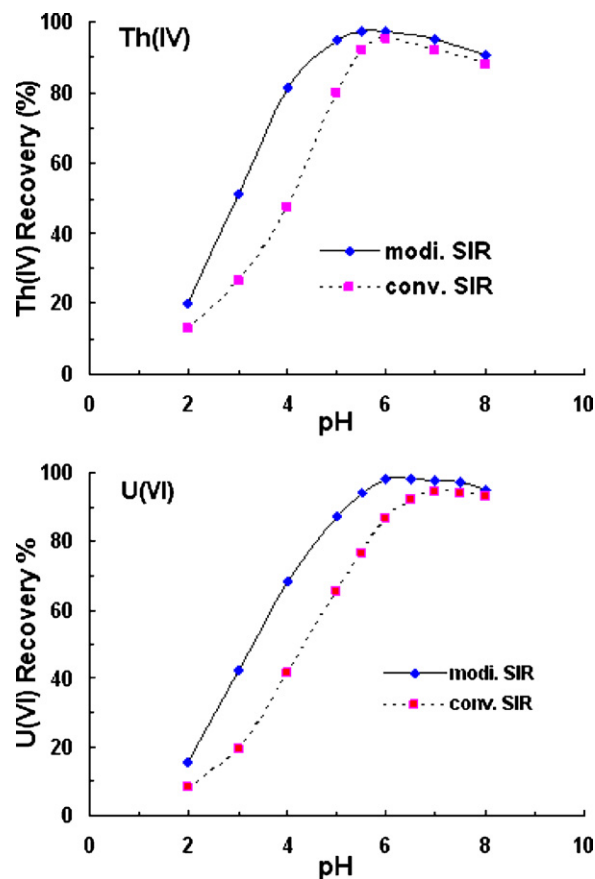


Fig. 4. Effect of pH on the recovery of thorium and uranium ions by both conventional and modified SIRs; batch experiments using 100 mL of solution of 5×10^{-6} M Th(IV) or U(VI), SIR amount of 500 mg, rpm 220 and contact time 70 min at 298 K.

both the conventional and modified SIRs. The amounts of maximum metal sorbed (q_{\max}) by the SIRs and energies of sorption were calculated from the slope and intercept of the plots, respectively. The linear equations, regression values, and the results obtained from these equations are given in Table 1.

3.3.2. Freundlich isotherm

The Freundlich isotherm can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption [35] and is expressed in linear form as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Obviously, the greater values of $1/n$, denotes on favorable sorption. For the sorption of Th(IV) and U(VI) ions onto both the conventional and modified SIRs, the linear plots of $\ln q_e$ versus $\ln C_e$ were plotted as shown in Fig. 6. The linear equations, regression values, and the results obtained from these equations are given in Table 1. As it is observed, a poor linearity is obtained according to the Freundlich model.

3.3.3. Dubinin–Radushkevich (D–R) isotherm

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich [36]. The D–R isotherm is expressed in the linear form as the following equation:

$$\ln q_e = \ln q_0 + \beta \varepsilon^2 \quad (3)$$

Table 1
Isotherms parameters and equations from Figs. 4–6 for both types of the SIR types.

Isotherm model	Equation and parameters			
Langmuir isotherm	Equation	R^2	q_{\max} (mmol g ⁻¹)	B (L mmol ⁻¹)
Th(IV)–conventional SIR	$y = 5.1939x + 0.3949$	0.9997	0.1934	13.15
U(VI)–conventional SIR	$y = 4.6614x + 0.3364$	0.9999	0.2152	13.86
Th(IV)–modified SIR	$y = 3.3151x + 0.0931$	0.9988	0.2873	48.50
U(VI)–modified SIR	$y = 3.3525x + 0.0781$	0.9997	0.2976	42.93
Isotherm model	Equation and parameters			
Freundlich isotherm	Equation	R^2	K_F (mmol ^{1-(1/n)} L ^{1/n} g ⁻¹)	n
Th(IV)–conventional SIR	$y = 0.5186x - 1.3948$	0.9239	0.2479	1.93
U(VI)–conventional SIR	$y = 0.5145x - 1.2751$	0.9177	0.2794	1.81
Th(IV)–modified SIR	$y = 0.3959x - 0.8486$	0.8720	0.4280	2.53
U(VI)–modified SIR	$y = 0.3972x - 0.8368$	0.8835	0.4331	2.52
Isotherm model	Equation and parameters			
D–R isotherm	Equation	R^2	E (kJ mol ⁻¹)	q_0 (mol g ⁻¹)
Th(IV)–conventional SIR	$y = -4.5E-9x - 7.0796$	0.9609	33.49	8.42E-4
U(VI)–conventional SIR	$y = -4.4E-9x - 6.9747$	0.9570	33.71	9.35E-4
Th(IV)–modified SIR	$y = -3.5E-9x - 6.7010$	0.9365	11.97	12.30E-4
U(VI)–modified SIR	$y = -3.3E-9x - 6.8645$	0.9352	12.40	10.24E-4

The ε and E parameters can be correlated to C_e and β using the following equations:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (5)$$

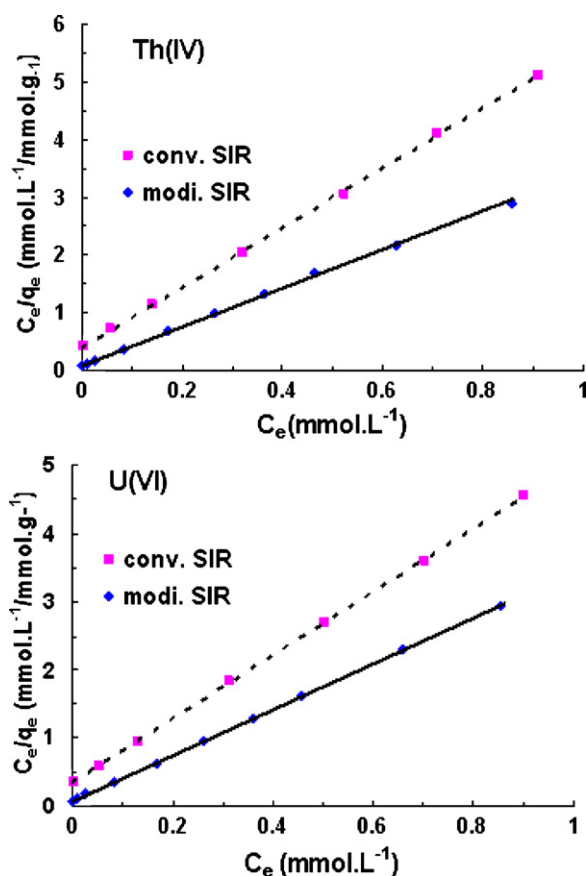


Fig. 5. Linearized forms of Langmuir sorption isotherm for sorption Th(IV) and U(VI) by both SIR (pH 6.0, rpm 200 and temperature 298 K).

Fig. 7 shows the plots of $\ln q_e$ versus ε^2 for the sorption of Th(IV) and U(VI) ions onto both the conventional and modified SIRs. Also, the calculated D–R constants for the sorption of Th(IV) and U(VI) ions onto both SIR samples are given in Table 1.

By considering the results obtained from the triple models, it is realized that the sorption process obeys the Langmuir model owing to the higher linearity and correlation coefficients obtained for Langmuir equation in comparison with the Freundlich and D–R

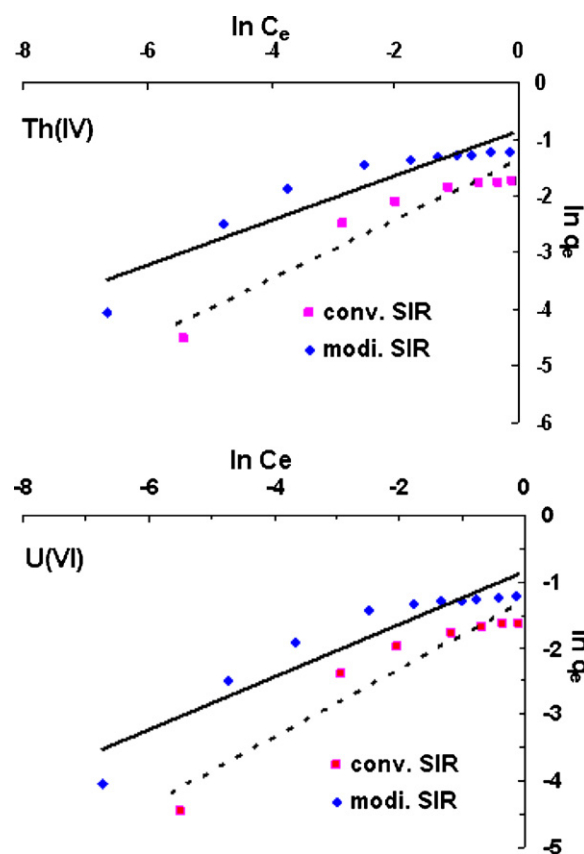


Fig. 6. Linearized forms of Freundlich sorption isotherm for sorption Th(IV) and U(VI) by both SIR (pH 6.0, rpm 200 and temperature 298 K).

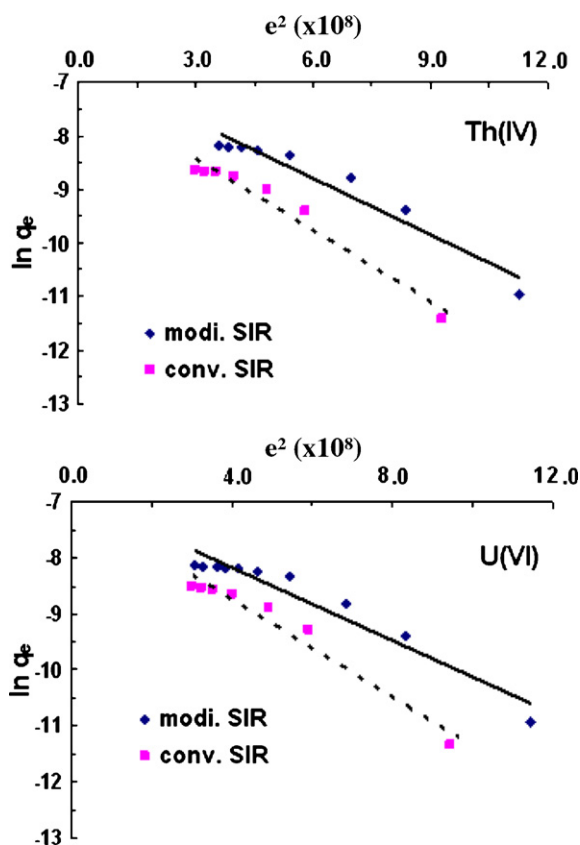


Fig. 7. Linearized forms D–R sorption isotherm for sorption Th(IV) and U(VI) by both SIR (pH 6.0, rpm 200 and temperature 298 K).

isotherm models. The fact that the Langmuir isotherm fits the experimental data satisfactorily may be owing to homogenous distribution of extractant molecules or active chelating sites on the polymeric surface of the resin beads, since the Langmuir equation assumes that the adsorbent surface is homogenous and the sorption is monolayer [37].

3.4. Metal sorption kinetic

First, the sorption of interested metal ions was studied at different agitation speed, ranging from 0 (without stirring) to 400 rpm while keeping other experimental parameters constant. The results indicated that the sorption rates of interested metal ions onto both SIRs increased with increasing agitation rate. For both SIRs, the change in sorption rate was negligible when the agitation speed increased from 200 to 400 rpm. Thus, the agitation speed of 220 rpm was selected for all the kinetic studies.

To evaluate the uptake rate of Th(IV) and U(VI), sorption capacity of the SIRs were monitored in various shaking times. From Fig. 8, it is established that complete sorption of the metal ions attained within 65 min and 45 min for the conventional and modified impregnated resins, respectively. The shortening time relevant to the modified resin, can be due to accelerating of metal ion attraction into the resin influenced on presence of $-\text{NO}_2$ group inside the resin since the liquid film around the resin beads is made narrower in comparison with the conventional resin.

Generally, the metal ion sorption onto the impregnated resins can be considered as a heterogeneous reaction between solid and solution. The sorption process can be defined by three steps: mass-transfer through the liquid film surrounding the resin beads (called external mass-transfer, or film diffusion), diffusion through the particle pores (called pore diffusion), and finally a chemical reaction

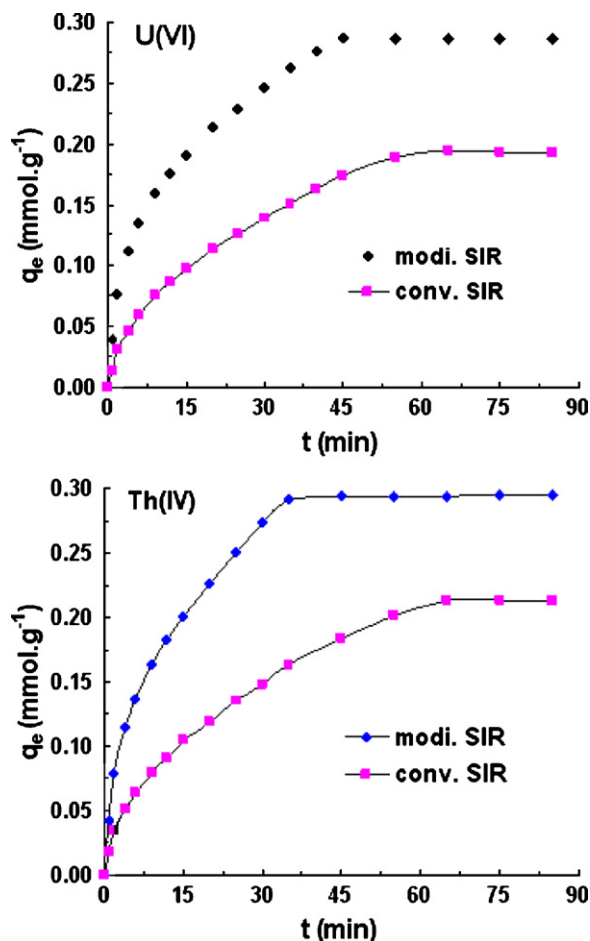


Fig. 8. Plots of sorption capacities of both conventional and modified SIRs versus time for Th(IV) and U(VI) ions. Experimental conditions: 100 mL of solution of 1×10^{-4} M Th(IV) or U(VI), SIR amount of 400 mg, pH 6.0, and rpm 220 at 298 K.

with the functional groups. Among them, the chemical reaction is being considered very fast in most cases. Inevitably, the first two steps can be the rate-controlling step, either singly or in combination. Therefore, for finding the rate-controlling step and explaining the nature of sorption process, kinetic studies were carried out using Homogenous Particle Diffusion Model (HPDM), which is a widely used kinetic model for describing the metal sorption data obtained from the various SIR systems [38–40]. In the HPDM model, the sorption mechanism involves counter diffusion of M^{n+} ions from the aqueous solution and H^+ ions from the resin phase through the above mentioned resistances. The exchange of M^{n+}/H^+ can be rigorously described by the Nernst Plank equation. This applies to counter diffusion of two species in a quasi-homogeneous media. When pore diffusion controls the mass transfer of metal ions from a volume of solution into a spherical ion-exchange particle, the relationship between the degree of fractional attainment to equilibrium (X_t) and the reaction time (s) is given as follows [41,42]:

$$-\ln(1 - X_t^2) = 2kt \text{ where } k = \frac{D_p \pi^2}{r_0^2} \quad (6)$$

If liquid film diffusion controls the sorption rate, the following analogous expression can be used:

$$-\ln(1 - X_t) = 2k_{li}t \text{ where } k_{li} = \frac{3DC}{r_0 \delta C_r} \quad (7)$$

In Eqs (6) and (7), r_0 is the average radius of the SIR particles (3.5×10^{-4} m), and X_t values are equal to q_t/q_e at various times. Linear plots based on the above equations are shown in Fig. 9 for the

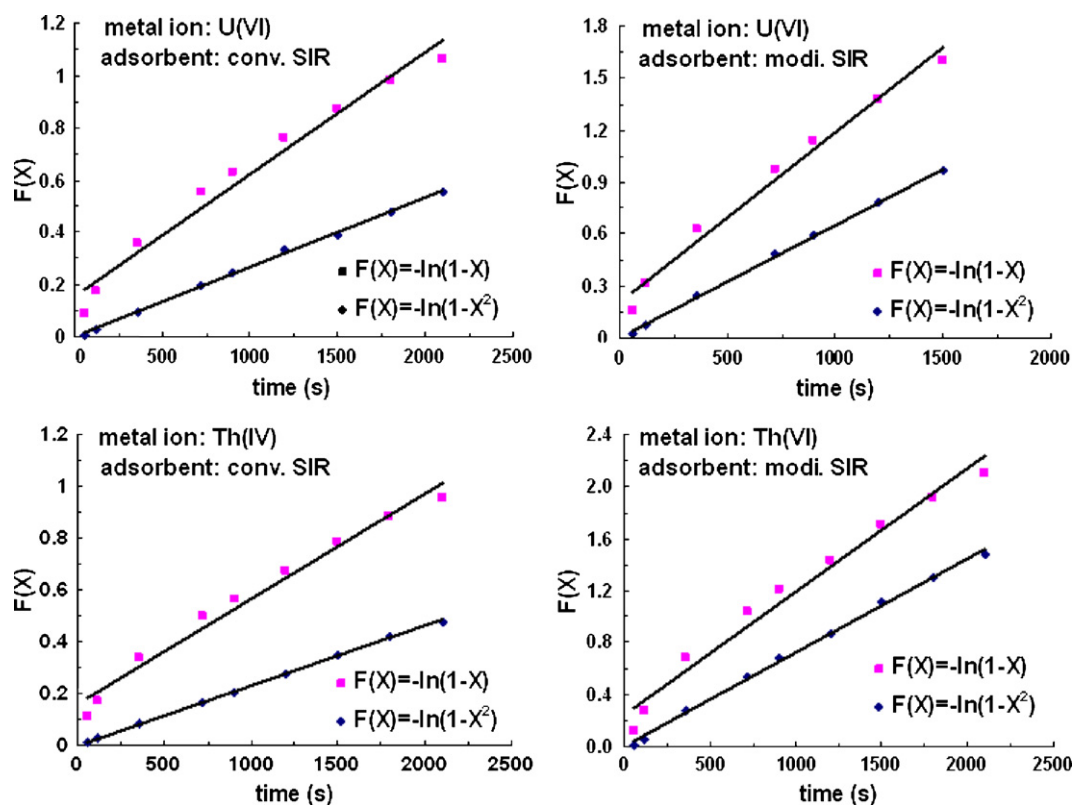


Fig. 9. Linear plots of functions $-\ln(1-X^2)$ and $-\ln(1-X)=2kt$ versus time (t) for the sorption of Th(IV) and U(VI) ions in/on both conventional and modified SIRs at the initial concentration of 1×10^{-4} M, pH 6.0, temperature 298 K and rpm 220.

sorption of Th(IV) and U(VI) ions onto/into both the conventional and modified SIR beads. Table 2 shows the results obtained from linear regression analysis of functions $-\ln(1-X^2)$ and $-\ln(1-X)$ versus time (t) at the initial concentration of 1×10^{-4} M, pH 6.0, temperature 298 K and rpm 220. It is observed for both types of SIRs that the film diffusion step can be discarded as the controlling step, since the fits do not give straight lines. In addition, the intercepts obtained from the linear plots are very high, which confirm this rejection. On the other hand, for both the conventional and modified SIRs, function of $-\ln(1-X^2)$ exhibits a satisfactory linearity over the entire range of time with a negligible intercept, indicating that the pore diffusion is the rate-controlling step in the sorption of U(VI) and Th(IV) ions onto the particles of SIRs. This can be explained by the fact that agitation reduces the film boundary layer surrounding the particles. Consequently, the mass transfer resistant made by the liquid film is decreased. At the conditions used in this study, when the SIR structure changes from conventional SIR to the modified one, the pore diffusion coefficients, D_p ($m^2 s^{-1}$) values calculated for both Th(IV) and U(VI) ions using the Eq. (6) respectively increase from 1.43×10^{-12} to $4.47 \times 10^{-12} m^2 s^{-1}$ and 1.68×10^{-12} to $4.04 \times 10^{-12} m^2 s^{-1}$. These data confirm that the presence of $-\text{NO}_2$ groups inside the resin structure dramatically increase the attraction of metal ions into the SIR beads, and accelerating the process of mass-transfer. In addition, the slightly greater

increase of D_p value for Th(IV) can be attributed to smaller radius and higher positive charge of Th^{4+} ion, which cause to better attraction of this ion into the SIR macroporous structure containing $-\text{NO}_2$ groups.

3.5. Desorption studies and stability tests

From the reusability point of view, the stability of SIR is of crucial importance and the adsorbed metal ions should be easily desorbed without destroying the SIR under the operation conditions. To find the convenient eluent for desorption the metal ions from the SIRs, various types of acid solutions including nitric, sulfuric, and hydrochloric acid were examined at different concentration values. The treatments involve stirring aliquots of 100-mL solution of 1.0×10^{-6} M metal ion with 0.05 g of each type of the SIRs for 4 h at room temperature. It was found that regardless of type of the acid, the elution process was not completed using the diluted solutions. The application of the concentrated solutions of nitric and sulfuric acids (more than 4 M) caused the SIRs to be slowly oxidized and diminish the reusability. Since the SIR exhibited a considerable stability in concentrated hydrochloric acid media, solutions with the appropriate concentration of this acid were chosen as the eluent. The experiments showed that 5 mL of 1.0 M HCl was sufficient for the complete elution of the total sorbed metal ions. The higher

Table 2

Linear regression analysis of functions $-\ln(1-X^2)$ and $-\ln(1-X)$ versus time (t) at the initial concentration of 1×10^{-4} M, pH 6.0, temperature 298 K and rpm 220.

Sorption system	$-\ln(1-X)=2k_{it}$		$-\ln(1-X^2)=2kt$	
	Equation	R^2	Equation	R^2
Th(IV)–conventional SIR	$y = 4.1E-4x + 0.1561$	0.9788	$y = 2.3E-4x - 5.9E-4$	0.9992
U(VI)–conventional SIR	$y = 4.7E-4x + 0.1532$	0.9730	$y = 2.7E-4x - 8.0E-4$	0.9982
Th(IV)–modified SIR	$y = 9.5E-4x + 0.2425$	0.9757	$y = 7.2E-4x - 2.6E-4$	0.9974
U(VI)–modified SIR	$y = 9.8E-4x + 0.2022$	0.9836	$y = 6.5E-4x - 6.7E-4$	0.9987

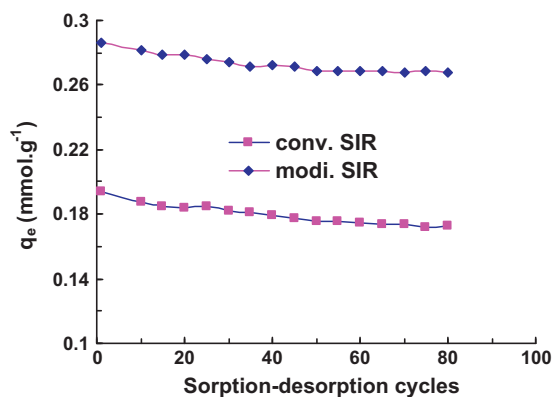


Fig. 10. Effect of the number of sorption-desorption cycles on the saturation capacities of SIR samples for Th(IV) metal ion.

Table 3

Tolerance ratio of foreign ions on the determination of 6×10^{-8} M of Th(IV) in aliquots of 1000-mL of the solution. The results are mean of three measurements.

Co-existing ions	Tolerance ratio (mol mol ⁻¹)
K ⁺ , Na ⁺ , Al ³⁺ , Fe ³⁺ , Cl ⁻ , I ⁻ , NO ₃ ⁻ , CrO ₄ ²⁻ , SO ₄ ²⁻	5000
Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Mn ²⁺ ,	1000
Pb ²⁺ , Co ²⁺ , Ln ³⁺ , MoO ₄ ²⁻	500
Cd ²⁺ , Cu ²⁺ , Ni ²⁺ , Zn ²⁺	100

desorption of interested metal ions by HCl is obviously due to the formation of rather stable metal ion complexes with chloride in the eluent solution.

To test the SIR stability, both the prepared SIRs were subjected to several loading and elution batch operations. The conditions employed for the study were: 0.05 g of the SIR beads was stirred with 100 mL solution of 1.0×10^{-3} M Th(IV) for 4 h at room temperature. After washing the Th(IV)-loaded SIR beads with 10 mL of distilled water, the elution operations were carried out by shaking the SIR with 5 mL of 1.0 M HCl solution for 20 min to ensure complete equilibration. The operating saturation capacity was calculated from the loading and elution tests. As shown in Fig. 10, the results obtained from both the prepared SIRs agreed within 2–5% error up to 40–50 cycles of repeated experiments. After that, the modified resin showed better reusability and stability towards this metal ion. This can be explained by considering that the impregnation of macroporous matrices leads to the immobilization of the extractant both in pores and in the gel regions of the polymer beads. The impregnating extractant located in the pore volume is weakly retained by the polymer (mainly due to the capillary forces) and can be easily leached out from the freshly prepared EIR samples during the first days of its use (unstable part of SIR capacity which is smaller than 5% for the both SIRs used in this study). The impregnating extractant taken up by the gel regions of the matrix represents the most stable part of the SIR capacity, which remains practically constant for a long period

Table 4

Tolerance ratio of foreign ions on the determination of 6×10^{-8} M of U(VI) in aliquots of 1000-mL of the solution. The results are mean of three measurements.

Co-existing ions	Tolerance ratio (mol mol ⁻¹)
K ⁺ , Na ⁺ , Al ³⁺ , Fe ³⁺ , Cl ⁻ , I ⁻ , CrO ₄ ²⁻ , SO ₄ ²⁻	5000
Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Mn ²⁺ , NO ₃ ⁻	1000
Pb ²⁺ , Co ²⁺ , Ln ³⁺ , MoO ₄ ²⁻	500
Cd ²⁺ , Cu ²⁺ , Ni ²⁺ , Zn ²⁺	100

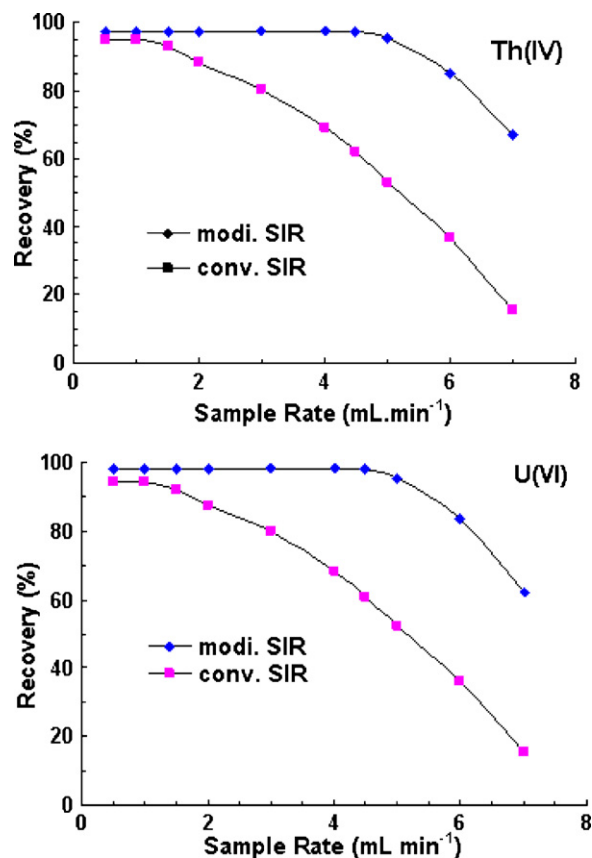


Fig. 11. Effect of flow rate of the sample solution on recovery of Th(IV) and U(VI) ions from the minicolumn.

3.6. Column-mode extraction study

For extraction of metal ions of interest using the columns packed with the of SIRs, several parameters, which influence on the performance was studied. These important parameters consist of sample and eluent flow rates, concentration of the eluent and enrichment factor.

The effect of sample and eluent flow rates on the extraction process were respectively examined in the flow rates range of 0.5–7 and 0.5–3.5 mL min⁻¹ using 100 mL of model solutions (1×10^{-7} M Th(IV) and 6×10^{-7} M U(VI)). When the influences of flow rates of sample were examined, the eluent flow rate was kept constant at 0.5 mL min⁻¹ and also the flow rate of sample was kept at 1 mL min⁻¹, when the effects of flow rates of the eluent were examined. As shown in Fig. 11, the sorption of Th(IV) and U(VI) were carried out quantitatively up to the sample flow rates of 4.5 and 1 mL min⁻¹ relevant to the modified and conventional SIRs, respectively. The optimized elution of Th(IV) and U(VI) could be carried out at the flow rates of 1.5 and 0.5 mL min⁻¹ in treatment with the modified and conventional SIRs, respectively.

For quantitative elution, HCl at various concentrations and volumes was examined. The experiments showed that these metal ions can be eluted thoroughly from the columns using 5 mL of 1 M HCl, irrespective to type of the SIRs.

The enrichment factor was studied in treatment with a series of solutions containing fixed amount of the examined metal ion (5×10^{-8} mol) at different volumes (50–3000 mL). The enrichment factor is calculated as the ratio of the highest sample volume to the eluent volume (5 mL). Irrespective of type the metal ions, it was found that the recoveries were >95% up to 1500 and 1250 mL, using the modified and conventional SIRs, respectively. In spite of this feasibility, owing to uniformity in measurements, aliquots of

Table 5
Application of the proposed method for the determination of Th(IV) and U(VI) in natural water samples. The results are mean of three measurements \pm standard deviation.

Samples	Spiked amount (nmol)		Measured (nmol)		Recovery%	
	Th(IV)	U(VI)	Th(IV)	U(VI)	Th(IV)	U(VI)
Ghazi spring	–	–	–	5.51 \pm 0.13	–	–
	50	50	48.05 \pm 1.22	51.76 \pm 1.08	96.1	93.2
Depth well water	–	–	–	–	–	–
	60	60	57.48 \pm 0.78	57.83 \pm 0.69	95.8	96.4
Semi-depth well water	–	–	–	–	–	–
	60	60	60.60 \pm 0.83	60.77 \pm 0.98	101.0	101.3

1000-mL of the sample solutions were preferred to use. Therefore, the enrichment factors calculated as the ratio of the sample volume to volume of the solution prepared for the absorbance measurements were found to be 100 for both metal ions of interest.

3.7. Analytical applications

By considering the above investigations, it was evident that applicability of the modified SIR is significantly better for extraction of these metal ions. Hence, in treatments with aliquots of 1000-mL of the solutions, the Th(IV) and U(VI) contents were extracted with the column packed with the modified SIR and then subjected to the determination processes. The calibration curves were linear in the ranges 2.5×10^{-8} – 4.5×10^{-7} and 1.0×10^{-8} – 1.5×10^{-7} M for Th(IV) and U(VI), respectively. The linear regression equations could be expressed as follows:

$$\text{Th(IV)}: A = 1.6562 \times 10^6 C + 0.0025; R^2 = 0.9992$$

$$\text{U(VI)}: A = 5.1774 \times 10^6 C + 0.0021; R^2 = 0.9990$$

where A is the absorbance, C is the molar concentration of the metal ion, and R^2 is the correlation coefficient. All of the statistical calculations were based on the average of three determinations. The limits of detection (LOD) corresponding three times to the standard deviation of the blank ($n=7$) were found to be 5.6×10^{-9} M and 1.6×10^{-9} M for Th(IV) and U(VI), respectively.

3.8. Effects of matrix ions interferences

To evaluate the analytical applications of the recommended procedure, the effect of some foreign ions which may interfere with the determination of these metal ions was examined. For this purpose, fixed amounts of metal ions of interest (6×10^{-8} M) were taken with different amounts of foreign ions and the recommended procedure was followed. The tolerance limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of metal ion of interest. The results are summarized in Tables 3 and 4. It was noteworthy that some ions including Ca^{2+} , Mg^{2+} , K^+ , Na^+ , HCO_3^- , Cl^- , and SO_4^{2-} as essential constituents of natural water are tolerable, considerably. The results also show that commonly occurring ions in water samples like many heavy metal ions have no pronounced interference effect even at much higher concentrations.

3.9. Analysis of real samples

The proposed method was applied for determination of metal ions of interest in spring, well and tap water samples collected from areas of Kashmar, a city in Iran, Khorasan Rasavi province. The water samples for such determinations were filtered through a membrane filter with a pore size of 0.45 mm before the determination. The accuracy of the determinations was investigated by spiking water samples with Th(IV) and U(VI) ions at various concentrations. The

results obtained are present in Table 5. As it can be seen from the results, the recoveries for the spiked amounts of these metal ions were found to be >93%, which confirmed the accuracy at the 90% confidence level for application of the proposed method.

4. Conclusion

The newly synthesized resin combined the benefits of chemical functionalized resins with impregnated techniques. The synthesis was initially progressed to nitration of the benzene rings present in backbone of resin before the impregnating process. This treatment gave rise to obtain an impregnated resin with considerable better properties in comparison with the conventional prepared SIR. The modified SIR exhibited some benefits such as faster rate of equilibrium, higher capacity and sorption rate. It could be recycled much more times than the conventional SIR without any lowering its sorption capacity. The results obtained show that the modified SIR has good potential for trace enrichment of Th(IV) and U(VI) ions. It combines efficient separation of these metal ions in the presence of various interfering ions with their spectrophotometric determinations. It is highly useful in the analysis of natural water samples since the modified SIR has negligible affinity for alkali and alkaline earth metal ions.

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