Extraction and determination of Th(IV) from aqueous acidic solutions using natural cassiterite adsorbent

Hany Lotfy Weheish¹ · Abdou Ali Abdou¹ · Wagiha Hamed Mahmoud² · Sherien Hussien Ahmed¹ · Ahmed Hussien Orabi¹

© Springer Nature Switzerland AG 2019

Abstract

This work concerned with the extraction of Th(IV) from aqueous solutions using natural cassiterite adsorbent natural tin oxide mineral (SnO_2). The achieved maximum Th(IV) adsorption efficiency (99.2%) depends mainly on some effective parameters such as pH value, contact time, dose of cassiterite, concentration of Th(IV) and temperature. The Langmuir and Freundlich models are used to simulate the sorption isotherms, respectively. On the other hand, not less than 99.6% of the uptaken Th(IV) was regenerated using 0.005 mol L^{-1} HCl solution by stirring for 25 min to yield Th(IV) concentrated solution. The concentrations of Th(IV) in all extraction process were spectrophotometric estimated using 1,4-di-hydroxy anthraquinone and Arsenazo(III) at λ_{max} 600 and 655 nm, respectively.

Keywords Thorium · 1,4-Di-hydroxy anthraquinone · Cassiterite

1 Introduction

Tin presently find extensive uses in industrial and domestic applications. It has been used extensively for soldering, corrosion prevention and food packaging. Tin is found in Egypt as cassiterite mineral and the main tin bearing deposits occur in the central part of the Eastern Desert of Egypt [1]. There are many industrial techniques for tin extraction from its ores depending on the type of the ore itself, oxide or sulfide. Each type of the ore should be treated by the suitable technique according to its chemical composition [2]. Tin is extracted from oxide ores usually by reduction smelting of the ore at high temperature (1200°C) using suitable fluxing agent silica or lime depending on the type and quality of the gangue material present in the ore [3].

Direct determination of uranium and thorium is still difficult because of insufficient sensitivity, lack of selectivity, presence of complex matrix, and poor precision and accuracy. To solve these problems, pre-concentration and

separation techniques have been used for uranium and thorium determination in environmental and biological samples. Online separation and pre-concentration of thorium and uranium is carried out by means of uranium and tetravalent actinides resin. After elution, Th(IV) and U(VI) are spectrophotometric detected after reaction with Arsenazo-III in different types of environmental sample matrices achieving high selectivity levels [4].

New surface ion-imprinted composite polymer was used for the extracting and pre-concentrating traces of Th(IV) ion prior to its photometric determination. The maximum uptake capacity of this material and that of the non-imprinted polymer at pH 4.5 are 56.8 and 26.3 mg g^{-1} , respectively. Recovery exceeds 95% and is complete within 5 min. The relative standard deviation is $< 2.5\%$, the detection limit is $0.54 \mu\text{g L}^{-1}$ (3σ). The imprinted polymer was coupled to spectrophotometry to separate and determine trace levels of Th(IV) in a soil standard material with satisfactory results [5]. More over different biomaterials of high Th(IV) sorption efficiency such as rice bran (RB) and wheat

✉ Abdou Ali Abdou, abdouchem76@gmail.com | ¹Nuclear Materials Authority, P.O. Box 530, El-Maadi, Cairo, Egypt. ²Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt.

bran (WB) in the strong acidic media. These sorbents have the sorption capacities 49.3 and 38.7 mg g⁻¹ for RB and WB respectively from distribution isotherms in 4 mol L⁻¹ HNO₃.

The mentioned biomaterials were already applied for the extraction of thorium from a real sample (monazite mineral) with achieved extraction efficiencies of 95.4 and 74.6% from 4 mol L⁻¹ nitric acid for RB and WB, respectively. The selected bio-sorbents have the potential to be applied on industrial scale because of economic and operational benefits. Tin dioxide belongs to the family of the equivalent element oxides AO₂ (SiO₂, MnO₂, TiO₂, SnO₂). These hydrous oxides show acidic and ion exchange properties due to Bronsted acidic groups. They behave either as cationic or anionic exchangers, depending upon the basicity of the central atom and the strength of the M–O bond relative to that of the O–H bond in the hydroxyl group, if the hydroxyl groups are the only Bronsted acidic groups present [6]. The equilibrium may be written as follows:

The acidity scale of these different oxides is established by comparison of the pH of the isoelectric points. We notice that the acidic strength decreases in the order SiO₂, MnO₂, TiO₂, SnO₂ and so do the capacities for cationic exchangers in the basic media. The values of the pH of the isoelectric points depend on the structures of the oxides.

The divalent transition elements are easily retained in acidic media although these oxides are anionic exchangers in such media; these elements are hydrolysable and have a great affinity for the oxygen atoms of the hydroxyl groups. The ion-exchange reaction may be represented:

The ion-exchange reaction may be represented as follows:

According to our results, the equilibrium for retention of M⁴⁺ may be written:

Frankly, hydrous Sn(IV) oxide used for separating Th(IV) exists in at least two distinct forms, often referred to as the α- and β-stannic acids and these exhibit

different adsorption properties to both anions and cations. The α-(or ortho) form is usually prepared by the low temperature hydrolysis of Sn(IV) salts in aqueous solution and is readily soluble in both acids and bases. On the other hand, the β-(or meta) form which is generally produced by the action of hot nitric acid on the tin metal, or by the high temperature hydrolysis of Sn(IV) salts is very much more stable [7].

In this context, the objective of the present paper is using the Egyptian natural cassiterite mineral for separating Th(IV) from both aqueous synthetic solutions and ore materials aqueous solutions. The extracted Th(IV) was spectrophotometric determined using 1,4-dihydroxy anthraquinone and Arsenazo(III) at λ_{max} 600 and 655 nm, respectively.

2 Experimental

2.1 Materials

2.1.1 Standard Th(IV) solution

A stock solution of 500 μg mL⁻¹ of thorium was prepared by accurately weighing 0.256 g of thorium nitrate tetrahydrate, [Th(NO₃)₄·4H₂O] dissolved in approximately 30 mL of double-distilled water and adjusted to pH 2.7 using dilute hydrochloric acid and closed up to 250 mL

in a volumetric measuring flask using double-distilled water. Solutions of lower concentrations were obtained via dilution process.

2.1.2 Preparation of cassiterite adsorbent

A weight 10 g of Egyptian cassiterite collected from Rasheid factory of black sand was ground to 0.297 mm and treated with 100 mL of 3 mol L⁻¹ hydrochloric acid and stirred for 48 h at 100–110 °C in atmospheric conditions. After filtration, the cassiterite residue left over the filter paper was washed carefully several times with distilled

Table 1 Complete chemical analysis of the cassiterite

Oxides	Wt%
SnO ₂	97.70
Ta ₂ O ₅	0.95
Nb ₂ O ₅	0.39
Fe ₂ O ₃	0.34
TiO ₂	0.40
SiO ₂	0.10
Total	99.88

water to remove any traces of chloride impurities and then dried at 100 °C for 2 h [8]. The chemical analysis of the purified cassiterite represents in Table 1 according to Abdel-Aal and Abdel-Hay [9].

3 Results and discussion

3.1 Structure characterization of cassiterite

The morphology structure of natural cassiterite sorbent was studied using scanning electron microscope (SEM) analysis. While the crystal structure of was characterized by X-ray diffraction (XRD) analysis. Infrared (FT-IR) analysis was used to confirm the present functional groups.

3.1.1 SEM analysis

Figure 1 represented SEM analysis of both natural (a) and purified cassitrite (b). This figure proved the necessary matter for purification of the natural cassiterite to be useful for application in the extraction process of Th(IV) from aqueous solutions. Chemical composition of natural cassiterite prior to the removal of impurities represented in Table 1

was found agreement with the mineralogy study of natural cassiterite which contains some associated minerals. The analyzed cassiterite especially after purification process have more than 97 wt% of SnO₂, [9].

3.1.2 XRD analysis

From the XRD pattern, the observed diffraction intense peaks at (39.9), (51.33), (57.81), (80.94), (86.25), and (99.7) °2 theta. Figure 2 shows the XRD pattern of the SnO₂ cassitrite mineral. Using the Debye–Scherrer equation [10], the mean crystallite size of the adsorbent was estimated as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

where λ , β , θ are the X-ray wavelength of radiation used. The XRD pattern of the adsorbent showed strong peaks of the cassiterite phase of SnO₂ along with some weak traces of metastable orthorhombic phase. X-ray diffraction revealed that the crystalline structure significantly.

Fig. 2 XRD pattern of the cassiterite mineral (SnO₂) **Fig. 1** ESEM analysis of cassiterite before (a) and after (b) purification

Fig. 3 Infrared spectra of cassiterite mineral

Fig. 4 Effect of pH on the Th(IV) uptake

3.1.3 FT-IR analysis

From the FT-IR spectra, Fig. 3 there are two broad bands at 3445 and 1645 cm^{-1} attributed to the O–H stretching vibration of water absorbed by the sample. The strong peak at 552 cm^{-1} agrees with the stretching vibrations of the Sn–OH bonds, while the peak at 632 cm^{-1} region assigned to the stretching modes of the Sn–O–Sn. The presence of these strong bands proved the hydration process of the natural SnO_2 as has been mentioned in Eq. (1) [6].

3.2 Optimization of Th(IV) adsorption

To optimize the Th(IV) adsorption process several effective parameters were studied including: pH value, the contact time, adsorbent dose, volume aqueous solution and the initial Th(IV) concentration.

3.2.1 Effect of pH on the Th(IV) uptake

Data, Fig. 4 represented the effect of changing pH values of the prepared Th(IV) solution from pH 2 to pH 7 upon Th(IV) adsorption efficiencies by mixing 0.25 g of cassiterite with 50 mL of Th(IV) solution assaying $50\text{ }\mu\text{g mL}^{-1}$

Fig. 5 Effect of contact time on the Th(IV) uptake

Fig. 6 Effect of adsorbents dose on the Th(IV) uptake

and shaking for 4 h at room temperature. The filtrates were analyzed for determining the percent uptake. It was noticed that, Th(IV) adsorption efficiency increased gradually up to 98.3% at the pH 6 and decreased gradually up to 76.6% at pH 7. From the adsorption mechanism Eq. (2), the presence of many OH groups at pH 6 led to encourage the adsorption process [6]. So, the suitable choice for the maximum adsorption efficiency of Th(IV) was pH 6.

3.2.2 Effect of contact time

To find out the optimum time required for the maximum adsorption of Th(IV) using cassiterite adsorbent, a weight 0.25 g of the adsorbent was mixed with 50 mL of Th(IV) solution assaying $50\text{ }\mu\text{g mL}^{-1}$ adjusted to pH 6 and shaking for different time intervals between 30 and 240 min. The filtrates were analyzed for determining the percent uptake for each shaking period. The obtained results, Fig. 5 revealed that the contact time of 210 min is found sufficient for the maximum uptake of Th(IV) not less than 98.7%.

3.2.3 Effect of adsorbents dose

This parameter was studied with different doses of cassiterite ranged from 0.04 to 0.4 g at the obtained optimal conditions. The obtained results, Fig. 6 proved that Th(IV)

Fig. 7 Effect of volume aqueous solution on the Th(IV) uptake

Fig. 8 Effect of initial concentration on the Th(IV) uptake

uptaken efficiency increased gradually from 10 to 99% with increasing the adsorbent dose from 0.04 to 0.3 g, due to high surface area and sufficient active sites for Th(IV) adsorption.

3.2.4 Effect of volume aqueous solution

To find out the effect of sample volume on uptake of Th(IV), solutions containing $50 \mu\text{g mL}^{-1}$ of Th(IV) (keeping the total amount of loaded metal ion constant) present in varying the volume from 25 to 250 mL of the aqueous solution was carried out by adjusting the pH to 6.0 and mixed with 0.3 g of adsorbents after 210 min. The obtained results, Fig. 7 revealed that Th(IV) uptake efficiency decreased gradually from 99.2 to 97.8% with increasing the volume aqueous solution.

3.2.5 Effect of initial Th(IV) concentration

This factor was studied using a sample volume (50 mL) of standard Th(IV) solution assaying different concentrations ranged from 50 to $350 \mu\text{g mL}^{-1}$ of Th(IV) under the optimum conditions previously studied. Results, Fig. 8 reflected that the maximum Th(IV) adsorption capacity increased up to 99.2% when Th(IV) concentration increased up to $300 \mu\text{g mL}^{-1}$ and then remains relatively constant.

Fig. 9 Effect of eluent concentration on the Th(IV) recovery

Fig. 10 Effect of contact time on the Th(IV) recovery

3.3 Optimization of Th(IV) elution process

Elution process is not only used to regenerate the loaded adsorbent, but also to have a concentrated aqueous solution suitable for determination of Th(IV). Several effective parameters were studied to optimize the elution process using HCl solution such as, concentration, contact time, eluent volume (S/L) ratio.

3.3.1 Effect of eluent concentration

This factor was already studied by mixing 0.3 g of the full saturated adsorbent with 25 mL of HCl solution of different concentrations varying between 0.0002 and 0.003 mol L^{-1} and stirred for 15 min. After filtration and analysis, the obtained data, Fig. 9 emphasized that the best Th(IV) elution efficiency of 90% was found at HCl concentration of 0.005 mol L^{-1} compared to the others. Elution process of the loaded cassiterite required the utilizing of dilute acid solution to avoid the free anion interfering in Th(IV) determination method.

3.3.2 Effect of contact time

Figure 10 represented the obtained data of varying the contact time periods from 10 to 30 min up on Th(IV) elution efficiency from the loaded cassiterite adsorbent by

mixing 0.3 g with 25 mL of 0.005 mol L⁻¹ HCl solution. It was observed that increasing the contact time has a remarkable effect on Th(IV) elution efficiency which achieved the maximum value (98.5%) at 25 min.

3.3.3 Effect of eluent volume (S/L) ratio

It is known that, minimum eluent volume is necessary to obtain higher pre-concentration factors. So, different volumes of 0.005 mol L⁻¹ HCl solution ranged from 5 to 40 mL were mixed with 0.3 g of the full saturated adsorbent and stirred for 25 min. It was shown in Fig. 11 that the best Th(IV) elution efficiency of 99.6% achieved using 35 mL of eluent solution by stirring for 25 min.

Finally, it can be concluded from this study that, at least 99.6% of Th(IV) could be regenerated from the loaded cassiterite using 35 mL of 0.005 mol L⁻¹ HCl solution by stirring for 25 min.

3.4 Effect of diverse ions

The interfering effect of various ions at mg levels on Th(IV) determination via the proposed method was examined. The results, Table 2 reflected that, the high concentrations of alkali elements e.g. Na, K, Ca and Mg and moderate concentrations of some transition elements e.g. Fe, V, Cu has very limit effect on Th(IV) determination while low concentrations of Zr, Hf and Ti ions led to more than $\pm 2.0\%$ error.

3.5 Equilibrium, kinetic and thermodynamic studies

3.5.1 Adsorption isotherms studies

Equilibrium data of the adsorption process is essential to develop an equation that used to compare different adsorbents under different operating conditions and to design and optimize an operating procedure. Adsorption isotherms provides rapid and concise information about adsorption process and explains the relationship between

Table 2 Effect various elements on separations of Th(IV)

Interfering ion	Amount mixture (mg L ⁻¹)	Th recovery (%)
Na ⁺ , K ⁺ , Ca ²⁺ and Mg ²⁺	1000	99.2
Fe ³⁺ , Al ³⁺ and Co ³⁺	500	98.8
Cr ⁶⁺ , VO ²⁺ and Cu ²⁺	300	98.5
Y ³⁺ , La ³⁺ and Ce ³⁺	300	98.8
Ti ⁴⁺ , Zr ⁴⁺ and Hf ⁴⁺	100	98.4
SO ₄ ²⁻ , Cl ⁻ and PO ₄ ³⁻	300	99.1

the amounts of species adsorbed by an adsorbent. In this work, two adsorption isotherm models were examined, namely Langmuir and Freundlich. Various concentrations of Th(IV) solution were prepared and the adsorption performance of cassiterite adsorbent was tested to investigate the adsorption isothermal equation.

Langmuir model is given as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (6)$$

The amount of adsorption was calculated by:

$$q_e = (C_i - C_e) \times \frac{V}{M} \quad (7)$$

The plot of C_e/q_e versus C_e gave a straight line, Fig. 12 where the adsorption behavior follows the Langmuir adsorption isotherm. $Q_{\max}$ and K_L were calculated from the slope and intercept of linear plots.

Freundlich isotherm assumed a heterogeneous surface and an exponential distribution of the energy of the active sites. Linearized equation of Freundlich model is given as follows:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (8)$$

The plot of $\log q_e$ versus $\log C_e$ gave a straight line, Fig. 13 so, the adsorption behavior follows the Freundlich

Fig. 11 Effect of eluent volume (S/L) ratio on the Th(IV) recovery

Fig. 12 Langmuir adsorption isotherm simulation of Th(IV) adsorption on cassiterite adsorbent

Fig. 13 Freundlich adsorption isotherm simulation of Th(IV) adsorption on cassiterite adsorbent

adsorption isotherm. K_f and n were calculated from the slope and intercept of linear plots.

Data, Table 3 confirmed that the equilibrium is best described by a Langmuir isotherm, with correlation coefficients above 0.977. Langmuir isotherm showed a better fit than the Freundlich isotherm, and indicating the applicability of monolayer coverage of Th(IV) on cassiterite. The maximum monolayer adsorption capacities of Th(IV) on cassiterite was found to be 61.46 mg g^{-1} .

3.5.2 Uptake kinetics studies

Adsorption rate established Th(IV) uptaken kinetics on cassiterite under various process conditions. Different kinetic models, such as pseudo first order kinetic model and pseudo second order kinetic model are used. The employed pseudo first order rate equation is given as follows:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

The plot of $\log (q_e - q_t)$ versus time gave a straight line, Fig. 14 shows that the adsorption behavior follows the pseudo first order. The pseudo first order rate constant K_1 was calculated from the slope. The employed pseudo second order rate equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

The plot of t/q_t versus time gave a straight line, Fig. 15 reflected that the adsorption behavior follows the pseudo

Fig. 14 Pseudo first order model rate constants for adsorption of Th(IV) ions by cassiterite

Fig. 15 Pseudo second order model rate constants for adsorption of Th(IV) ions by cassiterite

second order. The pseudo- second-order rate constant K_2 was determined from the slope and intercepts.

Table 4 indicates that the adsorption of Th(IV) onto cassiterite fits well pseudo second order according correlation coefficients. For this reason, the rate limiting step may be chemical sorption or chemisorption.

3.5.3 Thermodynamic studies

Thermodynamic parameters such as enthalpy (ΔH°), free energy (ΔG°), and entropy (ΔS°) of adsorption were estimated using the following equations:

$$\ln k_d = \frac{\Delta S^\circ}{R} + \frac{-\Delta H^\circ}{RT} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

Table 3 Comparison of the Langmuir and Freundlich, Parameters and correlation coefficients of isotherm models

Adsorbent	Langmuir parameters			Freundlich parameters		
	Calculated $Q_{\max}$ (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
Cassiterite	61.46	0.130	0.977	9.904	1.975	0.949

Table 4 The results of pseudo first order and pseudo second order rate constants for adsorption of Th(IV) ions by cassiterite adsorbent

Adsorbent	Pseudo first order model		Pseudo second order model	
	K_1 (m g ⁻¹)	R ²	K_2 (mg g ⁻¹ min ⁻¹)	R ²
Cassiterite	0.012	0.969	0.0028	0.990

Fig. 16 Thermodynamic parameters for Th(IV) adsorption onto cassiterite**Table 5** Thermodynamic parameters for Th(IV) adsorption onto cassiterite

Temperature (K)	Thermodynamic parameters for thorium adsorption onto cassiterite		
	ΔH° (KJ/mol)	ΔS° (KJ/K mol)	ΔG° (KJ/mol)
298	9.973	0.101	-20.196
308			-21.208
318			-22.220
328			-23.233

Distribution coefficient (K_d , mL/g) is also computed using the following equation:

$$k_d = \frac{C_i - C_e}{C_e} \times \frac{V}{M} \quad (13)$$

Table 6 Comparison of adsorption capacities of cassiterite and various adsorbents for Th(IV)

Adsorbent	Equilibrium time, min	Th(IV) efficiency (%)	Adsorption capacity, q (mg g ⁻¹)	References
Al-pillared rectorite	2880	99	81.2	[11]
Attapulgit	300	100	3.71	[12]
MX-80 bentonite	1440	95	23.2	[13]
Na-bentonite	2880	90	38.28	[14]
Illite	90	85	1.14	[15]
Activated bentonite	900	100	6.55	[16]
Cassiterite	210	99.2	61.46	This work

The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of $\ln K_d$ versus $1/T$ by using Eq. (12), Fig. 16. Gibbs free energy ΔG° was calculated for each working temperature by using Eq. (13).

Th(IV) results indicate that the adsorption process is spontaneous and endothermic dependent. The positive value of ΔS° suggests some structural changes in the adsorbate and adsorbent. The negative values for the Gibbs free energy change show that the adsorption process is thermodynamically feasible and the degree of spontaneity of the reaction increases with increasing temperature as seen in Table 5. This is indicating that the adsorption reaction is spontaneous.

3.6 Comparison with other inorganic mineral adsorbents

Studies on series of inorganic mineral adsorbents for Th(IV) adsorption have been widely reported in published journals recently. As some are listed in Table 6, on one hand, cassiterite is superior to some reported inorganic mineral adsorbents with shorter adsorption equilibrium time (210 min) and higher adsorption capacity (61.46 mg g⁻¹) for Th(IV), whereas it usually takes hours to arrive adsorption equilibrium for other listed inorganic mineral adsorbents, and the adsorption capacity is lower. For example, 2880 min and 81.2 mg g⁻¹ for Al-pillared rectorite [11], 300 min and 3.71 mg g⁻¹ for Attapulgit [12], 1440 min and 23.2 mg g⁻¹ for MX-80 bentonite [13], 2880 min and 38.28 mg g⁻¹ for Na-bentonite [14], 90 min and 1.14 mg g⁻¹ for Illite [15], 900 min and 6.55 mg g⁻¹ for activated bentonite [16].

4 Conclusion

Cassiterite is a tin oxide natural mineral (SnO₂) used for separation of Th(IV) from either aqueous solutions. The maximum Th(IV) uptaken efficiency of 99.2% was achieved using standard Th(IV) solution assaying 50 µg mL⁻¹ at pH 6 using 0.3 g of cassiterite adsorbent by stirring for 210 min. Applying the mentioned optimum adsorption conditions

on 1 g of cassiterite adsorbent and using different Th(IV) concentrations, it can be easily calculated the maximum Th(IV) adsorption capacity of natural cassiterite adsorbent which achieved 61.46 mg g^{-1} . Not less than 99.6% of Th(IV) could be regenerated from the loaded cassiterite using 35 mL of 0.005 mol L^{-1} HCl solution by stirring for 25 min. The extracted Th(IV) was determined using 1,4-di-hydroxy anthraquinone and Arsenazo(III) at λ_{max} 600 and 655 nm, respectively.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Sabet AH (1973) Tin-Tungsten mineralization in the Central Eastern Desert of Egypt. *Ann Geol Surv Egypt* 3:75–86
- Habashi F (1997) Handbook of extractive metallurgy, vol 2. Wiley, New York, pp 683–714
- Murach NN, Sevryukov NN (1964) Metallurgiya olova (Metallurgy of Tin). Metallurgiya, Moscow
- Avivar J, Ferrer L, Casas M, Cerdà V (2011) Smart thorium and uranium determination exploiting renewable solid-phase extraction applied to environmental samples in a wide concentration range. *Anal Bioanal Chem* 400:3585–3594. <https://doi.org/10.1007/s00216-011-5005-4>
- Cheng Z, Wang H, Wang Y, He F, Zhang H, Yang S (2011) Synthesis and characterization of an ion-imprinted polymer for selective solid phase extraction of thorium(IV). *Microchim Acta* 173:423–431. <https://doi.org/10.1007/s00604-011-0576-5>
- Monji AB, Ghoulipour V, Mallah MH, Mianji BM (2015) Selective sorption of thorium (IV) from highly acidic aqueous solutions by rice and wheat bran. *J Radioanal Nucl Chem* 303(1):949–958. <https://doi.org/10.1007/s10967-014-3559-2>
- Waters SL, Horlock PL, Kensett MJ (1983) The application of hydrous tin(IV) oxide in radiochemical separations and in particular, for the $^{68}\text{Ge}/^{68}\text{Ga}$ and $^{82}\text{Sr}/^{82}\text{Rb}$ generator systems. *Int J Appl Radiat Isot* 14(1):1023
- Firdiyono F, Andriyah L, Ainiz FN, Arini T, Lalasari LH (2018) Preliminary study on the dissolutions of Ce, Nd, Y and La from mineral cassiterite by acid and alkaline leaching. *Mater Sci Eng* 333(1):1–7. <https://doi.org/10.1088/1757-899X/333/1/012040>
- Abdel-Aal MA, Abdel-Hay ME (2012) Mineralogy and chemical distribution study of placer cassiterite and some associated new recorded minerals, east Rosetta, Egypt. *Arab J Geosci* 5(4):807–816. <https://doi.org/10.1007/s12517-011-0282-y>
- Tazikeh S, Akbari A, Talebi A, Talebi E (2014) Synthesis and characterization of tin oxide nanoparticles via the Co-precipitation method. *Mater Sci Pol.* <https://doi.org/10.2478/s13536-013-0164-y>
- Yu SM, Chen CL, Chang PP, Wang TT, Lu SS, Wang XK (2008) Adsorption of Th(IV) onto Al-pillared rectorite: effect of pH, ionic strength, temperature, soil humic acid and fulvic acid. *Appl Clay Sci* 38:219–226. <https://doi.org/10.1016/j.clay.2007.03.008>
- Chen L, Gao X (2009) Thermodynamic study of Th(IV) sorption on attapulgite. *Appl Radiat Isot* 67:1–6. <https://doi.org/10.1016/j.apradiso.2008.05.014>
- Lu S, Guo Z, Zhang C, Zhang S (2011) Sorption of Th(IV) on MX-80 bentonite: effect of pH and modeling. *J Radioanal Nucl Chem* 287:621–628. <https://doi.org/10.1007/s10967-010-0810-3>
- Pan D, Fan Q, Li P, Liu S, Wu W (2011) Sorption of Th(IV) on Na-bentonite: effects of pH, ionic strength, humic substances and temperature. *Chem Eng J* 172:898–905. <https://doi.org/10.1016/j.cej.2011.06.080>
- Hongxia Z, Xiaoyun W, Honghong L, Tianshe T, Wangsuo W (2016) Adsorption behavior of Th(IV) onto Illite: effect of contact time, pH value, ionic strength, humic acid and temp. *Appl Clay Sci* 127:35–43. <https://doi.org/10.1016/j.clay.2016.03.038>
- Yin Z, Pan D, Liu P, Wu H, Li Z, Wu W (2018) Sorption behavior of Th(IV) onto activated bentonite. *J Radioanal Nucl Chem* 316:301–312. <https://doi.org/10.1007/s10967-018-5716-5>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.