Research article

Extraction of Th(IV) metal ions with trioctylphosphine oxide dissolved in kerosene using multi-dropped liquid membrane technique

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ABSTRACT

In the present work, the experimental investigation and modeling of Th(IV) metal ions recovery have been carried out by using the recycling mode of the multi-dropped liquid membrane (MDLM) technique. Experiments were done at operational conditions: studies of the MDLM system with single and double reactor column (continuous system). The optimum condition for the extraction of Th(IV) was a 0.50 M HNO_3 solution as donor phase, 0.10 $molL^{-1}$ TOPO as a carrier, and 0.10 M H_2SO_4 as acceptor phase. The transport percentage of Th(IV) was increased up to >98% and the calculated activation energy which is 6.52 $kcalmol^{-1}$ indicated that the process was diffusion controlled by Th(IV) ions. The reuptake efficiencies of the extraction of Th(IV) ions in the presence of Cd(II), Cu(II), Ni(II), and Pb(II) separately under optimized experimental conditions were investigated. Therefore, the MDLM system might be useful for the design and the optimization of the recovery of Th(IV) in the recycling mode.

1. Introduction

Selective separation of heavy and toxic metal ions from waste solutions is often required in hydrometallurgical processes. Solvent extraction is a valuable method for separating some metal ions from the solution. The use of solvent extraction as a unit operation in hydrometallurgy is now widely used for metals of various types kinds of raw materials including low-grade ore, waste materials, and waste (Rydberg, 1992).

With the increasing demand for heavy metals as the main material in the production process, it is necessary to develop high-performance and economical separation methods to recover metals from low-grade ores and secondary sources. Ordinary solvent extraction techniques will require a large amount of extractant and a long time.

One of the effective methods to be used in the thorium purification process is solvent extraction. Long-chain amines have been utilized extensively as extracting agents for various elements including uranium and thorium. Several types of extractants that have been investigated or used commercially include tributyl phosphate, bis(2,4,4-trimethylpentyl) thiophosphinic acid, bis (2,4,4-trimethylpentyl) phosphinic acid, Adogen- 383 (secondary amine), Prime JM-T (primary amine) (Nasab, 2014). Tri-n-octyl phosphine oxide (TOPO) is one of the organo-phosphorus compounds that function as a substance forming complex organic phase compounds with the chemical formula $(C_8H_{17})_3PO$. TOPO oxide has physical properties such as wax crystals, melt at 51 °C, with a boiling point at 1.00 atm pressure of 200 °C. TOPO can dissolve in almost all hydrocarbon compounds. The highest solubility occurs in cyclohexane at a temperature of 25 °C, which is 0.9222 mol/g. The solubility of TOPO increases with temperature. Kerosene, varsol (saturated aliphatic and cyclic C7 to C12 hydrocarbons), and benzene are also quite good as TOPO diluents. Kerosene is both a high dispersion coefficient and a diluent compound for organic compounds. In addition, kerosene is easy to obtain and relatively cheaper than other solvents. The use of diluents in membrane systems is mainly to improve the physical properties of the organic phase. This compound has been widely used in separation and purification processes, especially on a laboratory scale (Purwani and Setyadji, 2015).

Research on thorium purification using TOPO extractant has also been carried out on monazite leached solutions. The results showed that the percentage of thorium extraction produced was higher when compared to other extractants (Afifi et al., 2012).

Extraction of Th(IV) across MDLM is investigated systematically under different experimental conditions such as studies of the MDLM system with a single reactor column, the concentration of TOPO in the membrane phase, the concentration of Th(IV) and HNO_3 acid in the feed solution, flow rate effect of membrane phase, and temperature effect. Transport of thorium ions through the MDLM in the presence of other metal ions is also investigated. The mathematical model describing the

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transport of Th(IV) across MDLM is developed and it is verified with experimental results.

2. Material and equipment's

Thorium nitrate (BDH) and TOPO (Fluka) were used without further purification. Kerosene was purified by distillation. Sulphuric acid (98%) (BDH), nitric acid (60%) (BDH), and Hydrochloric acid (36.5%) (BDH) were used throughout this work. Thorin [2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid] (Alfa Aesar) spectrophotometric reagent was used for Th(IV) ions determination. Deionized water was used for the preparation of aqueous solutions and for washing all glassware and MDLM systems. All pH measurements were carried out using a pH meter (HANNA HI 221). Weighing's were carried out on Analytical balance (Shimadzu AY 220). WiseCircu brand cryostat device was used to keep the solutions in the MDLM system at a constant temperature, and Longer Pump BT 300 2J brand peristaltic pump was used for the organic phase to pass between the phases under pressure. The spectrophotometric measurements were carried out using a double beam spectrophotometer (PerkinElmer Lambda 25).

2.1. Apparatus

In our experimental studies, the used experimental setup is given in Figure 1. Our experimental setup consists of two reactors and the dimensions of each reactor are the same. In the setup, D is symbolized as the donor phase (α), M as the organic phase (β), and the acceptor phase (γ). D Donor (α) phase; Acidic aqueous solution with sodium perchlorate containing thorium ions, M Organic (β) phase; TOPO solution prepared in freshly distilled kerosene, and A is the Acceptor (γ) phase solution containing sulfuric acid.

The system temperature was kept constant with the fluid circulated from the T-circulating constant temperature liquid bath. With the help of a P peristaltic pump, the organic phase was passed through the aqueous phases as particles at a constant flow rate, so that the thorium ion was taken from the donor phase and released into the acceptor phase. Thorium ion concentration in the donor phase and acceptor phase was calculated by reading the absorbance values of the samples taken from the D and A taps using the TOPO-Thorin method.

TOPO/Thorin method was used for quantitative analysis of thorium in the dilute aqueous medium. The basis of the method is to convert Th(IV) metal ions in the aqueous phase into a complex structure that can absorb in the visible region with the thorin reagent. In all studies, the mixture prepared by adding 0.5 mL of 20% HCl solution, 1 mL of 2% thorin reagent, and 7.5 mL of distilled water to 1 mL of sample for the Th(IV) concentration in the aqueous solution was shaken for a certain period of time. After shaking, it has been waited for 15 min and the absorbance value was determined at a wavelength of 549.5 nm, where the maximum absorbance was observed in the UV Spectrophotometer (Thomason et al., 1949; Rastegarzadeh et al., 2010; Khan et al., 2014). By reading the absorbance values of solutions with certain Th(IV) concentrations, the concentration-absorbance change graph and equation were determined to be used in other studies.

2.2. Data analysis

The transport reaction of Th(IV) metal ions with TOPO in the MDLM system is a consecutive reaction and the reaction mechanism is given in Eq. (1).
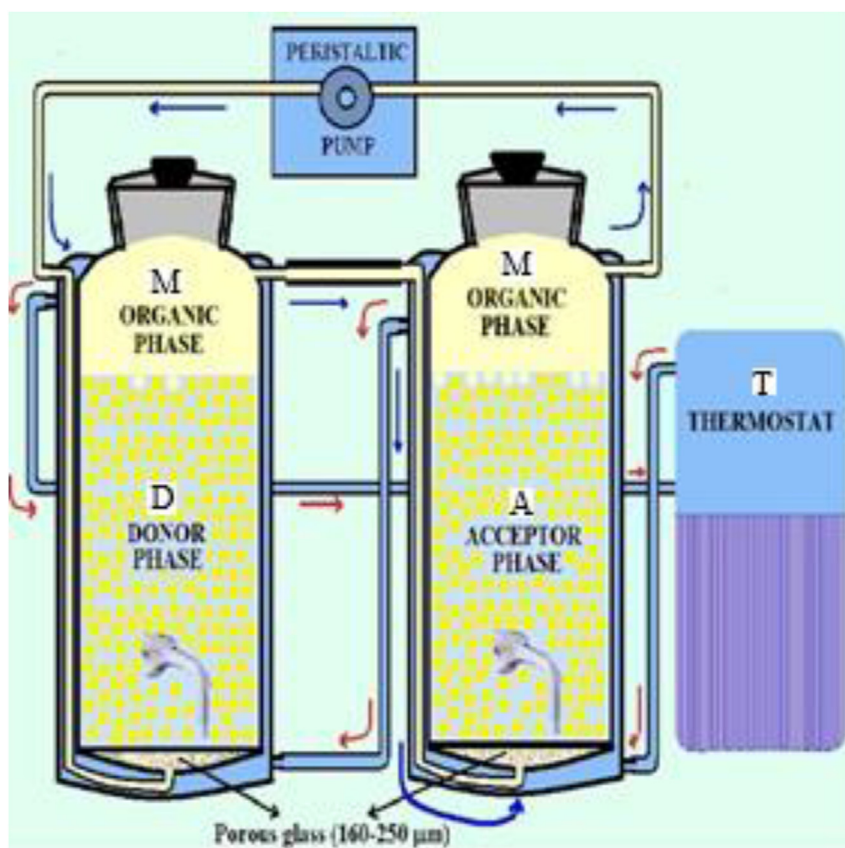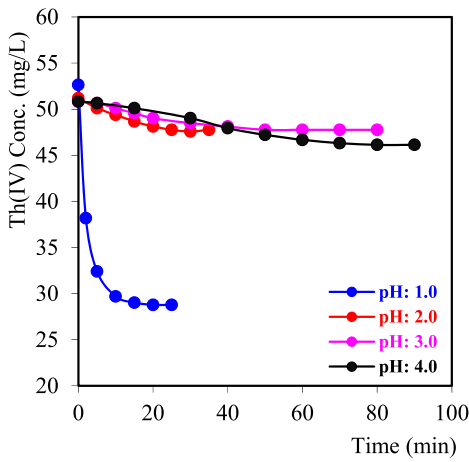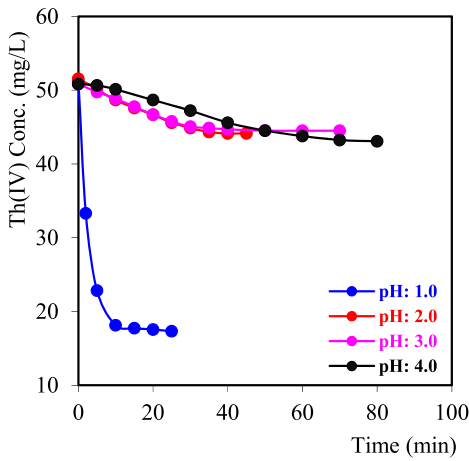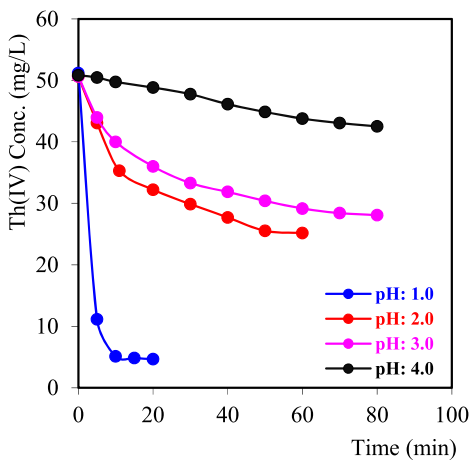
$$D_{Th(IV)} \xrightarrow{k_1} M_{Th(IV)} \xrightarrow{k_2} A_{Th(IV)} \tag{1}$$

Figure 1. Experiment setup used in the continuous extraction system.

a)

b)

c)

Figure 2. Variation of Th(IV) metal ions in the donor phase versus time at different pH and TOPO concentrations; a) 3.23×10^{-3}M, b) 4.31×10^{-3}M, c) 6.47×10^{-3}M.

$D_{Th(IV)}$, $M_{Th(IV)}$, and $A_{Th(IV)}$ given in the above equation are the concentrations of Th(IV) ions in the donor, organic (membrane) and acceptor phases, respectively. k_1 and k_2 are the extraction and back extraction rate constants for first order reactions.

The following Eqs. (2), (3), and (4) were used to calculate the values of $[D_{Th(IV)}, M_{Th(IV)}$, and $A_{Th(IV)}]$ Th(IV) metal ions in all three phases.
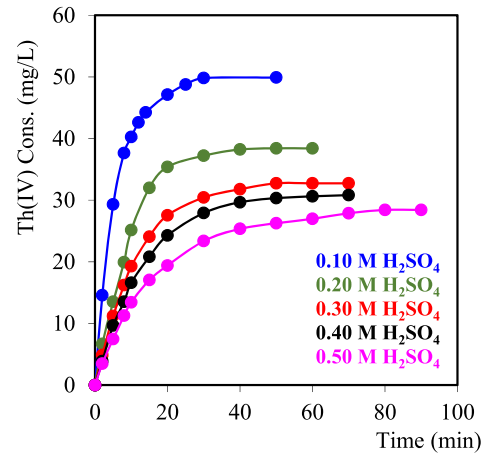

Figure 3. Variation of Th(IV) metal ion reuptake from the organic phase to acidic acceptor phase versus time.

$$D_{Th(IV)} = C_{Th(IV)} \ exp^{-k_1 t} \tag{2}$$

$$M_{Th(IV)} = \frac{C_{Th(IV)} \ k_1 \left[exp^{-k_1 t} - exp^{-k_2 t} \right]}{(k_2 - k_1)} \tag{3}$$

$$A_{Th(IV)} = C_{Th(IV)} \left[1 - \frac{\left[k_2 exp^{-k_1 t} - k_1 exp^{-k_2 t} \right]}{(k_2 - k_1)} \right] \tag{4}$$

where $C_{Th(IV)}$ is the initial concentration of Th(IV) metal ions.

The formulas used to calculate the time when the $M_{Th(IV)}$ value is maximum and the concentration at which the $M_{Th(IV)}$ value is maximum are given in Eqs. (5) and (6), respectively. These two relations give the maximum concentration of Th(IV) ions in the membrane phase and the magnitude of the maximum concentration.

$$t_{MTh(IV)}^{max} = \frac{ln\left(\frac{k_1}{k_2} \right)}{k_1 - k_2} \tag{5}$$

$$M_{Th(IV)}^{max} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}} \tag{6}$$

Eq. (7) was obtained by using Eqs. (5) and (6) together in calculating the k_2 value.

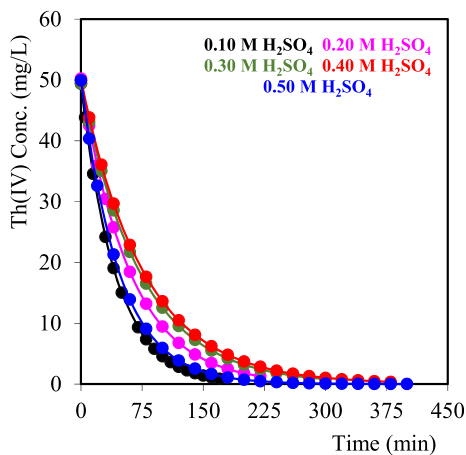$$k_2 = \frac{ln\left(\frac{1}{M_{Th(IV)}^{max}} \right)}{t_{MTh(IV)}^{max}} \tag{7}$$

The maximum fluxes in the MDLM system are obtained by substituting the expression $t_{MTh(IV)}^{max}$ given for Eq. (5) in Eqs. (8), (9), (10), and (11) (Donat et al., 2022):

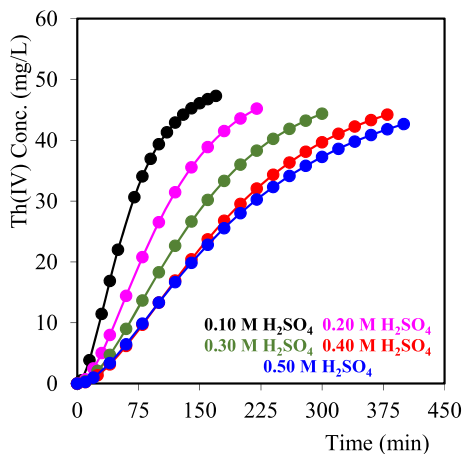$$\left[\frac{dD_{Th(IV)}}{dt} \right]_{max} = -k_1 \left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_1 - k_2}} = J_d^{max} \tag{8}$$

$$\left[\frac{M_{Th(IV)}}{dt} \right]_{max} = 0 \tag{9}$$

$$\left[\frac{A_{Th(IV)}}{dt} \right]_{max} = k_2 \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}} = J_a^{max} \tag{10}$$
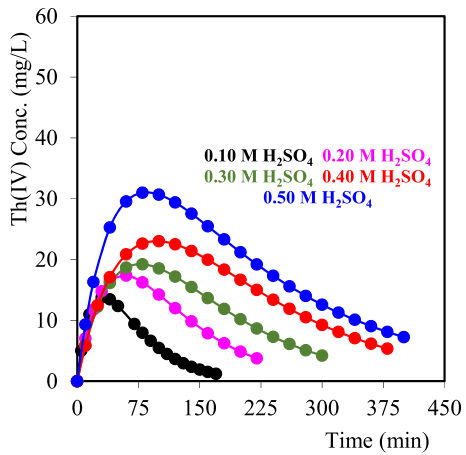
$$-\left[\frac{D_{Th(IV)}}{dt} \right]_{max} = +\left[\frac{A_{Th(IV)}}{dt} \right]_{max} \Rightarrow -J_d^{max} = +J_d^{max} \tag{11}$$

Figure 4. Time variation of Th(IV) metal ion concentration in a) Donor phase, b) Acceptor phase, c) Organic phase. (TOPO conc. 1.62×10^{-3} M).

In Eq. (12), maximum flux values at different temperatures are used to find the activation energy values from the Arrhenius equation.

$$\ln(J) = \ln(A) - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad (12)$$

The percentage of Th(IV) ion extraction successfully extracted in the MDLM system was done by measuring the amount of Th(IV) ion that
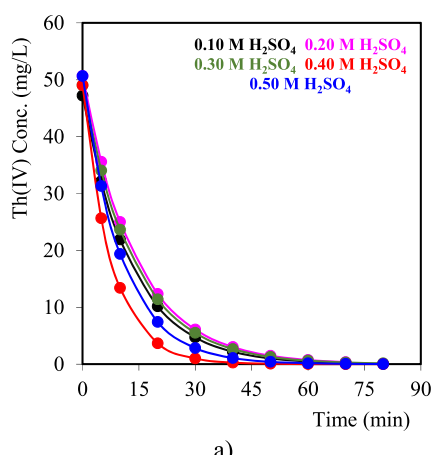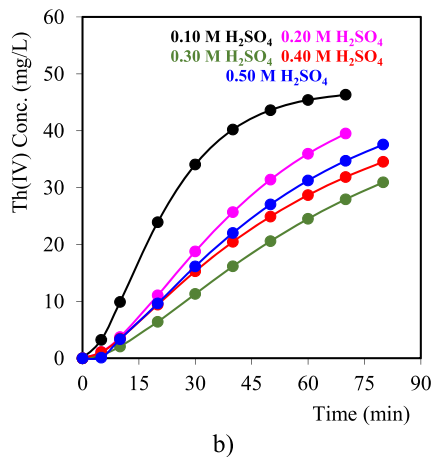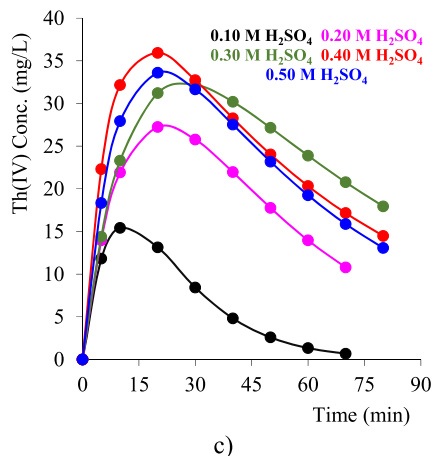

Figure 5. Time variation of Th(IV) metal ion concentration in a) Donor phase, b) Acceptor phase, c) Organic phase. (TOPO conc. 3.23×10^{-3} M).

passed into the acceptor phase. The following Eq. (13) was used to determine the percent reuptake of Th(IV) ion extraction obtained in this study:

$$E,\ \% = \frac{[\text{Th(IV)}]_{i,aq} - [\text{Th(IV)}]_{f,aq}}{[\text{Th(IV)}]_{i,aq}} \times 100\% \qquad (13)$$

where $[\text{Th(IV)}]_{i,aq}$ is: initial Th(IV) concentration in the aqueous phase and $[\text{Th(IV)}]_{f,aq}$ is: final Th(IV) concentration in the aqueous phase.
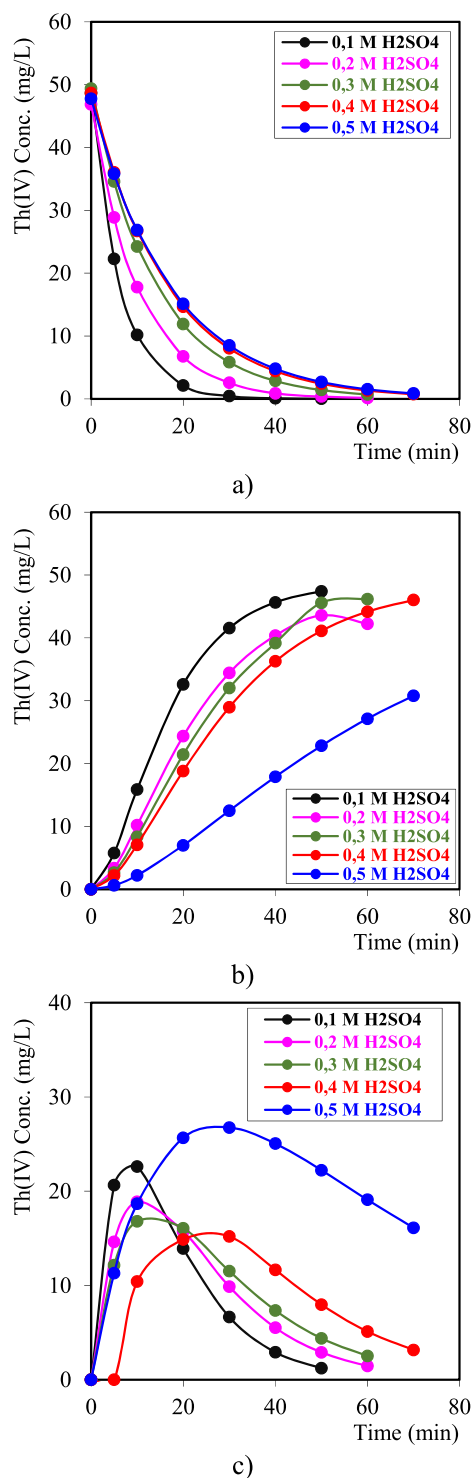
Figure 6. Time variation of Th(IV) metal ion concentration in a) Donor phase, b) Acceptor phase, c) Organic phase (TOPO conc. 4.31×10^{-3} M).

3. Result and discussions

3.1. Studies of the MDLM system with a single reactor column

3.1.1. Extraction of Th(IV) ions from the donor phase to the organic phase with a single column MDLM system

In our study, experiments were carried out with 50 mg/L Th(IV) aqueous solutions in the pH 1.00–4.00 (HNO$_3$) range to determine the most effective pH in the transport of Th(IV) ions from the aqueous phase

Table 1. Kinetic results of transport using TOPO at different acceptor concentrations.

1.62×10^{-3} M TOPO						
H$_2$SO$_4$ (M)	k_1x10^2 (min^{-1})	k_2 x10^2 (min^{-1})	$M_{MTh(IV)}^{max}$ (g/mL)	$t_{MTh(IV)}^{max}$ (min)	J_d^{max} x10^3 (min)	J_a^{max}x10^3 (min)
0.10	2.38	3.92	13.87	32.40	-11.00	11.00
0.20	1.67	1.54	19.23	64.40	-5.90	5.90
0.30	1.37	1.19	19.46	78.25	-4.69	4.69
0.40	1.30	0.691	24.37	103.77	-3.37	3.37
0.50	2.13	0.294	36.36	107.86	-2.14	2.14
3.23x10^{-3} M TOPO						
H$_2$SO$_4$ (M)	k_1x10^2 (min^{-1})	k_2 x10^2 (min^{-1})	$M_{MTh(IV)}^{max}$ (g/mL)	$t_{MTh(IV)}^{max}$ (min)	J_d^{max} x10^3 (min)	J_a^{max}x10^3 (min)
0.10	7.68	9.52	15.54	11.67	-3.13	3.13
0.20	7.06	2.75	27.75	21.87	-1.51	1.51
0.30	7.31	1.32	33.62	28.57	-0.90	0.90
0.40	12.76	1.60	36.40	18.60	-1.19	1.19
0.50	9.60	1.95	33.74	20.84	-1.30	1.30
4.31x10^{-3} M TOPO						
H$_2$SO$_4$ (M)	k_1x10^2 (min^{-1})	k_2 x10^2 (min^{-1})	$M_{MTh(IV)}^{max}$ (g/mL)	$t_{MTh(IV)}^{max}$ (min)	J_d^{max} x10^3 (min)	J_a^{max}x10^3 (min)
0.10	15.61	9.52	22.46	8.12	-4.39	4.39
0.20	9.73	7.52	19.50	11.66	-3.13	3.13
0.30	7.12	6.53	18.96	14.66	-2.51	2.51
0.40	6.00	6.22	17.57	16.37	-2.25	2.25
0.50	5.75	2.01	27.15	28.10	-1.14	1.14

to the organic phase. Concentrations of carrier reagent TOPO prepared in kerosene in the organic phase were used as $3.23.10^{-3}$, $4.31.10^{-3}$, $6.47.10^{-3}$ M. Experiments were carried out using a single reactor at a constant flow rate (120 rpm) and constant temperature (25 °C) in the form of droplets from the donor phase to the organic phase. The graph of the percentage extraction of Th(IV) metal ions as a function of acid concentration is shown in Figure 2.

The percentage of Th(IV) metal ions extraction increases with increasing acidity of the solution. However, when the nitric acid concentration exceeds pH: 4.00, the percentage of thorium extraction decreases. The results of this experiment are similar to the experimental results of thorium extraction with TOPO dissolved in toluene (Alin et al., 1987). The decrease in the percentage of thorium extraction can occur because the acid is also extracted by TOPO at an acid concentration that exceeds a certain level. Acid extraction by TOPO is shown in the following Eq. (14) (Xie et al., 2014).

$$H^+ + NO_3^- + TOPO \leftrightarrow HNO_3TOPO \qquad (14)$$
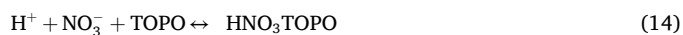
With the increase in pH value, Th(IV) ions in the solution undergo hydrolysis and pass from the state of Th(IV) to $[Th(OH)_n]^{(4-n)+}$. Although the Th(IV) ions are effectively complexed with the TOPO reagent, the hydroxy ions cannot be complexed. Therefore, as the hydroxy ion increases, the efficiency of the transition to the organic phase decreases. As the concentration of the carrier ligand (TOPO) decreases and the pH of the donor phase increases, the concentration of Th(IV) ions remaining in the donor phase increases. As seen in Figure 2, the transport time of Th(IV) ions from the donor phase to the organic phase also increases. It can be seen that the percentage of thorium extraction increased from the 2nd to the 10th minute and started to decrease at the 15th minute. This percentage trend of extraction is similar to the results of thorium solvent extraction using TOPO with nitrate-based artificial thorium solution (Alin et al., 1987). Considering the TOPO concentration, as the concentration decreases, the extraction rate decreases again because it reaches saturation quickly.
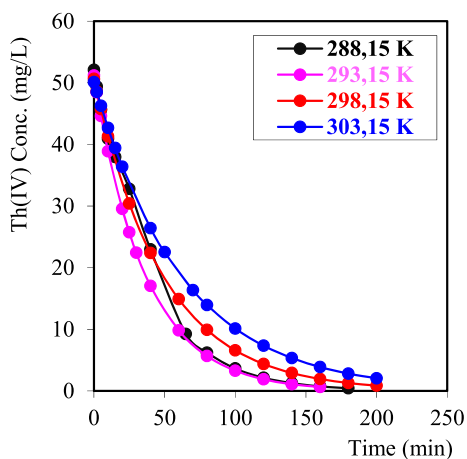
a)
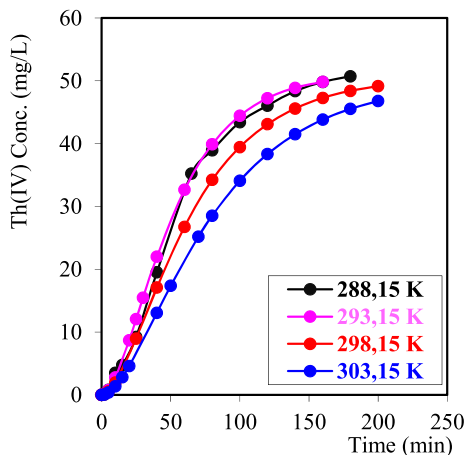
b)
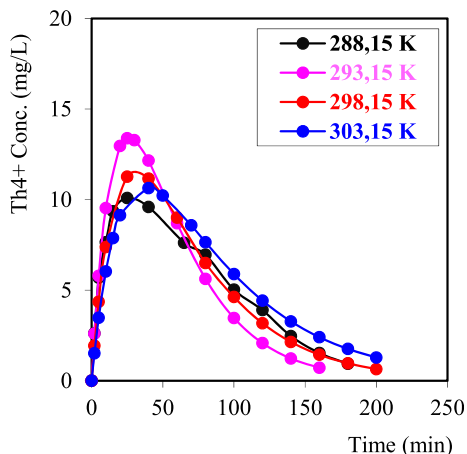
c)

Figure 7. Effect of four different temperatures on the extraction of Th(IV) ions for a) Donor phase, b) Acceptor phase, c) Organic phase.

The results of this experiment indicate that the extraction reaction of Th by TOPO is reversible where after equilibrium is reached and the stirring process is carried out for a longer time, the Th(NO$_3$)$_4$.nTOPO complex again decomposes into Th(IV) and $\mathbf{NO_3^-}$ which returns to the aqueous phase, as shown in the following Eq. (15).

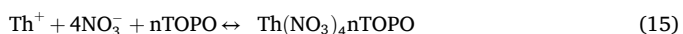$$Th^+ + 4NO_3^- + nTOPO \leftrightarrow Th(NO_3)_4nTOPO \qquad (15)$$

Table 2. Kinetic results of the calculated transport of Th(IV) ions at varying temperatures.

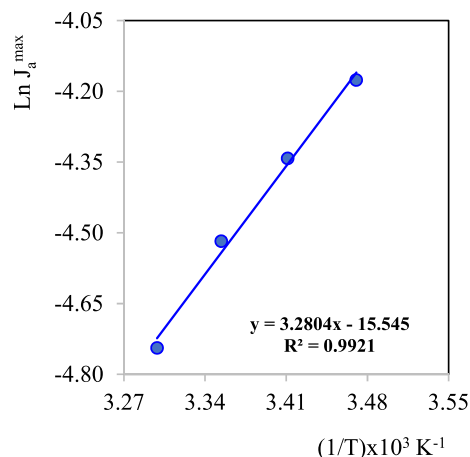| T (K)	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	$M_{MTh(IV)}^{max}$ (g/mL)	$t_{MTh(IV)}^{max}$ (min)
288.15	2.70	7.74	10.34	20.89
293,15	2.75	4.78	13.93	27.23
298.15	2.04	4.89	11.30	30.67
303.15	1.60	4.02	10.85	38.07

Figure 8. Arrhenius plot of the transport of Th(IV) metal ions by the carrier TOPO ligand at varying temperatures 1/T.

Based on the results of these experiments, the concentration of pH:1.00 nitric acid is the best concentration to perform the thorium extraction process with TOPO with a thorium extraction percentage of 92.26%. The transport that occurs is quite significant, starting at a pH of the feed phase 2.00 to 4.00, with the optimum transport occurring at pH 1.00.

3.1.2. Extraction of Th(IV) ions from the organic phase to the donor phase with a single column MDLM system

The solutions prepared at varying concentrations of H$_2$SO$_4$ were used in the uptake of Th(IV) metal ions taken into the organic phase to the acceptor phase. In order to determine the most effective concentration of the H$_2$SO$_4$ solution selected as the acceptor phase, batch extraction was carried out at a concentration range of 0.10–0.50 M, at a constant flow rate (120 rpm) and constant temperature (25 °C). $6.47.10^{-3}$ M TOPO containing 50 mg/L Th(IV) metal ions were used as the organic phase and the data obtained as a result of the experimental studies are given in Figure 3.

As seen in Figure 3, the H$_2$SO$_4$ concentration highly affects the re-uptake of Th(IV) ions from the organic phase. When the acceptor phase concentration of 0.10 M H$_2$SO$_4$ is used, high uptake Th(IV) ions pass into the acceptor phase. As the H$_2$SO$_4$ concentration increases, the uptake rate and capacity decrease. It was observed that the reuptake efficiency reached the highest value within thirty minutes when 0.10 M H$_2$SO$_4$ solution was used as the acceptor phase. As the concentration of the H$_2$SO$_4$ solution used in the reuptake trials increases, the reuptake becomes more difficult, while the uptake is 99.80% in 0.10 M H$_2$SO$_4$, it drops to 56.84% in 0.50 M H$_2$SO$_4$, and the reuptake time into the acceptor phase is prolonged.

3.2. Studies of the MDLM system with double reactor column (Continuous system)

3.2.1. TOPO carrier reactive concentration effect

In the MDLM system, donor phase pH: 1.0 (HNO$_3$) 50 mg/L Th(IV) aqueous solution, organic phase 4.31×10^{-3} M, 3.23×10^{-3} and $1.62 \times$
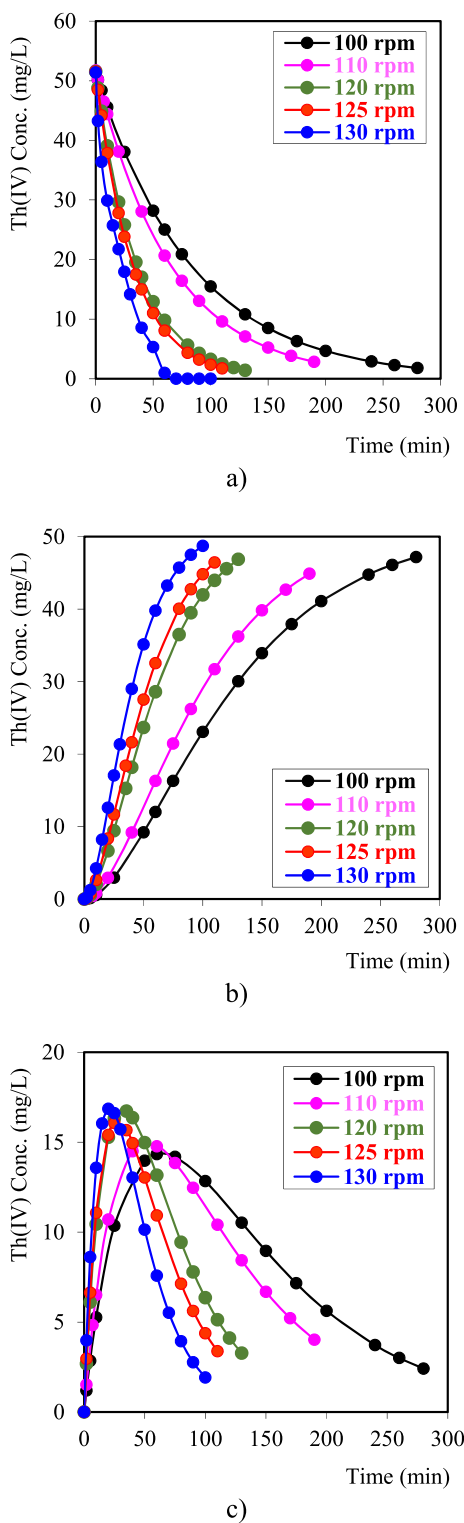
Figure 9. The variation of the concentration of Th(IV) ions versus time in the a) Donor phase, b) Acceptor phase, c) Organic phase at different flow rates of the membrane phase.

10^{-3} M kerosene solutions prepared in TOPO and 0.10–0.50 M concentration ranges of H_2SO_4 solution was used as the acceptor phase. Continuous extraction was performed with three different TOPO concentrations for each H_2SO_4 concentration. During the experiment, the flow rate of the organic phase of the system and the temperature were kept constant at 120 rpm 25 °C respectively. The data obtained are given in Figures 4, 5, and 6.

Table 3. Calculated kinetic data of Th(IV) transport at different flow rates of the membrane phase.

Flow rate (rpm)	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	$M_{MTh(IV)}^{max}$ (g/mL)	$M_{MTh(IV)}^{max}$ (min)
100	1.20	1.95	14.54	64.73
110	1.53	2.25	15.50	53.56
120	2.77	3.41	17.03	32.48
125	3.09	4.08	16.40	28.07
130	4.31	5.02	17.48	21.48

As seen in the graphs of change over time in continuous extraction using the concentration of carrier ligand $1.62.10^{-3}$ M, the extraction rate decreases as the concentration of the stripper H_2SO_4 in the acceptor phase increases (Figure 4). As can be seen in Table 1, the rate of uptake from the donor phase to the organic phase decreases by half, while the rate of uptake from the organic phase to the acceptor phase slows down by 6.5 times. Since the reuptake rate of the acceptor phase slows down, agglomeration occurs in the organic phase, which prevents the membrane from reaching equilibrium. Considering the test times, the test duration is 170 min at 0.10 M H_2SO_4. While the concentration increases, the time lengthens and the time reaches 400 min at 0.50 M H_2SO_4. As the concentration of the stripping phase decreases, the maximum membrane inlet (J_d^{max}) and outlet (J_a^{max}) velocities decrease up to 3.5 times.

In the continuous study using 3.23×10^{-3} M TOPO, as seen in Figure 5 and Table 1, there is a little difference in uptake from the donor phase to the organic phase, but the extraction rate decreases effectively from the organic phase to the acceptor phase. As the uptake decreases, agglomeration occurs in the organic phase, which increases the saturation time of the membrane and the saturation of the membrane. As the concentration of the stripping phase decreases, the maximum membrane inlet (J_d^{max}) and outlet (J_a^{max}) velocities decrease up to 3 times.

In continuous extraction using 4.31×10^{-3} M TOPO, uptake from the donor phase to the organic phase decreases three times with the increase in the concentration of the stripper phase. Since the TOPO concentration is higher, complexation is faster, which increases the extraction rate (Figure 6 and Table 1).

In general, as the TOPO concentration decreases in continuous operation, the uptake time from the donor phase to the organic phase and then from the organic phase to the acceptor phase decreases. While k_1 is 0.156 min^{-1} when $4.31.10^{-3}$ M TOPO is used: k_1 decreases to 0.024 min^{-1} when 1.62×10^{-3} M TOPO is used. Since there is not enough TOPO to form complexes with thorium ions in the donor phase, the uptake decreases. As the amount of H_2SO_4 in the acceptor phase increases, the uptake from the organic to the acceptor slows down and the uptake time increases. As uptake slows down, aggregation occurs in the organic phase. This increases the saturation time and concentration of the membrane. At the same rate, the membrane inlet (J_d^{max}) and outlet (J_a^{max}) velocities are effectively reduced.

3.2.2. Effect of temperature

Experiments were carried out at 288.15, 293.15, 298.15, and 303.15 K temperatures in order to determine the most effective temperature for the uptake from the donor phase to the organic phase followed by the organic phase to the acceptor phase in continuous operation. The donor phase pH is 1.00, the Th(IV) metal ions concentration is 50 mg/L, the acceptor phase is 0.10 M H_2SO_4, the carrier reagent concentration in the organic phase is kept constant as 1.62×10^{-3} M TOPO, and experiments are carried out at different temperatures at a flow rate of 120 rpm. The data obtained are given in Figure 7.

It was found that the most effective temperature for the removal of Th^{4+} metal ions from the aqueous phase to the organic phase and from the organic phase to the aqueous phase was 293.15 K (Figure 7). As the temperature increases, the k_1 value decreases. As the temperature decreases, the uptake from the donor phase to the acceptor phase increases. The k_2 value is the
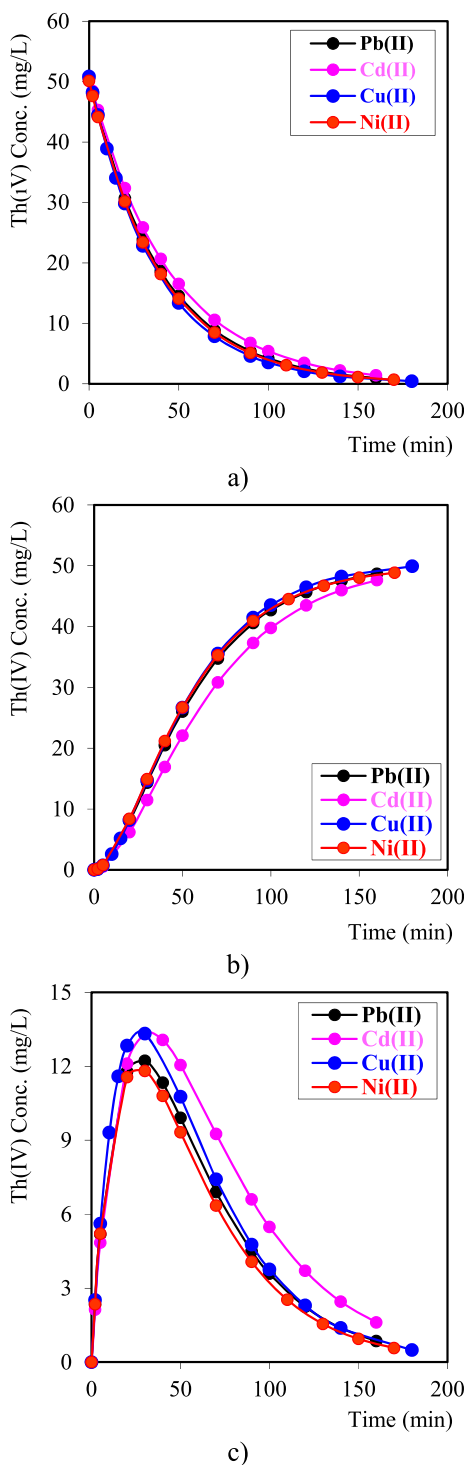
a)

b)

c)

Figure 10. a) Donor phase, b) Acceptor phase, c) Organic phase variation of Th(IV) metal ion concentrations versus time in the presence of different metal ions.

highest at 293.15 K, the k_2 value decreases with the increase and decrease of the temperature and the reaction rate decreases (Table 2). At 288.15 and 293.15 K, the k_1 values are close to each other, but considering the uptake into the acceptor phase, 293.15 K is the most effective. When the membrane flux is considered, the diffusion rate slows down with the increase in temperature and reaches its highest value at 293.15 K.

The activation energy (E_a) value of the transport of Th(IV) ions in our MDLM system was calculated from the slope of the line obtained by plotting the maximum membrane exit rates J_a^{max} versus $1/T$ (Figure 8). The

Table 4. Kinetic data of selective transport of Th(IV) ions in the presence of different metal ions.

Kinds of metal	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	$M^{max}_{MTh(IV)}$ (g/mL)	$t^{max}_{MTh(IV)}$ (min)
Pb(II)	2.49	4.91	12.73	28.06
Cd(II)	2.24	4.02	13.52	32.85
Cu(II)	2.67	4.62	13.86	28.19
Ni(II)	2.54	5.38	12.09	26.43

Table 5. Concentrations of metal ions that remain in the donor phase and pass into the acceptor phase after the extraction of Th(IV) ions.

Kinds of metal	$[C_i]$ (mg/L)	$[C_f]$ (mg/L)	Removal of metal ions (%)	Extraction Th(IV) ions (%)
	Donor	Acceptor		
Cd(II)	50.02	4.68	9.36	94.05
Cu(II)	49.88	2.00	4.00	98.22
Ni(II)	49.00	0.98	2.00	97.53
Pb(II)	49.50	0.87	1.76	96.45

activation energy value calculated as 6.52 kcal/mol for the transport of the Th(IV) ion for the TOPO carrier shows that the event is diffusion-controlled since it is less than 10 kcal/mol (Donat et al., 2015).

3.2.3. Flow rate effect

The organic phase is transferred between the aqueous phases at a regular flow rate with the aid of a peristaltic pump. Experimental studies were carried out in the range of 100–130 rpm flow rate to examine the change in extraction efficiency with the change of this transfer rate. Continuous extraction was carried out at 25 °C system temperature by taking the donor phase (50 mg/L Th(IV), pH:1.00), organic phase (1.62 × 10^{-3}M TOPO), and acceptor phase (0.1M H$_2$SO$_4$) as constants and the data obtained are given in Figure 9.

As the flow rate increases, uptake from the donor phase to the organic phase and from the organic phase to the acceptor phase increases effectively (Figure 9). As the flow rate increases, the convection event accelerates. While the uptake from the donor phase to the organic phase increases 3.55 times, the rate of uptake from the organic phase to the acceptor phase is accelerated by 2.72 times. Therefore, as the flow rate increases, there is a small amount of agglomeration in the organic phase ($M^{max}_{Th(IV)}$). The time for the membrane to reach equilibrium also decreases. As seen in Table 3, the rate of uptake from the organic phase to the acceptor phase is greater than the uptake from the donor phase to the organic phase. In the system, at speeds below 100 rpm, the organic phase transition is not homogeneous in the reactor in all parts of the column, and at speeds above 150 rpm, the experiment is disrupted due to foam formation. That's why between 100-150 rpm is most effective.

3.2.4. Extraction of Th(IV) ions in the environment of different metal ions

In order to examine the Th(IV) efficiency of our system at the pH and TOPO carrier reagent concentration studied, experiments were carried out with solutions containing different metals. In our experiment, four different studies were conducted with Pb/Th, Cd/Th, Cu/Th, Ni/Th solution mixtures containing 50 mg/L metal. The system temperature was set at 20 °C, the flow rate was 120 rpm and the TOPO concentration was 1.62 × 10^{-3} M. The data obtained by performing for experiments at pH:1.00 are given in Figure 10.

The concentrations of each metal at the beginning and at the end of the experiment were recorded by measuring AAS. In the light of experimental data, in the presence of multiple other heavy metals, the TOPO reagent can transport Th(IV) ions to the acceptor phase under optimum conditions.

As can be seen from Figure 10 and Tables 4 and 5 a quantitative and highly transport of Th(IV) ions with respect to four Pb(II), Cd(II), Cu(II), and Ni(III), has been achieved, under optimized experimental conditions. The transport from each metal to the acceptor phase varies between 2-5 mg/L, and the Th(IV) metal ion is transported to the acceptor phase with >94% efficiency.

The results of this study demonstrate the efficient extraction and transport of Th(IV) ions from aqueous solutions by the MDLM system. The proposed method is a simple and fast method for the separation of Thorium.

4. Conclusions

In this paper, various parameters were investigated in the recovery of thorium ions from an acidic environment using single and double reactors via the MDLM system. The findings of the most important experimental data obtained in the MDLM technique are given as follows:

- It has been found that the most effective acceptor phase solution for reuptake of Th(IV) ions in the organic phase is H_2SO_4. When the effect of H_2SO_4 concentration was examined, it was determined that the stripping from the organic phase to the acceptor phase effectively decreased with the increase of the concentration.
- Considering the effect of temperature, the increase in the transition from the donor phase to the organic phase at low temperatures indicates that this transition is exothermic. While the reaction rate constant (k_1) values for 15 and 20 °C are close to each other, the extraction efficiency decreases if the temperature in the organic phase is below or above 20 °C.
- The transport of Th(IV) ion was found to be 6.52 kcal/mol for the activation energy value in the interphase transport, and since this value is less than 10 kcal/mol, it shows that the transport is diffusion-controlled.
- The transition of other metals to the acceptor phase with Th(IV) ions occurs between 2-5 mg/L. Studied metals do not prevent Th(IV) transport in the working environment, and the transport is over 94%. In all continuous extraction studies for Th(IV) ions, it was found that more than >98% of the thorium ion in the aqueous phase could be taken into the acceptor phase.
- The obtained data were found to be in good agreement with the experimental results. This indicates that the developed model can be a useful tool for the design and scale-up of the MDLM process for thorium recovery from its acidic solution.

Declarations

Author contribution statement

Ramazan Donat: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Emrah Tavşan: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

Afifi, S.Y., El Sheikh, E.M., Elsayed, M.A.S., Mustafa, M.M., 2012. Extraction and determination of thorium and its application on geologic samples using trioctylphosphine oxide. Arab. J. Nucl. Sci. Appl. 45 (3), 35–51.

Alin, A., Miloud, M., Hossadi, A.E., Khaliquzzaman, M., 1987. Solvent extraction of thorium from mixed organic-aqueous nitric acid media by try-N-octyloxinephosphine oxide. J. Radioanal. Nucl. Chem. 116 (2), 271–286.

Donat, R., Durmaz, Ö., Cetisli, H., 2015. Transportation and kinetic analysis of Mo(VI) ions through a MDLM system containing TNOA as carrier. J. Hazard Mater. 294, 17–26.

Donat, R., Eyice, M.İ., Erden, K.E., 2022. Transportation and extraction of Cu²⁺ metal ions from acidic solution by MDLM technique. Resour. Conserv. Recycl. 179, 106124.

Khan, M.H., Hafeez, M., Manzoor, S., Bukhari, H., Ali, A., 2014. Spectrophotometric determination of micro amounts of thorium with thorin in the presence of cetylpyridinium chloride as surfactant in perchloric acid. J. Radioanal. Nucl. Chem. 301, 703–709.

Nasab, M.E., 2014. Solvent extraction separation of uranium (VI) and thorium (IV) with neutral organophosphorus and amine ligands. Fuel 116, 595–600.

Purwani, M.V., Setyadji, M., 2015. The influence of Tri-n-octyl phosphine oxide and extraction stage on purification of thorium concentrate. Eksplorium 36 (2), 100–124.

Rastegarzadeh, S., Pourreza, N., Saeedi, I., 2010. An optical chemical sensor for thorium (IV) determination based on thorin. J. Hazard Mater. 173, 110–114.

Rydberg, J., 1992. Principles and Practices of Solvent Extraction. Marcel D, New York, pp. 393–412.

Thomason, P.F., Perry, M.A., Byerly, W.M., 1949. Determination of microgram amounts of thorium. Anal. Chem. 21 (10), 1239–1241.

Xie, F., Zhang, T.A., Dreisinger, D., Doyle, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. Miner. Eng. 56, 10–28.