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Solvent Extraction and Separation of Thorium(IV) from Chloride Media by a Schiff Base

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Abstract The Schiff base extractant, (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt), for thorium(IV) ions was characterized in methylene chloride in chloride media. Analyses of the conventional $\log_{10} D$ versus pH and versus $\log_{10}$ thorium ion concentration plots of the extraction equilibrium data reveal that the thorium(IV) ions were extracted as a complex that is characterized by having one ionizable hydrogen ion and a metal:ligand ratio of 1:1. The effects of contact time, A:O phase ratio and temperature on the extraction and stripping were studied. Extraction and stripping isotherms were constructed to determine the theoretical stages of the extraction and stripping processes. The thermodynamic parameters Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes associated with the extraction processes were evaluated. Finally, the optimum parameters of solvent extraction were applied to a chloride leach liquor.

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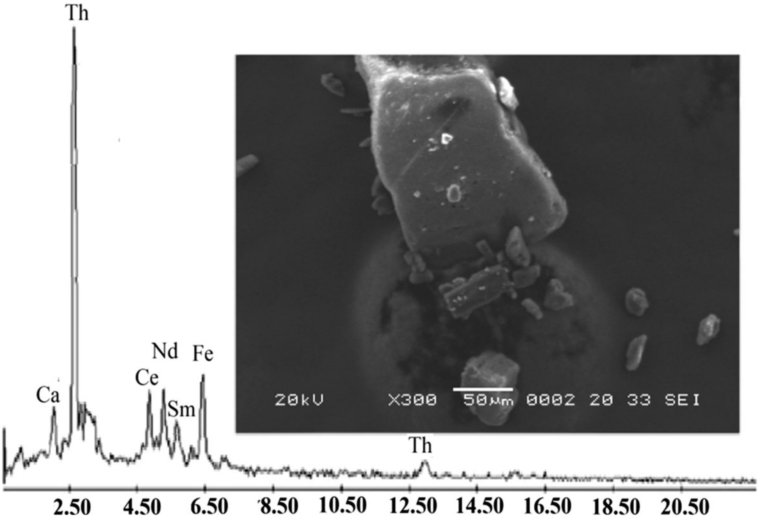
Graphical Abstract



Keywords Solvent extraction · Thorium · Schiff base · Chloride media · Isotherm

1 Introduction

Thorium has a great importance in the nuclear energy fields. Thorium is a naturally occurring, radioactive and widely distributed element, present in small amounts all over the earth's surface. It occurs in several minerals, the most common ones are monazite sand, thorianite, thorite and thoganite [1]. Thorium is used in industrial and technological applications. So, the separation, isolation, and recovery of thorium have their own importance. Solvent extraction has been the most commonly used technique for the separation and recovery of thorium [2].

Extensive efforts were recently focused on the solvent extraction of thorium(IV). Several organic extractants were used for the extraction of thorium(IV) such as di-(2-ethylhexyl)-2-ethylhexyl phosphonate [3], *bis*(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [4], organo phosphoric compounds in various media [5–13], *N*-*n*-heptylaniline [14], *N*-*n*-octylaniline [15], a mixture of *N*-*n*-octylaniline and trioctylamine [16], 2-octylaminopyridine [17], and TODGA in ionic liquids that were successfully employed for the recovery of thorium(IV) in industry [18]. Solvent extraction of thorium(IV) ions from perchlorate solution was carried out using didodecyl-phosphoric acid, DDPA, in chloroform diluents [19, 20]. Extraction of thorium(IV) by triphenylarsine oxide from salicylate media has also been carried out [21]. The stripping behavior of thorium(IV) from HEH/EHP (2-(ethylhexyl)phosphoric acid mono-2-ethylhexyl ester) with H_2SO_4, HCl and HNO_3 was studied [22]. The extraction of thorium by β-hydroxy naphthaldoxime in the presence of neutral organo-phosphorous compounds in *o*-xylene was studied [23].

The extraction of thorium(IV) from nitric acid solutions by di-*n*-butyl sulfoxide (DBSO) in *o*-xylene has been evaluated [24]. Tri-*n*-octyl phosphine oxide (TOPO) in cylcohexane was used to extract thorium(IV) from nitrate solutions [25]. Triphenylphosphine oxide (TPPO) dissolved in toluene was chosen for extraction of both uranium and thorium [26].

The behavior of thorium(IV) extraction from aqueous nitric acid was studied using 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) in the presence of tri-*n*-octyl phosphine oxide (TOPO) as well as tri-*n*-butyl phosphate (TBP) in xylene [27]. The extractive properties of diphenyl-*N*,*N*-dimethyl carbamoyl methyl phosphine oxide (DPDMCMPO) towards thorium(IV) and europium(III) ions were studied in dichloromethane in nitrate media at 293 K [28]. The synergistic effect of mixtures of Cyanex 923 and organophosphorus acids including P_2O_4, P_5O_7 and Cyanex 272 were applied to the extraction of Ce(IV) and Th(IV) from sulfuric acid solutions [29]. The extraction of thorium(IV) and uranium(VI) from nitric acid solutions using mixtures of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and dicyclo hexano-18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, or benzo-15-crown-5 was investigated [30]. Moreover, the liquid–liquid extraction of uranium(VI) and thorium(IV) by two open-chain crown ethers with two terminal quinolyl groups were also studied in chloroform [31].

In addition, the solvent extraction of thorium(IV) and uranium(VI) was carried out using mixtures of para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones and crown ethers [32]. The solvent extraction process for thorium(IV) and uranium(VI) from the sulfate leach liquor generated in the chemical treatment of monazite, using a solvent containing a mixture of Primene JM-T and Alamine 336, was described [33]. A calixarene derivative, 5,11,17,23-tetra-(diethoxyphosphoryl)-25,26,27,28-tetra acetoxycalix-4-arene (L), was used for the separation of thorium(IV) and rare earths in nitrate medium [34]. The extraction and stripping of thorium(IV) from the hydrous oxide cake of Egyptian monazite sands, obtained after alkaline dissolution followed by leaching with alkaline carbonate solution, has been investigated. This cake was dissolved in 4 mol·L^{-1} HNO_3 and thorium(IV) was extracted selectively by a counter-current extraction system using a mixer–settler contactor with Aliquat-336 in kerosene as extractant [35].

In the present study, a chelating agent Schiff base was synthesized and then applied to the extraction and separation of Th(IV) from hydrochloric acid solutions. The effects of various experimental parameters on the extraction of Th(IV) from the synthetic solution and the stripping from the loaded organic solution were studied. These factors include pH, extractant concentration, contact time, A:O ratio and temperature in the extraction process, while the stripping parameters include strippant concentration, contact time, phase volume ratio, and temperature. Finally, the optimum parameters are applied to Th(IV) extraction from the thorium leach liquor obtained from the cataclastic rock sample collected from South Eastern Desert, Egypt.

2 Experimental Section

2.1 Instrumentation

A double-beam recording UV/visible spectrophotometer model 160-A, Shimadzu, Japan, was used for measuring the absorbance of the solutions. The inductively coupled plasma-optical emission spectrometry (Prodigy high dispersion ICP, TELEDYNE, Leeman Labs, USA) was also used for measurement of thorium and trace elements. Absorption spectra in the IR region were collected using a Fourier transform infrared spectrometer (FT-IR) (Thermo Scientific, NICOLET iS10, USA); this spectrometer was used to characterize the major functional groups of the synthesized extractant and the complex formed. The elemental analyses of the Schiff base were carried out using a Perkin Elmer (Rotkreuz, Switzerland) elemental analyzer (Model 240C).

The scanning electron microscopy (SEM) image was taken using a Jeol (Tokyo, Japan) JSM 5600 LV scanning electron microscope equipped with an Oxford Instruments 6587 EDX microanalysis detector. An X-ray diffraction technique (XRD) was used to identify the unknown minerals.

2.2 Preparation of Main Working Solutions

2.2.1 Preparation of Thorium(IV) Solution

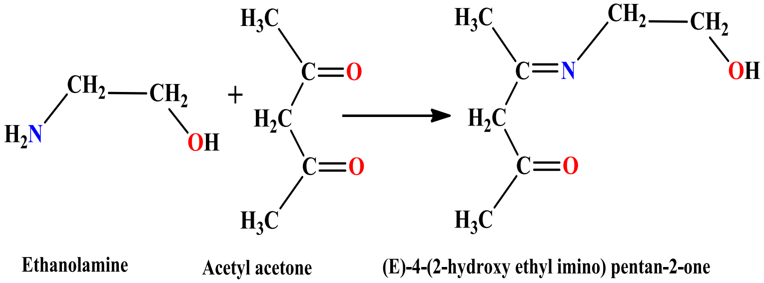
A standard stock solution of 4.3×10^{-3} mol·L^{-1} Th(IV) was prepared by dissolving 2.077 g of A.R. grade (BDH) hydrated thorium chloride ($ThCl_4 \cdot 6H_2O$, 99%) in 10 mL concentrated hydrochloric acid (Poch LTD, Poland, 99%) and diluted to 1 L with distilled water. The working solutions were prepared by appropriate dilution of the stock solution with distilled water. This solution was actually used to determine the relevant factors of thorium extraction using the prepared Schiff base.

2.2.2 Preparation of Some Ionic Solutions

Several standard stock solutions of 1 g of possible ions were prepared by dissolving suitable weights of their salts (A.R. grade, 99%) in 1 L distilled water, e.g. 3.56×10^{-2} mol·L^{-1} Si^{4+}, 3.71×10^{-2} mol·L^{-1} Al^{3+}, 2.49×10^{-2} mol·L^{-1} Ca^{2+}, 1.79×10^{-2} mol·L^{-1} Fe^{3+}, 2.09×10^{-2} mol·L^{-1} Ti^{4+}, 3.23×10^{-2} mol·L^{-1} P^{5+}, etc. These ions were used as the standard solutions during the determination of each ion in the thorium leach liquor.

2.2.3 Synthesis of (E)-4-(2-hydroxyethylimino)pentan-2-one

The Schiff base ligand (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) was synthesized by refluxing an ethanolic solution of 0.01 mol of acetylacetone (Sigma–Aldrich, 99%) with 0.01 mol of ethanolamine (Sigma–Aldrich, 98%) for 6 h [36]. Recrystallization from absolute ethanol, following filtration, and then washing using ethanol (Loba Chemie, India, 99%) and diethyl ether (Loba Chemie, India, 99%) afforded pure products. The preparation of the studied ligand containing nitrogen and oxygen donor atoms is shown in Scheme 1.



Scheme 1 (E)-4-(2-hydroxyethylimino)pentan-2-one synthesis

2.3 Experimental Procedures

The aqueous phase containing 0.43×10^{-3} mol·L^{-1} thorium(IV) was adjusted to the desired pH value with 1 mol·L^{-1} hydrochloric acid and 1 mol·L^{-1} sodium hydroxide solutions, and the aqueous phase was then equilibrated by shaking for a certain time in a separating funnel with an appropriate volume of the organic phase. The aqueous and organic phases, after equilibration, were allowed to settle and then were separated. The Th(IV) concentration in the separated aqueous phase was measured by the spectrophotometric technique using Thoron I reagent.

The extraction distribution ratio (D_e) was used as the most important index for determining the efficiency of the solvent extraction process and was calculated by the following equation [37]:

$$D_{\mathrm{e}} = \left(\frac{C_i - C_{\mathrm{A}}}{C_{\mathrm{A}}}\right) \cdot \frac{V_{\mathrm{A}}}{V_{\mathrm{O}}} \tag{1}$$

where the extraction distribution ratio (D_e) is defined as the concentration of species in the organic phase divided by the remained concentration in the aqueous phase. C_i is initial concentration of Th(IV), and C_A is the thorium(IV) concentration in the aqueous phase after the extraction procedure. The extraction percentage (E) was evaluated from the following equation:

$$E = \frac{100D_{\mathrm{e}}}{D_{\mathrm{e}} + \left(\frac{V_{\mathrm{E}}}{V_{\mathrm{O}}}\right)} \tag{2}$$

where V_A and V_O are the volumes of the aqueous and organic phases, respectively.

The stripping experiments were carried out by shaking different volumes of the organic phase solutions containing the extracted metal after extraction and the aqueous solution of the stripping agent (0.5 mol·L^{-1} HNO_3) under contact time ranging from 1 to 15 min at room temperature. After equilibration and settling, a complete separation of the two phases was obtained. Known aliquot portions were carefully withdrawn from the stripping aqueous phase for measuring the concentration of the stripped thorium(IV) ions.

The percentage of stripping (S) was calculated accordingly from the equation:

$$S = 100 - \left(\frac{100D_{\mathrm{e}}}{D_{\mathrm{e}} + \left(\frac{V_{\mathrm{A}}}{V_{\mathrm{O}}}\right)}\right) \tag{3}$$

All the extraction and stripping studies were carried out at ambient temperature (298 ± 1 K), except when studying the effect of temperature. All experiments were repeated several times in order to confirm the correctness of the obtained results. The relative errors are no more than 5%.

3 Results and Discussion

3.1 Characterization of the AcEt

The purity of the synthesized Schiff base was confirmed by its melting point, elemental analysis, and FT-IR analysis. The yield of yellow colored (E)-4-(2-

hydroxyethylimino)pentan-2-one (AcEt) was 84.8% (13.6 g), and melting point 338 K (Scheme 1). The elemental analysis: calculated % for $C_7H_{13}NO_2$ are: C, 58.72%; H, 9.17%; N, 9.78%. Found: C, 58.48 ± 0.54%; H, 9.15 ± 0.25%; N, 9.78 ± 0.30%.

Fourier transform infrared spectroscopy (FT-IR) was used to detect the various functional groups in the Schiff base ligand. The FT-IR spectra of the (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) and its complex with thorium ions are shown in Fig. 1. The FT-IR spectra of the AcEt ligand had a strong band, centered at nearly 3440 cm^{-1}, which could be due to the stretching vibration of the O–H group. The band ν(O–H) appeared as slightly broad which could be due to the presence of some intra- and/or intermolecular hydrogen bonds, but this also could be due to the overlapping of the symmetric stretching band with the asymmetric stretching band [38]. The red shift of the O–H band from 3440 to 3420 cm^{-1} in the AcEt–Th(IV) complex strongly indicates the interaction of this group in the chelate structure. The bands which appeared at 1630 and 1560 cm^{-1} could be due to the stretching vibration of the C=O and C=N bands, respectively. These bands shifted (10–15 cm^{-1}) towards lower wave number in the Th(IV) complex which reveals the participation of these groups in the chelate's structure.

The appearance of some new bands in complexes in the range around 600 and 450 cm^{-1} could be due to the formation of Th–O and Th–N bands, respectively [39]. Finally, according to the previous analysis, the structure of the complex could be postulated as follows (Scheme 2):

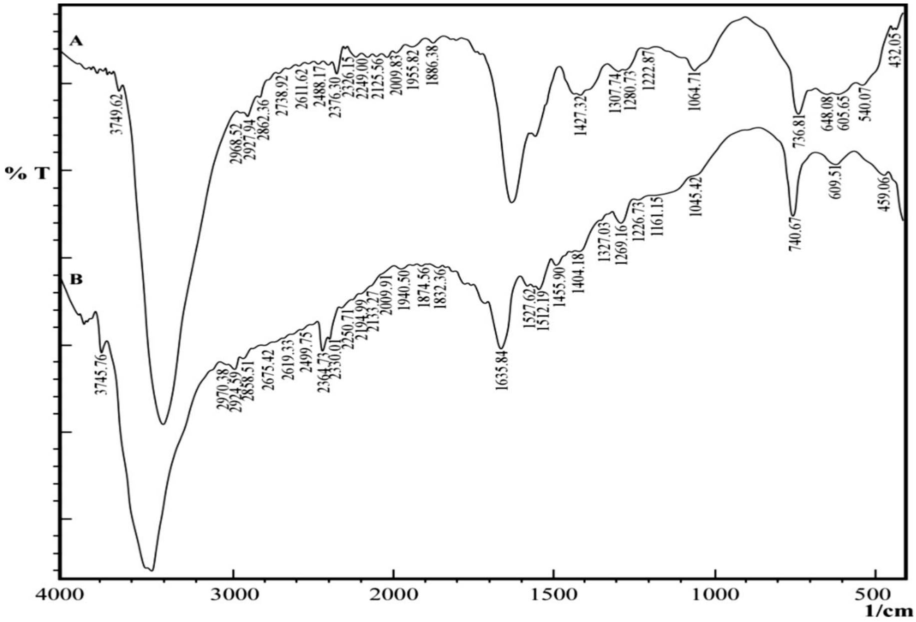


Fig. 1 FT-IR spectrum of **a** AcEt and **b** the AcEt–Th(IV) complex

3.2 Extraction Investigation

3.2.1 Effect of Diluent Type

The dissolution of the Schiff base (AcEt) was tested in various aromatic and aliphatic organic diluents, such as benzene, toluene, petroleum ether, kerosene, chlorobenzene, methylene chloride, chloroform, and diethyl ether. The purities of all diluents were 99% and obtained from Loba Chemie, India. From the obtained results, it was found that the (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) was completely dissolved in methylene chloride. Therefore, methylene chloride was used to dissolve the AcEt in the next studies.

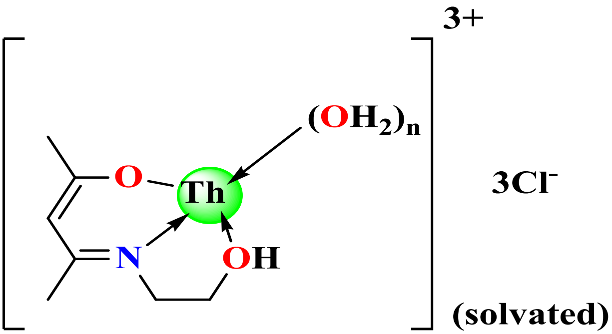
3.2.2 Effect of pH

The influence of pH on the extraction behavior of thorium(IV) with the chelating extractant (AcEt) was studied; various experiments were performed at pH values ranging from 1 to 9 with the other parameters held constant at 0.4×10^{-3} mol·L^{-1} Th(IV) in the aqueous solution, 0.17% ($0.012\ \text{mol·L}^{-1}$) AcEt in methylene chloride and 3:1 aqueous to organic phase ratio for 7 min contact time at room temperature. From the obtained results shown in Fig. 2, it is clearly evident that the thorium(IV) extraction efficiency gradually increased with increasing pH until reaching a maximum value at pH 6.5.

At low pH, the hydrogen ions will be in excess in the acidic solution, which could lead to the protonation of the oxygen atoms of the studied Schiff base. As a result of the increasing acidity, the hydrogen ions competes with the thorium ions during the extraction. Consequently, the thorium(IV) extraction efficiency decreased at low pH. With increasing pH, the hydrogen ion concentration decreased; therefore, the reaction of hydrogen ions with the internal oxygen atoms of AcEt decreased and the Th(IV) complex was increasingly produced, leading to a higher extractability of Th(IV). Hence, the selected pH 6.5 was used for the Th(IV) extraction using the studied extractant, since it gave the highest uptake.

The $\text{pH}_{0.5}$ in solvent extraction is the pH at which the extraction efficiency for metal ions is 50% or the value of pH in an aqueous phase at which the distribution ratio (D) is unity. From the obtained data, the quantitative extraction of thorium(IV) for AcEt ligands at pH 4.5 became 57.03%. Therefore, the $\text{pH}_{0.5}$ value is 3.95.

A plot of $\log_{10} D$ against pH gave a straight line whose slope is 0.84 (Fig. 3). The slope value represents the number of hydrogen ions released during the formation of the



Scheme 2 The postulated structure of the AcEt–Th(IV) complex

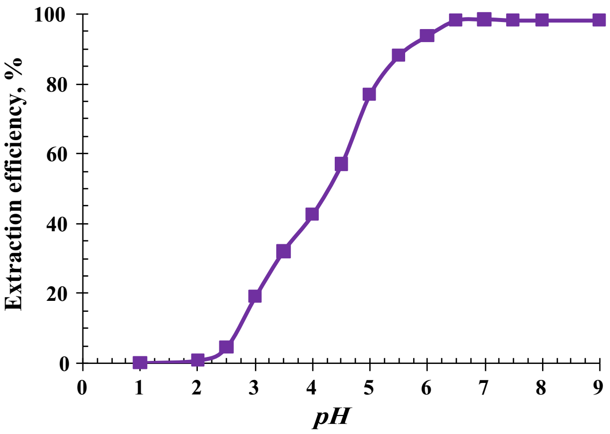


Fig. 2 Effect of pH on the Th(IV) extraction using AcEt extractant (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), 0.012 mol·L^{-1} AcEt in methylene chloride, 3:1 A:O phase ratio, 7 min contact time, room temperature)

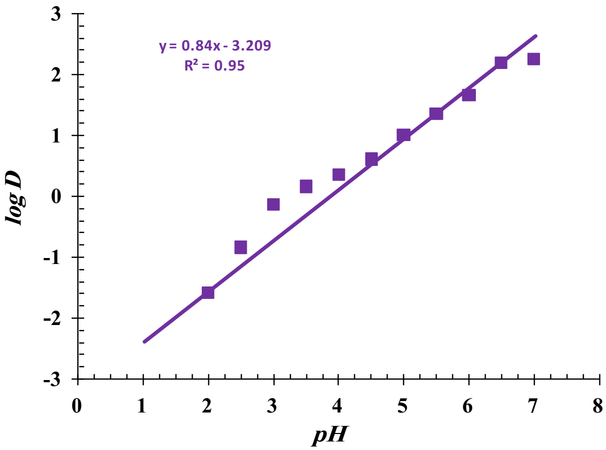
thorium–AcEt complex, so it indicates that one hydrogen ion was released in the aqueous medium during the extraction procedure.

It was visualized that the large size of thorium(IV) would assist in reducing the hydrolysis and steric hindrance that is experienced by the incoming organophilic oxo donor, thereby increasing the metal ion's extractability. However, thorium may also form several monomeric hydroxo or chloro species owing to its partial hydrolysis in the solutions. Based on the experimental evidence, primarily on the slope analyses of the extraction results, the following equation is recommended for the Th(IV) extraction by the studied extractant (HY) into the methylene chloride diluent:

$$\mathrm{Th^{+}Cl_{3(A)}} + \mathrm{HY_{(O)}} \rightleftharpoons \mathrm{Th \cdot Y(Cl)_{3(O)}} + [\mathrm{H^{+}}]_{(A)}$$

where HY is the monoanionic Schiff base, the subscripts, A and O donate the aqueous and organic phases respectively. At pH 6.5, the extraction mechanism corresponds to a cation

Fig. 3 $\log_{10} D$ against pH plot for the Th(IV) extraction efficiency using AcEt extractant (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), 0.012 mol·L^{-1} AcEt in methylene chloride, 3:1 A:O phase ratio, 7 min contact time, room temperature)



exchange, in which a complex of stoichiometric formula Th·Y(Cl)$_3$ is possibly formed in the organic phase, liberating at the same time 1 mol of H^+ ions in the aqueous phase. In this case, the extraction constant (K_{ex}) can be expressed as follows:

$$K_{ex} = \frac{[Th \cdot Y(Cl)_3]_{(O)}[H^+]_{(A)}}{[ThCl_3^+]_{(A)}[HY]_{(O)}} \tag{4}$$

$$K_{ex} = \frac{D[H^+]_{(A)}}{[HY]_{(O)}} \tag{5}$$

$$\log_{10} D = \text{pH} + \log_{10} K_{ex} + \log_{10}[HY] \tag{6}$$

According to Eq. 6, a plot of $\log_{10} D$ against pH yields a straight line, the slope of which is equal to the number of hydrogen ions released during the formation of the thorium–ligand complex.

3.2.3 Effect of Extractant Concentration

The effect of AcEt concentration in methylene chloride on the Th(IV) extraction efficiency was studied in the concentration range from 0.001 to 0.030 mol·L^{-1} at pH 6.5 for 7 min shaking time and 3:1 A:O phase ratio at room temperature (Fig. 4).

The data show that the Th(IV) extraction progressively increased from 66.25 to 98.18% with increasing concentration of (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) from 0.001 to 0.012 mol·L^{-1} (0.17%). Upon further increase in the extractant concentration, up to 0.030 mol·L^{-1}, the extraction efficiency did not change significantly and showed a plateau due to the excess of the free extractant. Hence, 0.012 mol·L^{-1} AcEt was the optimum concentration chosen for subsequent experiments.

To confirm that the composition of the extracted complex depended on the HY-to-Th(IV) concentration ratio, the thorium extraction dependence on its concentration was studied in the HCl media. The plot of $\log_{10} D$, which is the logarithm of distribution ratio of Th(IV) extraction, versus the logarithm of ligand concentration at equilibrium was studied. The equivalent results of the linear plot could explain the reaction mechanism between (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) and thorium(IV) ions in the

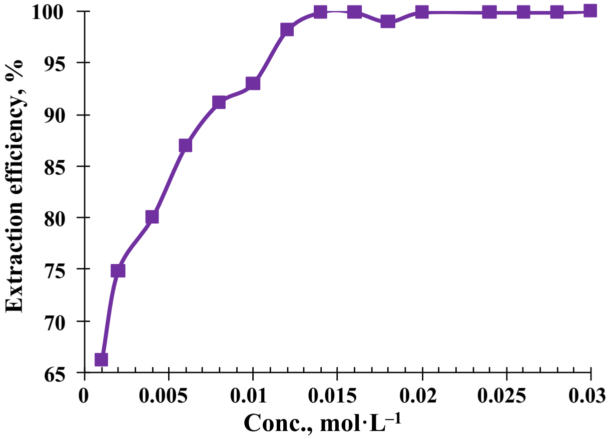


Fig. 4 Effect of AcEt extractant concentration on the Th(IV) extraction (extraction conditions: 0.43 × 10^{-3} mol·L^{-1} Th(IV), pH 6.5, 3:1 A:O phase ratio, 7 min contact time, room temperature)

chloride medium as presented in Fig. 5, which shows an approximately linear correlation ($R^2 = 0.90$) with a slope of 1.09, indicating the requirement of 1 mol of AcEt for each 1 mol of Th(IV) in the extracted complex. Therefore, the predicted extraction mechanism is as shown in the following equation:

$$\mathrm{ThCl}^{+}_{3(\mathrm{A})} + \mathrm{HY}_{(\mathrm{O})} \rightleftharpoons [\mathrm{ThY}]\mathrm{Cl}_{3(\mathrm{O})} + \mathrm{H}^{+}_{(\mathrm{O})}$$

3.2.4 Effect of Contact Time

It is clear that an increase in agitation time results in more contact between the two phases, consequently mass transfer will be increased. The effect of contacting time on Th(IV) extraction ranging from 1 to 10 min was carried out using the above optimum parameters.

The results in Fig. 6 reveal that the Th(IV) extraction increased with increasing agitation time until 5 min and subsequently the Th(IV) extraction efficiency reached a plateau. So, a contact time of 5 min is long enough to achieve the maximum extraction. Therefore, the next experiments were performed with contact of the two phases for 5 min.

3.2.5 Effect of Aqueous: Organic Phase Ratio

The phase ratio (A:O) is one of the most important factors that effects the extraction efficiency. The effect of A:O ratio on Th(IV) extraction was investigated in the range 7:1 to 1:4 using 0.012 mol·L^{-1} AcEt in methylene chloride. Mixing of the aqueous solution containing 0.43×10^{-3} mol·L^{-1} Th(IV) at pH 6.5 with the organic phase was followed by the separation of the two phases in which the thorium(IV) concentration was determined in the aqueous solution and the obtained results are plotted in Fig. 7. From the obtained data, it is quite clear that the maximum extraction efficiency remained relatively constant from 3:1 until 1:4 A:O ratio. Therefore the 3:1 ratio is set as the optimum A:O phase ratio.

3.2.6 Extraction Isotherm

At equilibrium, metallic cations are only partially transferred from the aqueous to the organic phase. Consequently, a number of stages of contact should be used in order to

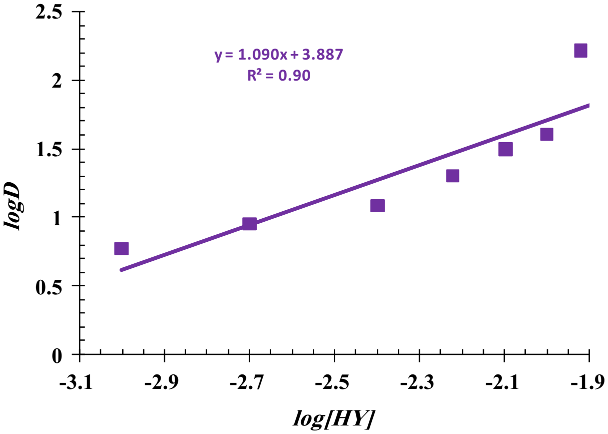


Fig. 5 A plot of $\log_{10} D$ versus $\log_{10}$ [HY] of Th(IV) extraction (where HY = AcEt) (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), pH 6.5, 3:1 A:O phase ratio, 7 min contact time, room temperature)

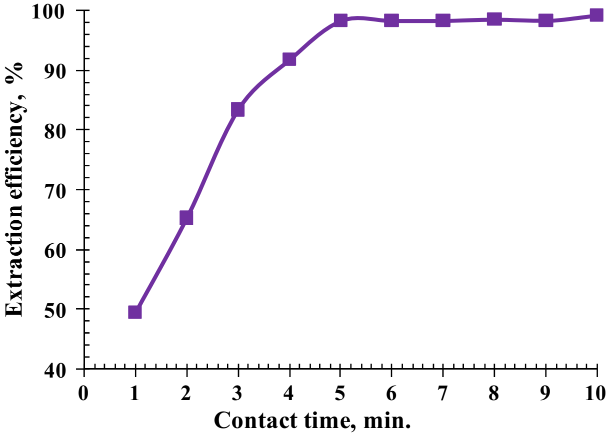


Fig. 6 Effect of contact time on the Th(IV) extraction using AcEt extractant (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), pH 6.5, 0.012 mol·L^{-1} AcEt in methylene chloride, 3:1 A:O phase ratio, room temperature)

recover the maximum amounts of metallic species. In this work, the McCabe–Thiele construction was used to determine the number of theoretical stages required for achieving a desired separation [40].

The equilibrium curve was generally obtained by shaking of different ratios of aqueous leach liquor and the suitable organic solvent. In the present work, the corresponding McCabe–Thiele diagram was then constructed using a 3:1 A:O volume ratio. The practical number of stages was stepped up as shown in Fig. 8. From the obtained results, it is obvious that two stages were quite adequate to almost saturate the organic phase and to deplete the mother leach liquor of Th(IV) for AcEt extractant with an A:O ratio 3:1.

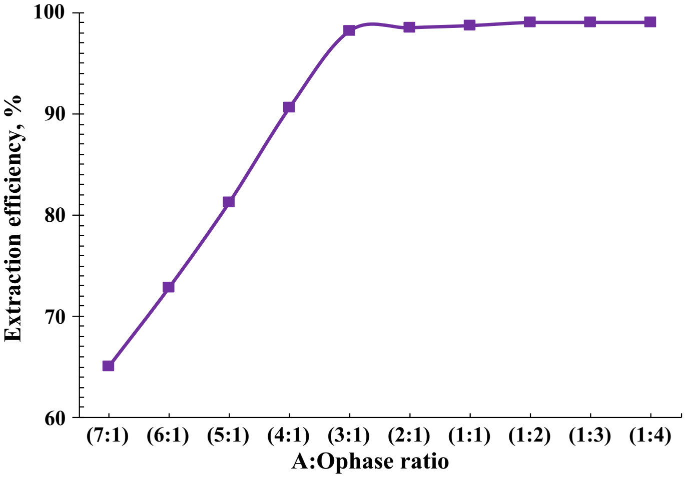


Fig. 7 Effect of the A:O phase ratio on the Th(IV) extraction using AcEt extractant (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), pH 6.5, 0.012 mol·L^{-1} AcEt in methylene chloride, 7 min contact time, room temperature)

3.2.7 Influence of Temperature

The influence of temperature on Th(IV) extraction was performed in the range of 298–333 K using the above optimum conditions. From the obtained results, plotted in Fig. 9, it was found that the Th(IV) extraction slightly increased with increasing temperature from 298 to 333 K. According to the feasibility study, room temperature is the best extraction temperature. Consequently, the maximum efficiency of thorium extraction with the synthesized extractant AcEt in methylene chloride was 98.2%, which is equivalent to 0.75 mol·L^{-1}. In other words, the experimental thorium(IV) extraction capacity of AcEt extractant was 173.3 (g-Th)·L^{-1} (extractant). However, the extraction capacity of AcEt is really equivalent to 173.3 g thorium ions per 1 kg of AcEt extractant. Therefore, the extraction processes were clearly favored at room temperature.

3.2.8 The Thermodynamic Parameters

A number of experiments were carried out to determine the corresponding thermodynamic parameters of the system. The reaction extent may increase or decrease with increasing temperature; temperature changes may also accelerate or slow down the reaction. Metal complex extraction into an organic phase involves large changes in enthalpy (solvation processes) and in entropy (solvent orientation and restructuring), leading to considerable temperature effects [41].

The thorium(IV) extraction with (E)-4-(2-hydroxyethylimino)pentan-2-one (AcEt) was studied by varying the temperature from 298 to 328 K while the other factors were kept constant at the above conditions. The variations of thorium extraction data with temperature for thorium(IV) extraction were used to evaluate thermodynamic parameters including the standard Gibbs energy ($\Delta G°$/kJ·mol^{-1}), the enthalpy ($\Delta H°$/kJ·mol^{-1}), and the

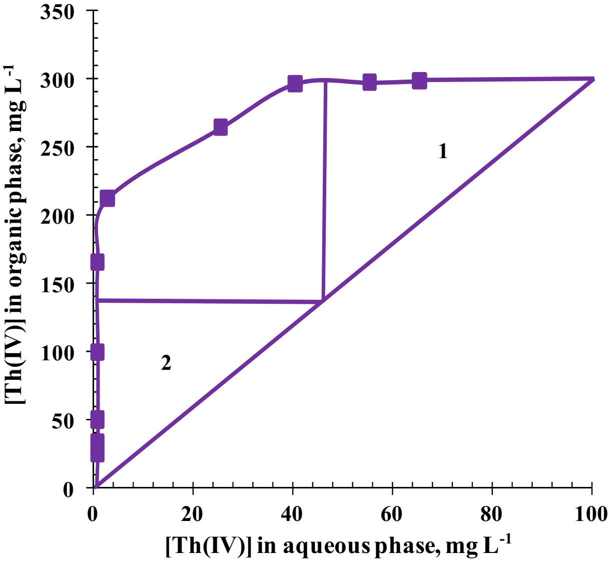
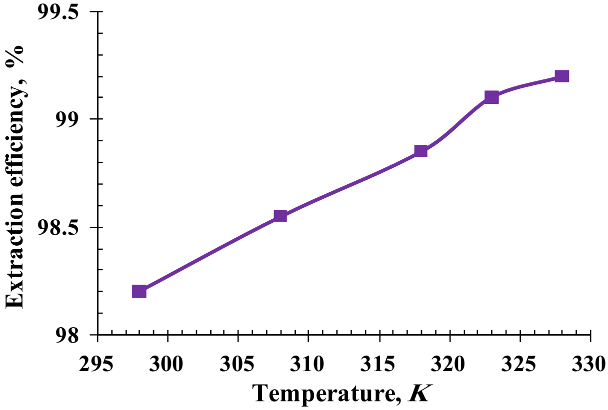


Fig. 8 McCabe–Thiele diagram for Th(IV) extraction using AcEt extractant (extraction conditions: 0.43 × 10^{-3} mol·L^{-1} Th(IV), pH 6.5, 0.012 mol·L^{-1} AcEt in methylene chloride, 7 min contact time, room temperature)

Fig. 9 Influence of temperature on Th(IV) extraction using AcEt extractant (extraction conditions: 0.43×10^{-3} mol·L^{-1} Th(IV), pH 6.5, 0.012 mol·L^{-1} AcEt in methylene chloride, 3:1 A:O phase ratio, 7 min contact time)



entropy ($\Delta S°$/J·mol^{-1}·K^{-1}). These parameters were determined using the following van't Hoff equations [41], Eqs. 7–9:

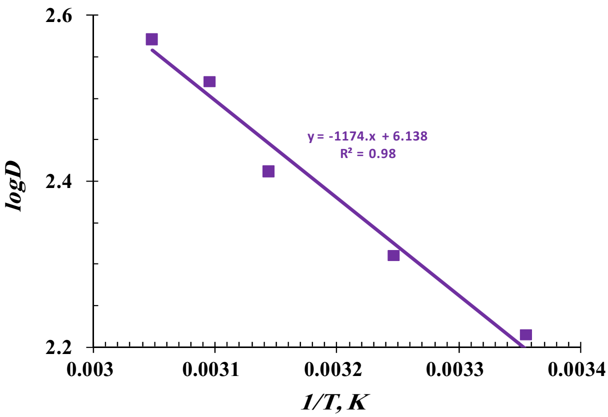
$$\log_{10} D = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{7}$$

$$\Delta G^\circ = -2.303RT \log_{10} D \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where D is the distribution ratio and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}). The corresponding result of $\log_{10} D$ versus $1/T$ was the straight line with a correlation coefficient of 0.98 as seen in Fig. 10. Consequently, the values of both the enthalpy $\Delta H°$ and the entropy $\Delta S°$ were simultaneously evaluated from the slope ($-\ \Delta H°/2.303R$) and intercept ($\Delta S°/2.303R$) of the diagram, respectively. The obtained values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for thorium extraction in the system are reported in Table 1. It should be mentioned in this regard that the obtained negative value of the standard Gibbs energy confirms the feasibility and the positive value of $\Delta H°$ reflects the endothermic nature of the extraction processes, while the positive value of entropy $\Delta S°$ suggests an increase in randomness

Fig. 10 Plot of $\log_{10} D$ versus $1/T$ of the thorium(IV) extraction using AcEt extractant (extraction condition: 0.43×10^{-3} mol·L^{-1} Th(IV), pH 6.5, 0.012 mol·L^{-1} AcEt in methylene chloride, 3:1 A:O phase ratio, 7 min contact time)



during the extraction system which favors the stability of the extracted complex via chelation.

3.3 Stripping Investigation

3.3.1 Effect of Stripping Concentration

To study the effect of the stripping agent concentration, Fig. 5 demonstrates that low Th(IV) extraction was detected at low pH values, which implies that its stripping from the loaded chelating ligand will occur with increasing acid concentration. For this purpose, nitric acid at different concentrations from 0.01 up to 1 mol·L^{-1} was selected and examined while the other stripping conditions were fixed at an A:O ratio of 1:2 for 7 min contact time at room temperature. From the results given in Fig. 11, it is clear that 0.5 mol·L^{-1} HNO_3 gave the maximum thorium stripping efficiency of about 98.5% from the loaded AcEt.

3.3.2 Effect of Contact Time

The effect of contact time on Th(IV) stripping efficiency by 0.5 mol·L^{-1} HNO_3 from the loaded AcEt in methylene chloride was studied in the time range from 1 to 15 min at the fixed conditions of A:O ratio of 1:2 at room temperature. From the data shown in Fig. 12, it is indicated that the stripping efficiency for thorium(IV) increases from 74.22 to 98.5%, upon increasing the contact time from 1 min to 7 min. A contact time beyond 7 min did not perceptibly increase the Th(IV) stripping from the loaded extractant beyond 98.5%. Thus, a 7 min shaking time could be considered sufficient for quantitative stripping.

3.3.3 Effect of Aqueous to Organic Phase Ratio

In order to study the effect of the A:O phase ratios on Th(IV) stripping from the loaded AcEt in methylene chloride (0.75 mol·L^{-1}), several stripping experiments were done at A:O ratios varying from 1:5 to 3:1 with 0.5 mol·L^{-1} HNO_3 as stripping agent for 7 min contact time at room temperature. From the data in Fig. 13, it is seen that the maximum stripping was achieved at an A:O ratio of 1:2 and remained constant thereafter.

3.3.4 Stripping Isotherm

To determine the number of theoretical stages required for Th(IV) stripping from the loaded AcEt in methylene chloride (0.75 mol·L^{-1}), a series of stripping experiments were carried out under the optimum conditions. The data were then used to construct the matching McCabe–Thiele stripping diagram for plotting the obtained equilibrium isotherm and to which a proper operating line was fitted (Fig. 14). From the latter, it can be seen that the possibility of quantitative stripping of thorium(IV) ions should be possible using two countercurrent theoretical stages and an A:O ratio 1:2 with 0.5 mol·L^{-1} nitric acid.

3.3.5 Effect of Temperature

To examine the effect of temperature on the Th(IV) stripping by 0.5 mol·L^{-1} nitric acid from the loaded AcEt in methylene chloride, various experiments were conducted in the

Table 1 Thermodynamic parameters for Th(IV) extraction using AcEt extractant

ΔH° (kJ·mol^{-1})	ΔS° (J·mol^{-1}·K^{-1})	ΔG° (kJ·mol^{-1})				
		298 K	308 K	318 K	323 K	328 K
22.48 ± 0.12[a]	117.52 ± 0.33[a]	–12.54 ± 0.11[a]	–13.72 ± 0.14[a]	–14.89 ± 0.15[a]	–15.48 ± 0.17[a]	–16.07 ± 0.21[a]

[a] Standard deviation, $n = 3$

Fig. 11 Effect of HNO_3 concentration on Th(IV) stripping from the loaded extractant (stripping conditions: 1:2 A:O ratio, 7 min contact time, room temperature)

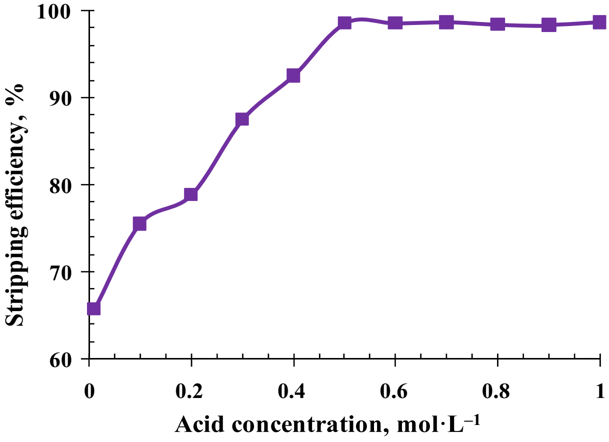


Fig. 12 Effect of contact time on Th(IV) stripping from the loaded extractant (stripping conditions: 0.5 mol·L^{-1} HNO_3, 1:2 A:O ratio, room temperature)

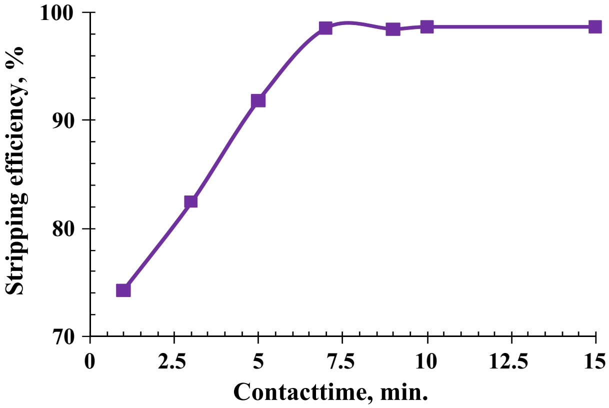
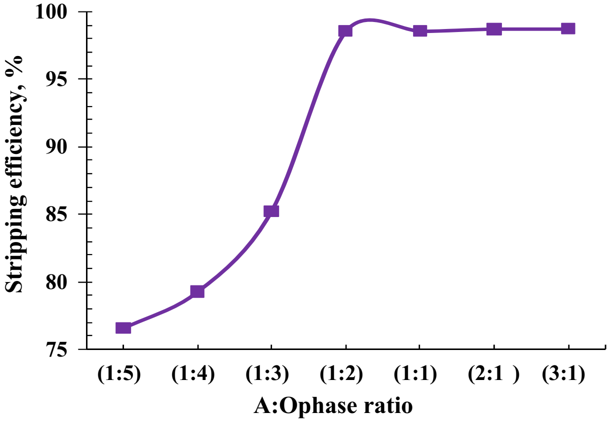


Fig. 13 Effect of A:O phase ratio on Th(IV) stripping from the loaded extractant (stripping conditions: 0.5 mol·L^{-1} HNO_3, 7 min contact time, room temperature)



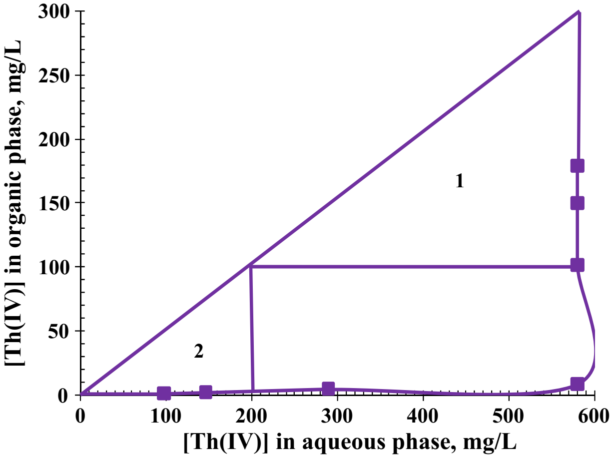


Fig. 14 McCabe–Thiele diagram for Th(IV) stripping from the loaded extractant (stripping conditions: 0.5 mol·L^{-1} HNO_3, 7 min contact time, room temperature)

range from 298 up to 328 K at 7 min contact time and an A:O phase ratio of 1:2. From the data shown in Fig. 15, it is obvious that with raising the temperature from 298 to 328 K, the stripping progressively decreased from 98.5 down to 85.3%. These results could be described by an exothermic reaction in the stripping process. Therefore, room temperature can be considered as the best temperature for the re-extraction process.

3.4 Extractant Reusability

For the reusability of the studied extractant (AcEt), the used organic phase was contacted with an equal volume of DI (de-ionized) water for 30 min. The phases were separated and the pH of the aqueous phase was measured. The organic phase was obtained and repeated with a number of contacts using fresh DI water until there was no change in pH. The organic phase was then reused.

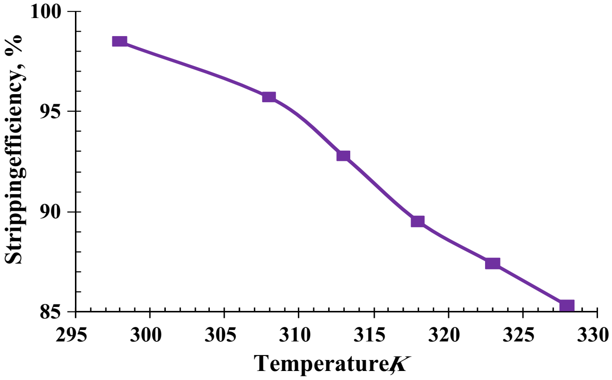


Fig. 15 Effect of temperature on Th(IV) stripping from the loaded extractant (stripping conditions: 0.5 mol·L^{-1} HNO_3, 1:2 A:O ratio, 7 min contact time)

3.5 A Case Study

The representative cataclastic rock sample was collected from the Abu Rushied area of the South Eastern Desert, Egypt, and was subjected to complete analysis for the determination of major and trace elements using reported methods [42, 43]. From these results, the concentration of silica, alumina, Fe_2O_3, CaO, MgO, K_2O and Na_2O assayed at 64.88 ± 1.2, 13.76 ± 0.5, 4.8 ± 0.3, 5.2 ± 0.5, 1.2 ± 0.1, 3.66 ± 0.2 and 4.92 ± 0.4%, respectively, while the trace elements such as total REEs, Ba, Sr, Zn and Zr ions were 0.060 ± 0.01, 0.016 ± 0.001, 0.018 ± 0.002, 0.040 ± 0.01 and 0.026 ± 0.004%, respectively; moreover, the thorium concentration was 0.033 ± 0.003%.

The thorium leach liquor was prepared by treating 1 kg of the ground rock sample (200 mesh size) with 3 L of 1 $mol\cdot L^{-1}$ hydrochloric acid solution and 150 rpm agitating speed for 4 h agitation time at room temperature. The insoluble gangue was then filtered off and the obtained leach liquor was found to assay 99 $mg\cdot L^{-1}$ of thorium ions indicating a leaching efficiency of 90.13 ± 0.1% using a spectrophotometric technique. On the other hand, the interesting associated ions in the prepared leach liquor were analyzed using the ICP-OES technique. From the obtained data in the Table 2, the leach liquor contained different concentrations of associated metal ions; therefore, it is recommended that the leach liquor requires further purification or addition of masking agents to obtain a high grade of the thorium ions.

Based on the above results, the optimum parameters of extraction and stripping of thorium(IV) ions from synthetic solution using the synthesized AcEt Schiff base were directly applied to the prepared leach liquor. The extraction process was carried out on 3 L of the prepared leach liquor which contained 0.43 $mol\cdot L^{-1}$ Th(IV) (297 mg total content of Th(IV) ions in the pregnant liquor) and its associated ions using 1 L of 0.012 $mol\cdot L^{-1}$ AcEt in methylene chloride at the optimum conditions of pH 6.5 of leach liquor for 5 min contact time at room temperature. From the data, the Th(IV) content on the AcEt/methylene chloride was 294 mg Th(IV) ions in the 1 L organic phase (1.7 g of AcEt in 1 L in methylene chloride) after two stages. The working thorium-loaded AcEt/methylene chloride (1 L) was agitated using 500 mL of 0.5 $mol\cdot L^{-1}$ HNO_3 for 7 min contact time at ambient temperature by two stages. The Th(IV) concentration in the aqueous phase was

Table 2 Chemical analysis of the working leach liquor

Constituents	Conc. ($mol\cdot L^{-1}$)
Si^{4+}	0.063 ± 0.002[a]
Al^{3+}	0.0900 ± 0.0012[a]
Ti^{4+}	0.0006 ± 0.00001[a]
Fe^{3+}	0.0258 ± 0.00015[a]
Ca^{2+}	0.0524 ± 0.00026[a]
Mg^{2+}	0.0132 ± 0.00005[a]
P^{5+}	0.00226 ± 0.00007[a]
Th^{4+}	0.00043 ± 0.00001[a]
REE^{3+}	0.00131 ± 0.00009[a]
Ba^{2+}	0.00032 ± 0.00005[a]
Zn^{2+}	0.00177 ± 0.00012[a]
Zr^{4+}	0.00080 ± 0.00006[a]

[a] Standard deviation, $n = 3$

spectrophotometrically determined. The thorium content was found to assay 294 mg Th(IV) ions in 0.5 L aqueous phase.

The precipitation process was carried out by adjusting the pH to 2.5 using ammonia solution followed by adding 30% oxalic acid to precipitate thorium as $Th(C_2O_4)_2{\cdot}xH_2O$ (0.95 g) which was roasted at 973 K to decompose the oxalates. The final product was a ThO_2 cake that weighed 0.38 g.

The obtained thorium oxide cake was identified using the scanning electron microscope (SEM), and the corresponding EDX spectrum of thorium oxide cake (Fig. 16). Furthermore, it was quantitatively analyzed using ICP-OES technique to determine its chemical constituents in oxide forms (Table 3). According to the obtained data, the thorium oxide was found to assay 94.35 ± 1.5%. The obtained X-ray diffraction spectrum showed distinct peaks indicating crystallized ThO_2. The diffractogram of the calcined thorium oxalate displayed a maximum number of peaks due to Th^{4+} between 2θ of 27.68°, 2θ of 32.04°, 2θ of 37.02°, 2θ of 44.49° and 2θ of 60.35° as illustrated in Fig. 17. Significantly, the d values of most of the peaks correspond to thorium oxide [44]. Finally, a schematic flow sheet of recovery of thorium ions was constructed and presented in Fig. 18.

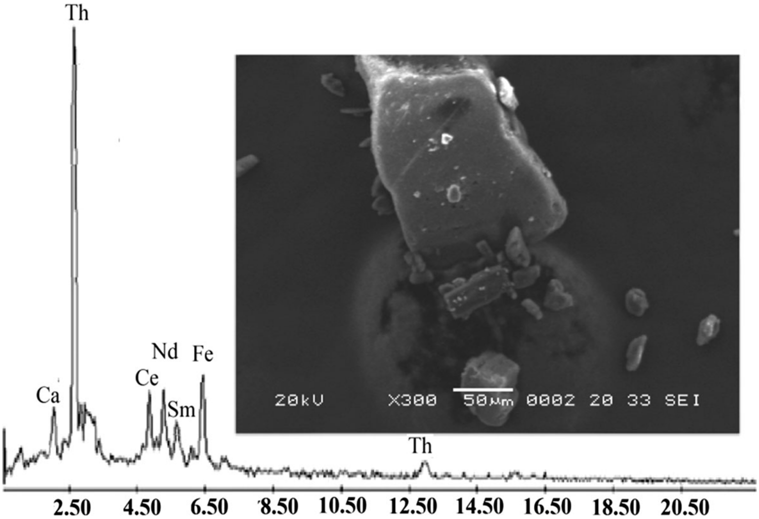


Fig. 16 Scanning electron microscope image of the ThO_2 cake

Table 3 Chemical analysis of thorium oxide product

Constituents	Conc. (%)
ThO_2	94.35 ± 1.5[a]
TiO_2	0.07 ± 0.01[a]
Fe_2O_3	0.15 ± 0.05[a]
RE_2O_3	3.92 ± 0.55[a]
CaO	0.19 ± 0.03[a]
MgO	0.12 ± 0.02[a]

[a] Standard deviation, $n = 3$

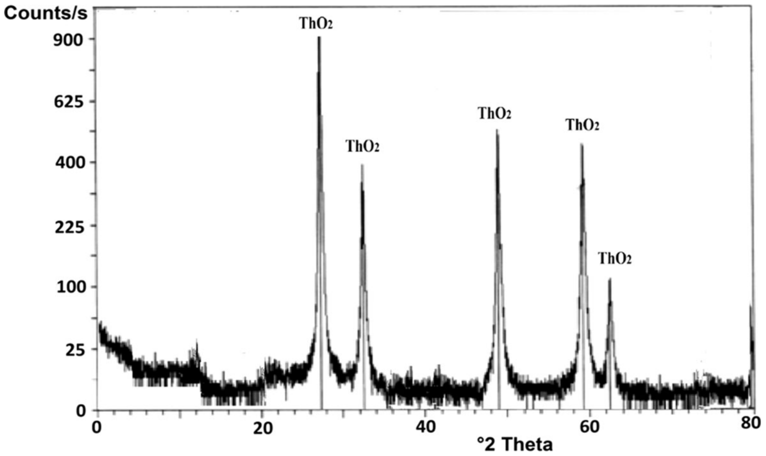


Fig. 17 X-ray diffraction spectrum of the ThO_2 cake

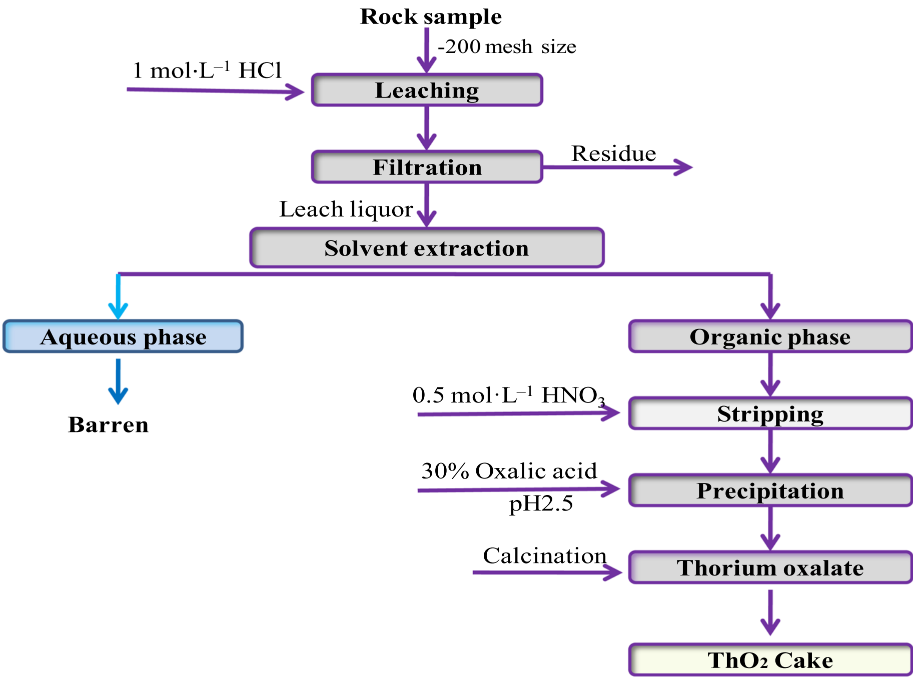


Fig. 18 A schematic flow sheet for recovery of thorium ions from studied rock sample

4 Conclusions

The present investigations have resulted in the submission of a convenient solvent extraction technique for the extraction and separation of thorium(IV) from hydrochloric acid solutions using the prepared Schiff base, (E)-4-(2-hydroxyethylimino)pentan-2-one

(AcEt) as an extractant, yielding a higher extraction percentage under various operating conditions. The best extraction conditions were pH 6.5, 0.012 $mol \cdot L^{-1}$ (0.17%) AcEt in methylene chloride and 3:1 aqueous to organic phase ratio for 5 min equilibrium contact time at room temperature.

The Th(IV) extraction capacity is 0.75 $mol \cdot L^{-1}$ (294.6 $mg\text{-}Th \cdot L^{-1}$ AcEt in methylene chloride). Moreover, the working thorium-loaded AcEt was agitated using 0.5 $mol \cdot L^{-1}$ HNO_3 and a 1:2 A:O phase ratio for 7 min contact time at room temperature. The number of extraction and stripping stages were theoretically determined to be two by the McCabe–Thiele diagrams. Furthermore, the negative value of the standard Gibbs energy indicates the feasibility of extraction while the positive values of ΔH° and ΔS° reflected the endothermic nature and an increase in randomness which favors the extraction of Th(IV) ions.

The proposed method for Th(IV) extraction using AcEt in methylene chloride is simple, easy, selective and reproducible for the isolation and separation of Th(IV) from its leach liquor with 98.2% extraction efficiency and 98.5% stripping efficiency.

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