



# Thorium ions recovery using activated carbon modified with triphenyl phosphine oxide: kinetic and equilibrium studies

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## Abstract

Activated carbon (AC) modified with triphenyl phosphine oxide (TPPO) was tested for thorium(IV) adsorption. Different factors affecting the adsorption process such as pH, contact time, modified AC dose, initial thorium concentration, triphenyl phosphine oxide (TPPO) concentration and temperature were investigated to optimize Th(IV) adsorption operating conditions. Kinetic and equilibrium studies of the adsorption process have been studied. The obtained most favorable conditions for Th(IV) adsorption were: pH 3.6, 40 min contact time, 0.5 g modified AC dose, 0.02 M TPPO in toluene and 400 mg/L of thorium concentration at room temperature. The maximum sorption capacity according to Langmuir isotherm reached 71.94 mg/g for modified AC. Adsorption kinetics obeys pseudo-second order kinetic model. Thorium(IV) was efficiently desorbed from the loaded composite using 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The optimized factors have been carried out to recover thorium(IV) from Abu Rusheid leach liquor, south Eastern Desert, Egypt.

**Keywords** Modified AC · TPPO · Thorium · Recovery

## 1 Introduction

Thorium is widely distributed in trace amounts throughout the earth's crust, occurring mainly within several minerals, such as monazite sands, thorianite, thorite and thoganite [1]. Thorium is three times more abundant than uranium in the earth's crust. Direct toxicity with thorium is low due to its stability at ambient temperatures [2, 3]. Thorium reactors produce less waste than conventional uranium based ones. Waste solutions bearing thorium can accidentally contaminate underground waters, which is considered as an environmental concern [4, 5]. Thorium was used in a variety of applications during the last century. It has been paid more attention recently as a potential nuclear resource due to the large demand of energy. Thorium is an important alloying agent, as it offers alloys greater strength at high temperatures, making it useful in manufacturing jet engines [6]. Thorium dioxide is added to glass to increase its refractive index, producing thoriated glass for use in high-quality camera lenses [7]. <sup>227</sup>Th is an

alpha-particle emitting isotope that can be used to create localized tumor-killing cancer treatments [8].

Various methods have been developed for separation and utilization of Th(IV). Such methods include biosorption [9], liquid-liquid extraction [10] and solid-phase adsorption [11, 12]. Adsorption based on carbon materials, such as activated carbon were used due to their high adsorption capacity as well as elevated thermal and radiation stability [13].

Adsorption is a low cost uptake alternative, which is simple and effective. It is obvious that utilizing adsorbents in metal recovery offers more advantages over liquid-liquid extraction technique. The simplicity of equipment and overall operation and the possibility of regenerating the solid adsorbent is a striking feature of the process. Cost is an important parameter for comparing the adsorbent materials. However, the expense of utilizing individual adsorbents varies depending on the degree of processing required and their availability. Although, the development of chelating ion exchangers is of considerable interest,

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SN Applied Sciences (2019) 1:974 | <https://doi.org/10.1007/s42452-019-1006-2>

Received: 20 May 2019 / Accepted: 29 July 2019 / Published online: 3 August 2019

there are still many difficulties related to their preparation and cost. Due to such difficulties, the concept of using solvent impregnated sorbents has been widely utilized and developed [14, 15].

Activated charcoals possess high degree of surface reactivity due to the favorable pore size distribution, which makes their surface accessible and enhances their adsorption rate without sacrificing their mechanical strength [16]. Due to such advantages, activated carbon materials have found their way in many industrial separation and purification applications, such as the removal of different contaminants from water supplies [17].

The concern of this investigation is to introduce activated carbon modified with TPPO as an effective adsorbent for thorium ions.

## 2 Experimental

### 2.1 Materials

All the chemicals and reagents used in this work are of the analytical grade. Thorium stock solution was prepared by dissolving 2.38 g of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in 1000 mL of double-distilled water to prepare 1000 mg/L stock solution, that was diluted into other desired concentrations throughout the study. Thorium concentration was determined photometrically using Arsenazo III complex, [18].

### 2.2 Apparatus

Thorium, silica, alumina,  $\text{TiO}_2$ , and  $\text{P}_2\text{O}_5$  were measured spectrophotometrically using Metertech Inc, model SP-8001, UV-Visible spectrophotometer. Sodium and potassium were determined by a Sherwood flame photometer model 410 (England), using a series of chemical solutions, while CaO, MgO and  $\text{Fe}_2\text{O}_3$  were determined by titration [19]. Trace elements were analyzed using ICP-OES.

The Fourier Transform Infrared Spectrometer (FT-IR) (Thermo Scientific - NICOLET IS10 USA) spectrometer has been used to characterize the major functional groups of AC modified with TPPO before and after adsorption of thorium. Scanning electron microscope (SEM) was used for the specification of the modified AC before and after adsorption of thorium, as well as the final obtained thorium oxide precipitate. The modified activated carbon was identified at laboratories of the Atomic Energy Authority, Anshas, Egypt using X-ray fluorescence (XRF) "JSX-3222 Element Analyzer" with automatic sample changer (JEOL) PW 1510, connected to a computer system using X-40 program for spectroscopy with a detection limit of 5.0 mg/L.

### 2.3 Preparation of activated carbon

Commercial grade activated carbon was calcinated at 500 °C for 4 h. The powder was stirred with 10% hydrochloric acid solution for 4 h in order to remove any adsorbed species. The residue was filtered off and washed with double distilled water to retain neutral pH. The purified activated carbon was stirred with 10% mixture of  $[\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$  for 3 h and solid/liquid (S/L) ratio 1/5 followed by a rewashing step. The oxidized product was dried in a drying oven at 110 °C for 4 h to enhance the hydroxyl capacity of AC, and (HO-AC) was obtained [20].

### 2.4 Preparation of modified activated carbon

A series of different concentrations (0.005–0.03 M) of triphenyl phosphine oxide (TPPO) were used to modify activated carbon by dry technique; 0.5 g of activated carbon was stirred with different TPPO in toluene concentrations with S/L ratio (1/10) for 40 min at room temperature till the toluene was evaporated. The modified AC was dried at room temperature.

### 2.5 Preparation of Abu-Rusheid sample

The studied sample from Abu Rusheid area (south Eastern desert, Egypt) was leached using mixture of acids HF,  $\text{HNO}_3$ ,  $\text{HClO}_4$  and HCl, to determine the percent of major oxides (Table 1). Trace elements (mg/kg) were determined using ICP-OES technique as shown in (Table 1).

### 2.6 Preparation of Abu-Rusheid leach liquor

The studied sample was subjected to thorium leaching using optimum conditions that verify the best thorium leaching efficiency (90%), while ensuring the minimal dissolution of unwanted impurities. The optimum conditions are – 200 mesh size ground sample, 3 M  $\text{H}_2\text{SO}_4$  as a leaching agent, 1/5 solid/liquid ratio, 200 rpm stirring speed for 0.5 h at room temperature. Thorium was measured in filtered leach liquor and found to be 1800 mg/L.

### 2.7 Adsorption procedures

Batch adsorption studies were conducted by stirring the solution bearing thorium with a certain amount of modified activated carbon for a period of time at constant temperature till equilibrium was achieved. In order to predict the most favorable conditions, such procedures were carried out at different pH values ranging from 1 to 7, different thorium

**Table 1** Chemical composition of major oxide (wt %) and trace elements content (mg/kg) using ICP-OES technique

Major oxides	wt%
SiO <sub>2</sub>	73.51
Al <sub>2</sub> O <sub>3</sub>	12.50
TiO <sub>2</sub>	0.12
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	5
CaO	1.0
MgO	0.63
Na <sub>2</sub> O	0.63
K <sub>2</sub> O	3.5
P <sub>2</sub> O <sub>5</sub>	0.12
L.O.I	1.08
Trace elements	(mg/kg)
Th	10,000
Zr	194.83
Sr	16.28
Cr	8.762
Cd	3.37
Co	0.58
Cu	63.56
Zn	1977.91
Pb	61.86
Li	1146.09
Mn	210.72
Mo	1.79
Ni	5.36
Tl	5.67
V	1.55
Ba	63.49
As	1.04
Sb	6.38
Sn	20.02
B	12.81

concentrations varying from 50 to 1000 mg/L, different time intervals ranging from 10 to 90 min., different temperatures and different adsorbent doses while keeping the agitation speed constant at 200 rpm. The adsorbent was separated thorium was measured in the filtrate. The thorium uptake capacity ( $q_e$ , mg/g), adsorption efficiency (E %) and distribution coefficient ( $K_d$ ) were calculated from the following equations:

$$q_e = (C_o - C_e) \times v/m \quad (1)$$

$$E(\%) = 100(C_o - C_e)/C_o \quad (2)$$

$$K_d = [(C_o - C_e)/C_e] \times V/m \quad (3)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium thorium (IV) concentrations (mg/L), respectively,  $V$  is the volume of the aqueous solution (L) and  $m$  is the dry resin weight (g).

### 3 Results and discussions

#### 3.1 Characterization of the synthesized modified activated carbon

##### 3.1.1 Fourier-transform infrared spectrometer characterization

FTIR is a useful tool to identify molecular functional groups [21]. FTIR model Thermo Scientific Nicolet IS10 instrument via the KBR pressed disc method was used in a range starting from 400 to 4000  $\text{cm}^{-1}$  wave numbers. The (FTIR) results of AC modified with TPPO before and after adsorption of thorium are given in (Fig. 1A, B). The obtained (FTIR) results of prepared AC modified with TPPO showed peaks at 3852.96, 3728.69, 3703.62, 3625.37, 3601.97 and 3352.23  $\text{cm}^{-1}$  corresponding to AC-OH stretching. The peaks at 1735.42 to 1654.30  $\text{cm}^{-1}$  corresponding to mono substituted aromatic. The bands 1576.70 and 1503.74  $\text{cm}^{-1}$  are related to C=C ring stretching. While, the bands 1483.25 and 1413.39  $\text{cm}^{-1}$  are attributed to asymmetric  $\text{CH}_3$  stretching. Two bands 1357.12, and 1332.67  $\text{cm}^{-1}$  are related to  $(\text{Ar})_3\text{-P=O}$  stretching. One peak at 1167.16  $\text{cm}^{-1}$  is related to P=O aromatic stretching. The peaks at 799.93, 720.53, 681.02, 668.88, 657.67 and 617.95  $\text{cm}^{-1}$  are corresponding to out of plane C-H aromatic bending. Finally, peaks at 539.64, 511.30, 473.13, and 463.45  $\text{cm}^{-1}$  are attributed to hydrogen bond out of plane OH (Fig. 1A). While, after adsorption of thorium the peaks at 1413.39, 1357.12, 720.53 and 617.95  $\text{cm}^{-1}$  disappeared and new peak appeared at 1384.10  $\text{cm}^{-1}$ . Most bands are shifted which indicated the adsorption of thorium onto AC modified with TPPO (Fig. 1B).

##### 3.1.2 Scanning electron microscope (SEM)

SEM and EDX of the AC modified with TPPO before and after adsorption of thorium were shown in (Fig. 2a, b). Results show the presence of thorium after adsorption onto the modified AC surface.

##### 3.1.3 X-ray fluorescence (XRF)

Both the synthesized and loaded modified AC were identified by X-ray fluorescence (XRF) as shown in (Fig. 3a, b). The results show that thorium was

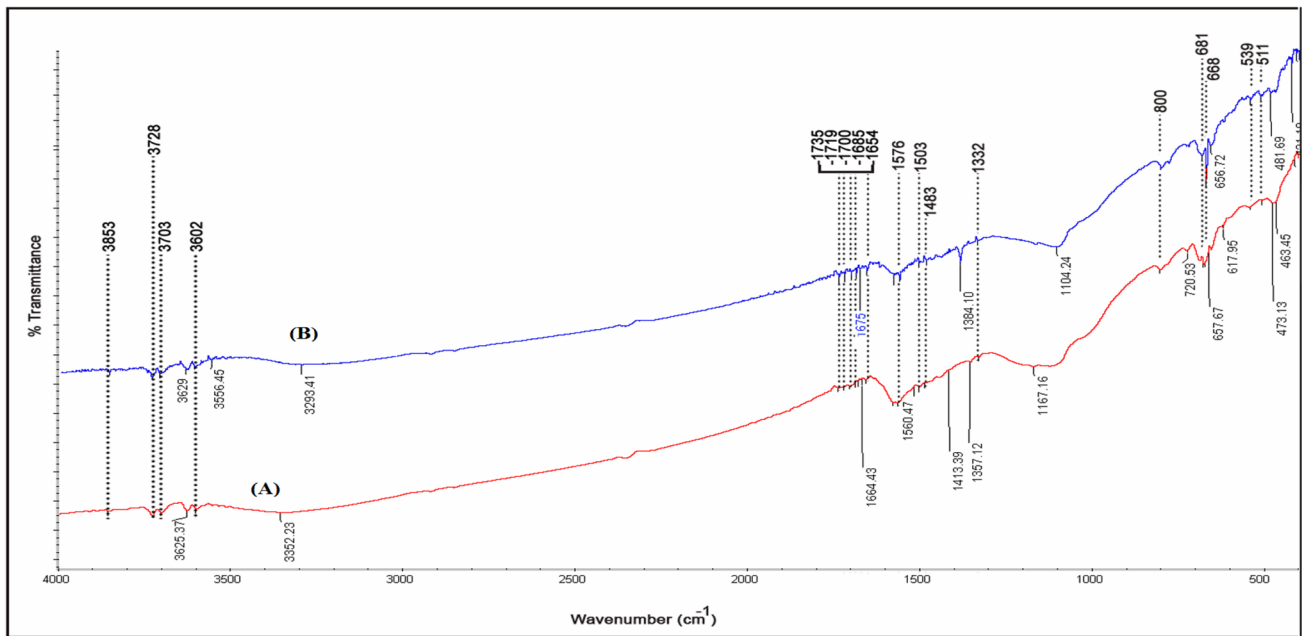


Fig. 1 FTIR chart of the AC modified with TPPO before (A) and after (B) the adsorption of thorium

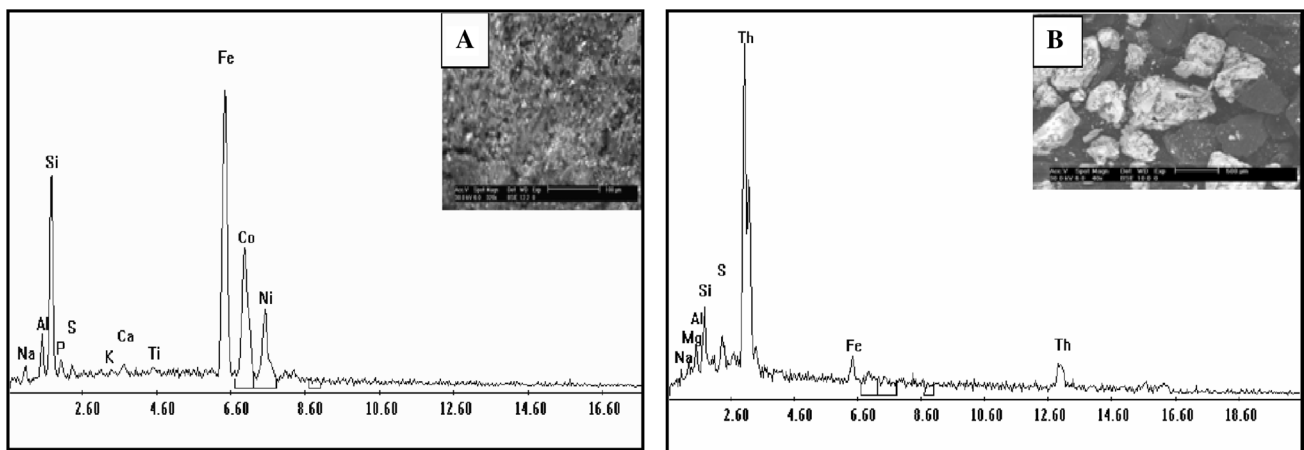


Fig. 2 SEM and EDX of AC modified with TPPO before (a) and after (b) the adsorption of thorium

successfully adsorbed onto the surface of the modified AC.

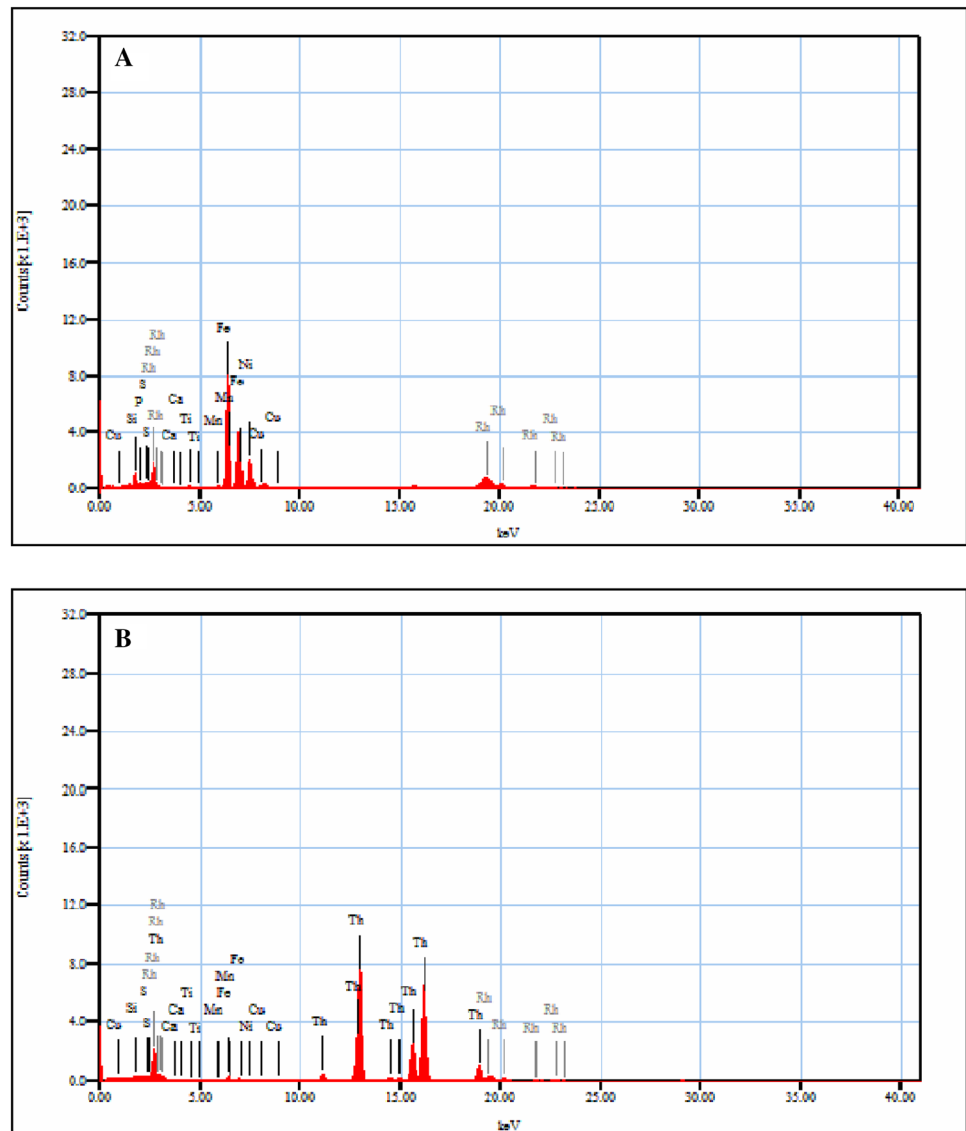
### 3.1.4 Effect of pH

Proton availability is important for metal adsorption nearly by all adsorbents. The pH directly influences the aqueous chemistry of thorium and the properties of the sorbent's active sites [22]. The retention of thorium(IV) on the prepared modified AC was studied in the pH range from 1 to 7 using 100 mL thorium solution assaying 400 mg/L, 0.5 g modified AC and 200 rpm stirring speed for 40 min at room temp. The obtained results indicated that thorium(IV)

adsorption efficiency increases with increasing the pH from 1 to 3.6, where it reaches a maximum of 89% at pH 3.6 then adsorption efficiency decreases with increasing pH up to 7 (Fig. 4). This is due to electrostatic repulsion of the protonated active sites with the positively charged of thorium ion species.

From the obtained results, it is clear that the efficiency of thorium adsorption depends on pH dependent and that maximum adsorption occurs at pH 3.6 due to surface properties of the modified AC as well as the variation of thorium complex species distribution at different pH values [23]. The dominant thorium species at pH 3.6 are  $\text{Th}(\text{OH})_2^{2+}$  or  $\text{Th}(\text{OH})^{3+}$ . The adsorption percent was low

**Fig. 3** XRF analysis of the AC modified with TPPO before (a) and after (b) the adsorption of thorium



at pH values below 3, due to the protonation of residual oxygen-containing groups on the modified AC as well as the competition between  $H^+$  and  $Th^{4+}$  ions for the same adsorption sites [24]. However, on increasing the pH beyond 4, hydrolytic precipitation of thorium ions results in declining the adsorption capacity. At  $pH > 4$ , thorium precipitates as  $Th(OH)_4$ . At higher pH values, monomer and polynuclear species of thorium may include  $Th(OH)^{3+}$ ,  $Th(OH)_3^+$ ,  $Th(OH)_2^{2+}$ ,  $Th_2(OH)_2^{6+}$ ,  $Th_2(OH)_4^{4+}$ ,  $Th_4(OH)_8^{8+}$ , and  $Th_6(OH)_{14}^{8+}$  [25].

### 3.1.5 Effect of contact time

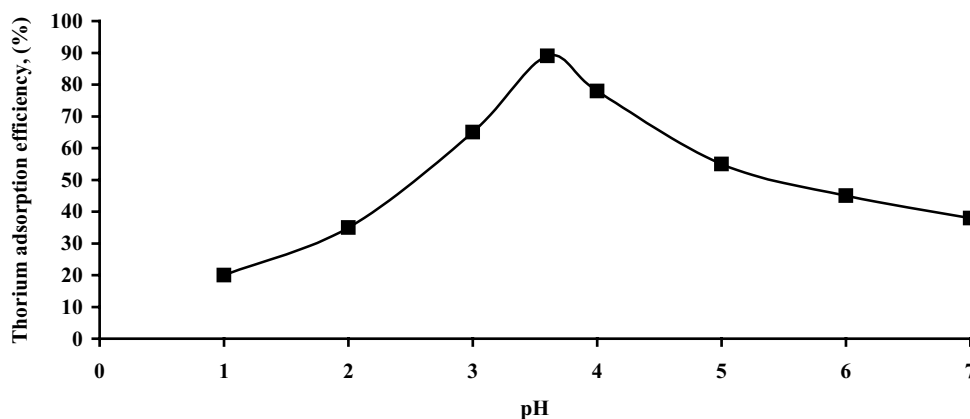
The effect of contact time was studied while keeping other parameters affecting the adsorption constant. Time was varied from 10 to 90 min. It was found that thorium adsorption efficiency increased with increasing the

contact time (Fig. 5). The adsorption efficiency of thorium increased from 55% at 10 min to 89% at 40 min. Sorption reached apparent equilibrium after about 40 min. No significant change in thorium adsorption efficiency was noticed beyond that time, revealing that a state of equilibrium was reached. This indicates that adsorption occurred as monolayer on the surface of the adsorbent. When all the adsorption sites were saturated, the increase in metal ions uptake was seized [26]. Further increase in time encountered a decrease in metal uptake due to intra-particle diffusion processes dominating over adsorption [27].

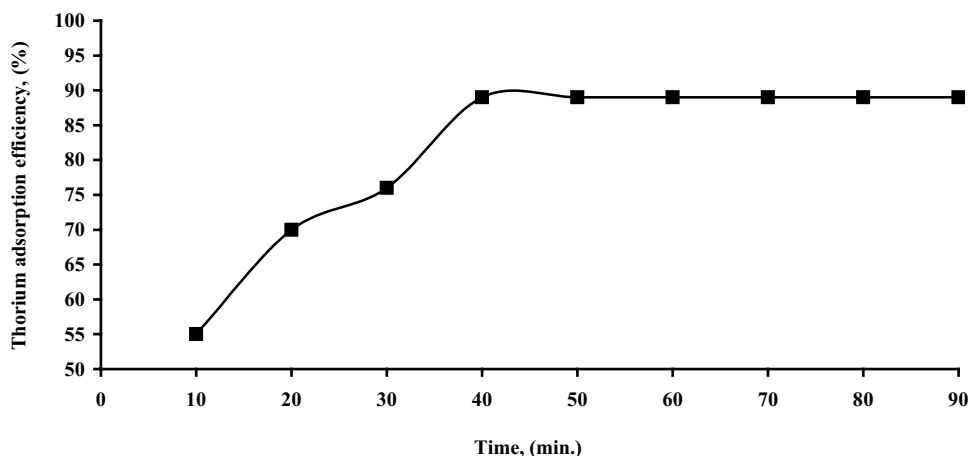
### 3.1.6 Effect of triphenyl phosphine oxide (TPPO) concentration

A series of experiments were performed using 0.5 g of activated carbon stirred for 40 min with different

**Fig. 4** Effect of pH on Th<sup>4+</sup> adsorption efficiency using AC modified with TPPO. Adsorption conditions: 400 mg/L thorium concentration, 40 min contact time, room temperature, 100 mL of thorium solution and 0.5 g modified AC with TPPO



**Fig. 5** Effect of contact time (min) on Th<sup>4+</sup> adsorption efficiency using AC modified with TPPO. Adsorption conditions: 400 mg/L thorium concentration, pH 3.6, room temperature, 100 mL of thorium solution and 0.5 g modified AC with TPPO



concentrations of (0.005 to 0.03 M) TPPO in toluene with S/L ratio (1/10) at room temperature (Fig. 6). The obtained results indicate that thorium adsorption efficiency increased with increasing the concentration of (TPPO) until reaching maximum value at 0.02 M TPPO.

### 3.1.7 Effect of initial thorium concentration

A series of prepared 100 mL solutions of different initial thorium concentrations ranging from 50 to 1000 mg/L were mixed with 0.5 g of modified AC at pH 3.6 and 200 rpm stirring speed for 40 min at room temperature. The effect of initial thorium concentration is expressed in terms of uptake capacity ( $q_e$ ) (Fig. 7). Accordingly, 400 mg/L of thorium was found optimum to yield maximum uptake capacity, ( $q_e = 71.2$  mg/g for AC modified with TPPO).

Increasing thorium concentration results in higher molecular competition on the available surface active sites on the surface of the adsorbent, thus, leading to a decrease in the overall adsorption efficiency [28].

### 3.1.8 Effect of temperature

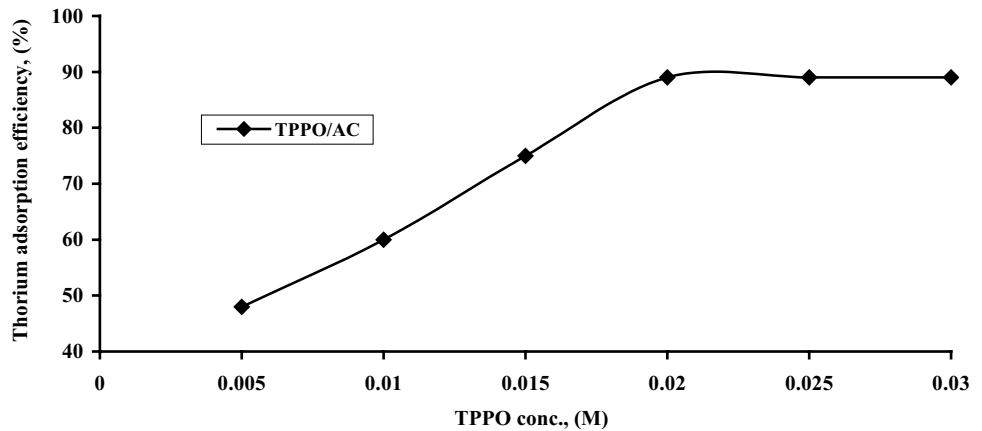
Several experiments were performed at temperatures ranging from 25 to 70 °C. Other parameters were fixed at 400 mg/L thorium, pH 3.6 and 200 rpm stirring speed for 40 min. The maximum adsorption efficiency was 89% at 25 °C and dropped down to 50% at 70 °C, (Fig. 8). Such results show that room temperature is the most favorable temperature for thorium adsorption by the modified AC.

### 3.1.9 Effect of modified AC dose

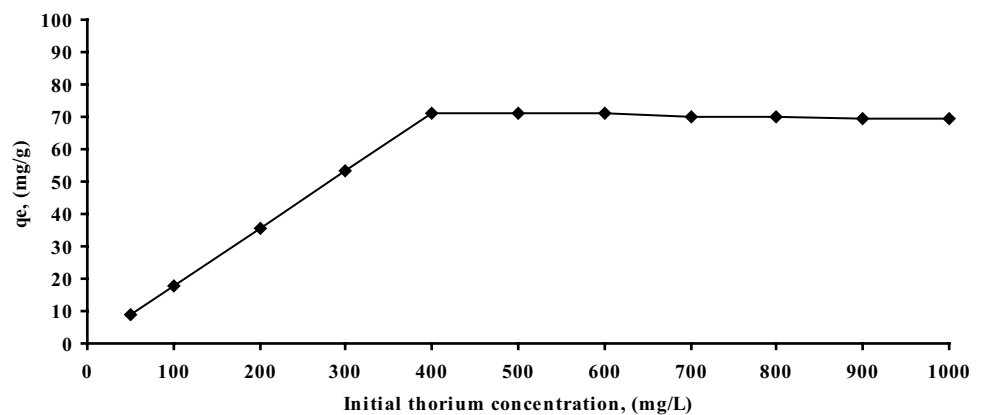
Different amounts of modified AC ranging from 0.1 to 1 g were mixed with 100 mL of thorium solution at optimum conditions. Thorium adsorption efficiency increased from 55% with 0.1 g to reach 89% with 0.5 g, (Fig. 9). Furthermore, the adsorption efficiency decreased by increasing the adsorbent dose. At low adsorbent doses, all the active sites are available for thorium adsorption. On the other hand, at higher adsorbent amounts, the crowdedness of thorium ions will lead to difficulty to fill the remaining sites due to electrostatic repulsion between thorium ions [29, 30].



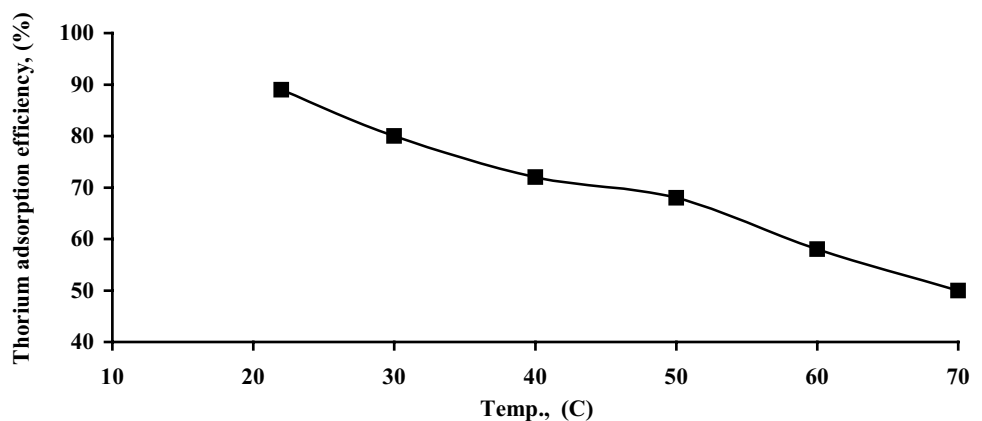
**Fig. 6** Effect of TPPO concentration on  $\text{Th}^{4+}$  adsorption efficiency using AC. Adsorption conditions: pH 3.6, 40 min contact time, room temperature, 100 mL of thorium solution and 0.5 g of AC



**Fig. 7** Effect of initial thorium concentration (mg/L) on the uptake capacity of AC modified with TPPO. Adsorption conditions: pH 3.6, 40 min. contact time, room temperature, 100 mL of thorium solution and 0.5 g of modified AC with TPPO



**Fig. 8** Effect of temperature on  $\text{Th}^{4+}$  adsorption efficiency by AC modified with TPPO. Adsorption conditions: 400 mg/L thorium concentration, 40 min contact time, pH 3.6, 100 mL of thorium solution and 0.5 g of modified AC with TPPO

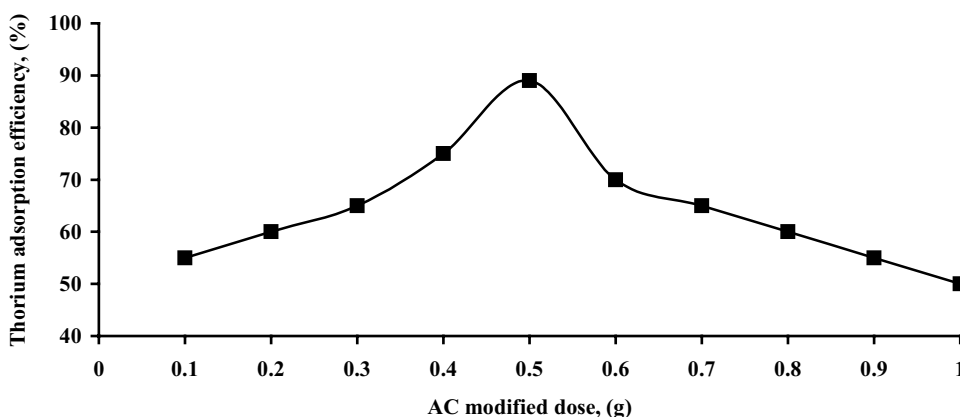


### 3.1.10 Desorption and regeneration of modified activated carbon

Desorption enhances the economic value of the overall adsorption process [31]. Three mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ) having the same concentration (1 M) were examined using 100 mL of diluted acid solution to elute thorium loaded on to 0.5 g modified AC for 30 min at room temperature. From (Table 2), sulfuric acid was found the most suitable acid to elute loaded thorium.

In order to determine the optimum  $\text{H}_2\text{SO}_4$  concentration, a series of 100 mL of different acid concentration solutions ranging from 0.1 to 1.0 M were mixed with 0.5 g of modified AC at room temperature for 40 min. Table 2 shows that  $\text{Th}(\text{IV})$  elution efficiency increases from 42% with 0.1 M  $\text{H}_2\text{SO}_4$  till 93% at 0.5 M. Further increase in sulfuric acid concentration shows no enhancement to the elution efficiency. The optimum sulfuric acid concentration sufficient to elute  $\text{Th}(\text{IV})$  efficiently was 0.5 M  $\text{H}_2\text{SO}_4$ .

**Fig. 9** Effect of modified AC dose on Th<sup>4+</sup> adsorption efficiency. Adsorption conditions: 400 mg/L thorium concentration, 40 min. contact time, room temperature, pH 3.6 and 100 mL of thorium solution



**Table 2** Effect of different eluting agents with emphasis on H<sub>2</sub>SO<sub>4</sub> concentration on Th<sup>4+</sup> elution efficiency (%)

Eluting agents (1 M)	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Thorium elution efficiency (%)	75	93	56
H <sub>2</sub> SO <sub>4</sub> conc. (M)	Thorium elution efficiency (%)		
0.1	42		
0.2	58		
0.3	65		
0.4	75		
0.5	93		
0.6	93		
0.75	93		
1	93		

Regeneration is an important feature of the studied adsorbent in order to ensure its economic applicability and reuse. The adsorption–desorption cycle was repeated five times with the same loaded adsorbent using 0.5 M H<sub>2</sub>SO<sub>4</sub>. Table 3 shows that the adsorption capacity of Th(IV) decreased slightly after 5 regeneration cycles from 71.2 to 68 mg/g, while the adsorption efficiency decreased from 89 to 85%. After the fifth cycle, the adsorption efficiency decreased sharply to 50%. Thus, the studied modified AC possesses excellent reusability features.

### 3.1.11 Adsorption equilibrium studies

Adsorption isotherms can clearly characterize the interaction pathway of Th(IV) with the modified AC adsorbent. Equilibrium studies are generally used for both the design of sorption process and understanding the sorption mechanism. Thorium ions can be adsorbed onto the surface of a solid support by several mechanisms. The operative mechanism depends on the nature of sorption sites, surface properties, affinities of the sorbent, the type of the sorbate and the bulk properties of the aqueous solution [32].

In the current study, both Langmuir and Freundlich isotherm models were used to correlate experimental data at the determined optimum conditions. Sorption experiments were conducted by mixing 10 mL of solution of an initial thorium concentration 400 mg/L with 0.5 g of the modified AC at pH 3.6 and 200 rpm agitation speed for 40 min at room temperature.

Langmuir adsorption model assumes that adsorption occurs mainly as a saturated monolayer of adsorbate on the surface of the adsorbent. This model assumes too that the energy of adsorption is constant and there is no transmigration of the adsorbed molecules on the adsorbent surface [33]. Langmuir isotherm model can be expressed in the following form:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

where C<sub>e</sub> is concentration of thorium in solution at equilibrium (mg/L), q<sub>e</sub> is the amount of thorium adsorbed per weight unit of adsorbent at equilibrium (mg/g), q<sub>max</sub> is the saturated monolayer maximum adsorption capacity (mg/g) and b is Langmuir constant (L/mg). The linear plots of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> are shown in (Fig. 10). The maximum calculated adsorption capacity (q<sub>max</sub>) was close to experimental data and the correlation coefficient was 0.9977 at room temperature, (Table 4). The value of saturation capacity determined from Langmuir isotherm model was 71.94 mg/g at room temperature which is near to the experimental value of 71.2 mg/g. The tested modified AC showed high sorption capacity compared to other adsorbents [34–40]. From Langmuir assumptions, thorium uptake has occurred on a homogeneous surface as a monolayer and all the metal binding sites are energetically the same [41].

The dimensionless constant called separation factor; R<sub>L</sub>, can be used to predict whether the sorption system is favorable or unfavorable. This parameter can be calculated from the following equation [42]:



**Table 3** Five cycles of Th<sup>4+</sup> adsorption–desorption with 0.5 M H<sub>2</sub>SO<sub>4</sub> acid

Cycle	Adsorption (%)	q <sub>e</sub> (mg/g)	Desorption (%)
1	89	71.2	93
2	88	70.4	91
3	87	69.6	90
4	86	68.8	89
5	85	68	88

*Adsorption conditions* 400 mg/L thorium concentration, 40 min contact time, room temperature, pH 3.6, 100 mL of thorium solution and 0.5 g of modified AC with TPPO

$$R_L = 1/1 + bC_o \tag{5}$$

where b is the Langmuir constant and C<sub>o</sub> is the initial Th(IV) concentration (mg/L). The value of R<sub>L</sub> indicates the nature of the isotherm; if (R<sub>L</sub> = 0) then irreversible, if (0 < R<sub>L</sub> < 1) then favorable and if (R<sub>L</sub> > 1) then unfavorable. The obtained data shows that the values of R<sub>L</sub> are > 1, indicating a favorable sorption process under the conditions applied.

On the other hand, The Freundlich isotherm model assumes that the adsorption process is carried out on a surface of adsorbent with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [43]. The Freundlich isotherm model is represented by the equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

where C<sub>e</sub> is the equilibrium concentration of thorium in the solution (mg/L), q<sub>e</sub> is the amount of thorium adsorbed per weight unit of modified AC at equilibrium (mg/g), K<sub>f</sub> is the adsorption capacity (mg/g) and 1/n is the Freundlich constant related to the intensity of adsorption (L/mg).

The Freundlich constants K<sub>f</sub> and 1/n are calculated from the slope and intercept of the log q<sub>e</sub> versus log C<sub>e</sub>

**Table 4** Adsorption isotherms of thorium by AC modified with TPPO

Adsorption isotherm models	Parameters	298 K
Langmuir isotherm	Equation	Y = 0.0139x + 0.2218
	q <sub>max</sub> (mg/g)	71.94
	b (L/mg)	0.062
	R <sup>2</sup>	0.9977
Freundlich isotherm	Equation	Y = 0.3425x + 1.0031
	k <sub>f</sub> (mg/g)	10.07
	1/n (mg min/g)	0.3425
	R <sup>2</sup>	0.7099

*Adsorption conditions* 400 mg/L thorium concentration, 40 min contact time, room temperature, 0.5 g modified AC TPPO dose, pH 3.6 and 100 mL of thorium solution

plots (Fig. 11). The adsorption parameters are shown in (Table 4). The value of K<sub>f</sub> (mg/g) is lower than the experimental capacity of Th(IV) on modified AC at room temperature. From the obtained data, the calculated by Freundlich isotherm model does not fit with experimental data.

### 3.1.12 Sorption kinetics studies

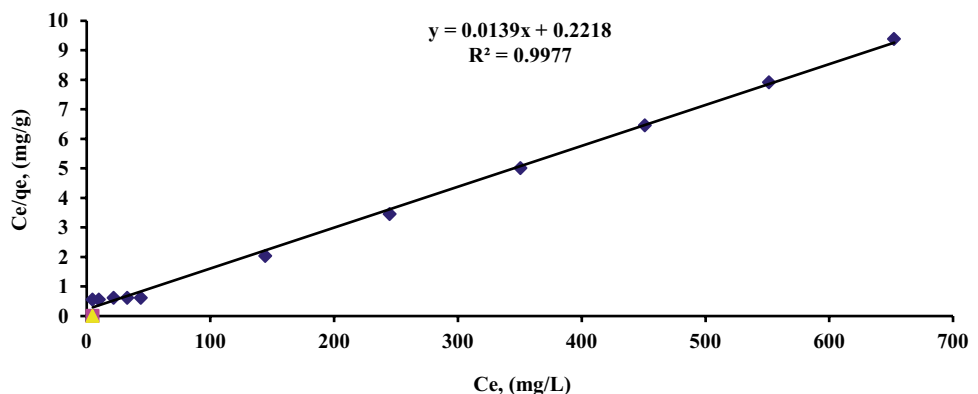
Kinetic studies are helpful for the prediction of adsorption rate and gives important information for designing and modeling extraction processes. Two kinetic models including pseudo-first order and pseudo-second order diffusion models were applied to analyze the kinetics of the sorption process. Thorium sorption kinetics was studied at 400 mg/L concentration, pH 3.6 and stirring speed of 200 rpm at room temperature.

The linear form of pseudo-first order kinetic model can be represented by following equation [44]:

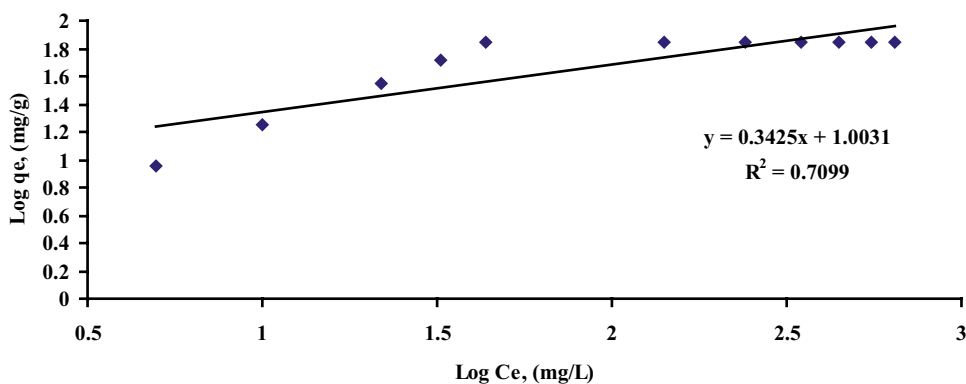
$$\text{Log}(q_e - q_t) = \text{log } q_e - (K_1/2.303)t \tag{7}$$

where q<sub>t</sub> and q<sub>e</sub> are the amounts of thorium ions adsorbed in (mg/g) at time t (min) at equilibrium. The constant k<sub>1</sub> is

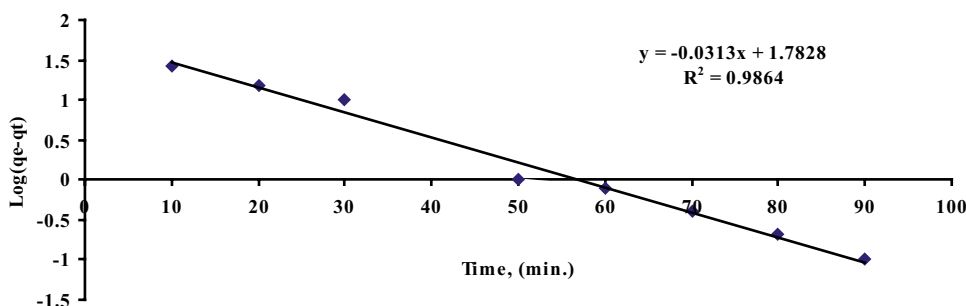
**Fig. 10** Langmuir isotherm model of Th<sup>4+</sup> adsorption by the AC modified with TPPO



**Fig. 11** Freundlich isotherm model of Th<sup>4+</sup> adsorption by AC modified with TPPO



**Fig. 12** Pseudo first order adsorption model of Th<sup>4+</sup> by AC modified with TPPO



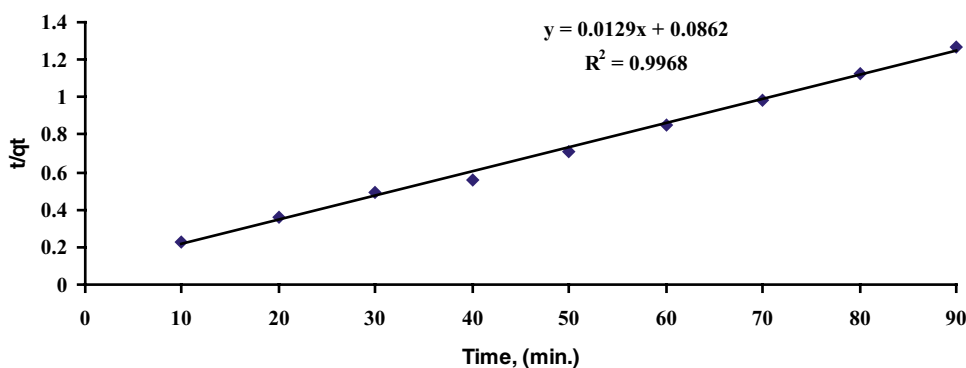
**Table 5** Sorption kinetics of thorium by AC modified with TPPO

Kinetic of sorption	Parameters	298 K
Pseudo first order	q <sub>e</sub> (mg/g)	60.64
	K <sub>1</sub> (min <sup>-1</sup> )	0.072
	R <sup>2</sup>	0.9864
Pseudo second order	q <sub>e</sub> (mg/g)	77.51
	K <sub>2</sub> (g/mg min)	0.00193
	R <sup>2</sup>	0.9968

*Adsorption conditions* 400 mg/L thorium concentration, 40 min contact time, room temperature, pH 3.6, 100 mL of thorium solution and 0.5 g modified AC dose

the adsorption rate constant (min<sup>-1</sup>), which is determined by plotting Log (q<sub>e</sub> - q<sub>t</sub>) versus t (Fig. 12).

**Fig. 13** Pseudo second order model of Th<sup>4+</sup> adsorption by AC modified with TPPO



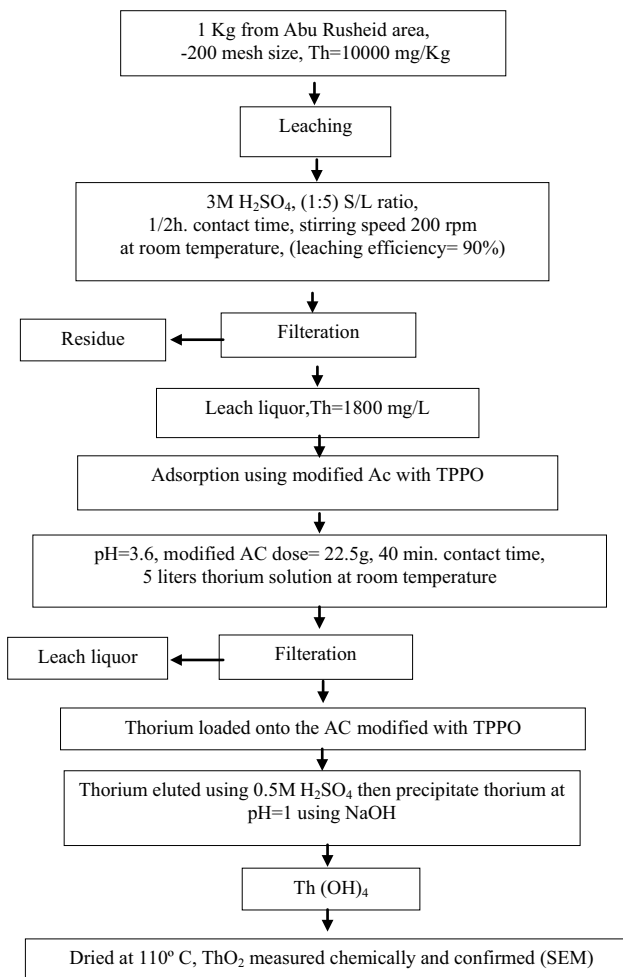
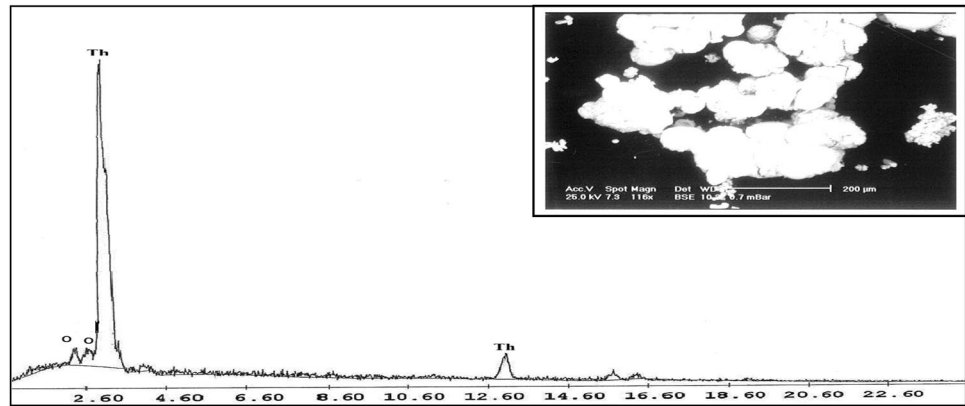
From the data in (Table 5), the sorption capacity was found 60.64 mg/g, and R<sup>2</sup> value was 0.9864. Accordingly, the adsorption processes for the modified AC does not fit a pseudo-first order kinetic model.

Results were also applied to the pseudo-second order kinetic model which is given in the following form [45]:

$$t/q_t = 1/k_2q_e^2 + (1/q_e)t \tag{8}$$

where k<sub>2</sub> is the rate constant (g/mg min). The slope of the straight lines of plots of t/q<sub>t</sub> versus t stands for 1/q<sub>e</sub> while the intercept stands for 1/k<sub>2</sub>q<sub>e</sub><sup>2</sup> (Fig. 13). The calculated value (q<sub>e</sub>) for modified AC was found to be 77.51 mg/g and the correlation coefficient (R<sup>2</sup>) = 0.9968, (Table 5). The obtained experimental data fit well with the pseudo-second order kinetic model. Accordingly, the pseudo second order model is the most suitable model to describe the

**Fig. 14** SEM and EDX analyses of the thorium precipitate



**Fig. 15** Schematic flow diagram for the recovery of thorium from Abu-Rusheid area ore sample, SE desert, Egypt

kinetic process of thorium adsorption by the modified AC. This kinetic process is mainly controlled by the chemisorption which involves chemical bonding between thorium ions and the active sites of the modified AC [46, 47].

**Table 6** Comparison of uptake capacities (mg/g) of different adsorbents towards Th<sup>4+</sup>

Adsorbent	Uptake capacity (mg/g)	References
Lewatit S1468	499.91	[48]
Carbamoylmethylphosphine oxide—crosslinked polymer (CMPO)	25.98	[49]
Merrifield polymer-DMDBMA	15.54	[50]
Magnetic chitosan composite	312.5	[51]
Water hyacinth roots	20	[52]
PEO/PLLA fibrous membranes	50.1	[53]
Methacrylic acid/bentonite	111.36	[54]
Impregnated XAD-7 resin	136.88	[55]
AC modified with TPPO	71.94	Present study

#### 4 Case study

Obtained sample of Abu Rusheid weighing 1 kg with thorium content 10,000 mg/kg was ground to particle size – 200 mesh and was subjected to acid leaching with 3.0 M H<sub>2</sub>SO<sub>4</sub> with S/L ratio of 1:5 for 30 min at room temperature. The leach liquor was filtered and thorium was measured in solution was found 1800 mg/L; leaching efficiency was 90%. Five liters of leaching solution were stirred with 22.5 g of modified AC at pH 3.6 at 200 rpm stirring speed for 40 min. Thorium(IV) was eluted from the loaded modified AC using 0.5 M H<sub>2</sub>SO<sub>4</sub> acid and was precipitated using sodium hydroxide at pH 1 as thorium hydroxide then dried at 110 °C as thorium oxide powder. The thorium assayed 83% in the product with 94.3% purity. The chemical composition of thorium precipitate was characterized by SEM and EDX analyses, (Fig. 14). Finally, a schematic flow diagram for the process is presented in (Fig. 15). A comparative study [48–55] of thorium uptake capacities (mg/g) of different adsorbents is shown in (Table 6).

## 5 Conclusion

Activated carbon modified with TPPO was used for thorium(IV) adsorption at optimum conditions: pH 3.6, 200 rpm agitation speed for 40 min at 25 °C. The maximum uptake capacity of the modified AC was 71.94 mg/g. The obtained data obeyed pseudo-second order kinetic model. Langmuir adsorption isotherm model was found to be the most suitable model for explaining the adsorption process. Finally, the optimized factors have been carried out for thorium adsorption and precipitation from the studied leach liquor of a geologic sample. The final thorium precipitate was measured chemically and characterized by SEM and EDX analyses.

**Acknowledgements** This research paper was carried out as a part of the research activities of the authors. This article was reviewed and approved for publishing by the Nuclear Materials Authority. Despite that all the laboratories, instrumentations and chemicals were provided by the Nuclear Materials Authority; the authors still maintain the full right to publish the manuscript wherever they decide without any conflict of interest with the Nuclear Materials Authority.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Disclosures and disclaimer** This work was funded by the Nuclear Materials Authority as a part of its research activities. This article was reviewed and approved for publishing by the Nuclear Materials Authority with no obligation on the authors' part to revise the manuscript.

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Informed consent** None.

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