

DESIGN OPTIMIZATION OF EXTRACTION PROCEDURE FOR TERBIUM (III) BY SUPPORTED LIQUID MEMBRANE USING D2EHPA AND TOPO AS A CARRIER

Sid Ahmed Elhabiri, Mohamed A. Didi*

*Tlemcen University, Faculty of Sciences, Department of Chemistry,
Laboratory of Separation and Purification Technologies, Box 119,
13000, Algeria*

*Corresponding author: madidi13@yahoo.fr

Received: May, 22, 2017

Accepted: April, 16, 2018

Abstract: The extraction of terbium (III) from aqueous nitrate solutions with a supported liquid membrane was investigated using a mixture of di-(2-ethylhexyl phosphoric acid (D₂EHPA) and tri-octyl phosphine oxide (TOPO) with a molar ratio 1/0.4. The mixture was dissolved in diethyl ether which served as a carrier. The hydrophobic polyvinylidene fluoride (PVDF) membrane was used as a solid support. SEM images and FTIR spectra showed that the PVDF membrane was modified after impregnation. The sorption process followed a *pseudo-second-order* kinetics. 8.29 mg·g⁻¹ was extracted using a supported liquid membrane (SLM). The mixture D₂EHPA / TOPO (1/0.4) presented a synergistic effect. The influence of the ionic strength, stirring rate, extraction time, and the interactions between them on the extraction yield of terbium (III) ions was investigated using the factorial designs. The analysis of variance (ANOVA) was used to show the relative importance of the extraction process parameters. Student's t-test to the results of the factorial plane 3³, with 30 runs for terbium (III) extraction, showed that the stirring rate in the studied ranges was statistically important. The amount of Tb (III) extracted after 12 cycles was 73.624 mg·g⁻¹.

Keywords: *analysis, D₂EHPA, rare earth, recovery, SLM, TOPO*

INTRODUCTION

Recently new chemical separation techniques have gained increasing interest, and this is confirmed by the large number of contributions that appeared in the scientific literature on this subject during the last two decades. This is largely due to increasing concerns about environmental problems, energy saving and to the optimization of industrial extraction, as described in [1]. In these extraction techniques, use was made of the properties of the membrane which is a thin layer and which serves as a barrier capable of preferential or selective transfer of the components of the mixture [2]. The liquid membrane (LM) separation technique is an advanced solvent extraction technique, which provides an effective and simple method for separating metal ions [3]. The use of liquid membrane processes is becoming increasingly important in the separation and recovery of toxic metals and valuable metals as well as in the treatment of effluents containing low concentrations of solutes in large volumes, without generating any secondary waste [4]. Consequently, several methods for the removal of these solutes from the environment have been reported. Among these, the supported liquid membrane (SLM) extraction technique has emerged as a new, economical and green technology. The SLM method usually consists of an organic solution immobilized in the pores of a hydrophobic microporous membrane that contains a complexing agent (carrier), which selectively extracts one of the components from the feed solution [5]. In a supported liquid membrane with a carrier, the extraction with the acidic extractant is performed by the diffusion of metal ions from the feed phase toward the membrane where the metal-complex forms; then, it is back-extracted into the strip phase due to the proton gradient between the strip and the feed phases. This provides the driving force for the mass transfer, as indicated in [6]. The removal of rare earth elements (REEs) can be achieved by the supported liquid membrane extraction process [7 – 8]. Several membrane supports, such as polypropylene (PP) [1], polyvinylidene difluoride (PVDF) [9] and polytetra-fluoroethylene (PTFE) [10 – 15], were reported in various publications and have been used to make supported liquid membranes (SLMs). One of the characteristics of lanthanides is that their chemical properties are very similar, causing difficulties in separating these elements. Although some highly sensitive and selective methods for the detection and determination of rare earth elements are described, the number of related studies remains insufficient. In most cases, the methods used for the pretreatment of samples include procedures such as separation, concentration and removal of REEs. The pre-treatment approach is particularly important for complicated matrices containing terbium, which is an important member of the rare earth family; it is widely used in cathode ray tubes, optical magnets, computer memories and magnetostrictive alloys [11, 12]. Researchers in bio-inorganic and bio-organic chemistry are getting more and more interested in terbium determination as it is increasingly found in industrial waste. Terbium is primarily used in phosphors, particularly in fluorescent lamps, and in high-intensity green emitters used in projection televisions. The principal sources of rare-earth elements are monazite, xenotime, and bastnasite [13]. The removal of terbium from aqueous solutions may be achieved using techniques such as solid-liquid extraction (SLE) [11], liquid-liquid extraction (LLE) [13] and sorption on transcarpathian clinoptilolite [14].

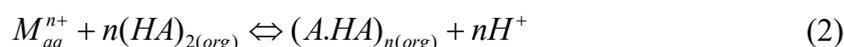
The separation of terbium from the lanthanide series was also possible via a membrane using solid phase surface fluorescence [15].

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is a derivative of *orthophosphoric acid* whose two hydrogen atoms are substituted by the alkyl ($-\text{OC}_8\text{H}_{17}$) and phosphoryl ($\text{P}=\text{O}$) groups of a typical organophosphorus acidic extractant and HA is the organophosphorus acidic extractant itself. Whether the metal-extractant complex formed will be a monomer or polymer depends on the metal loading level of the extractant. The following reactions 1 and 2 were suggested in the case of low and high levels of metal loading conditions [16]:

- for high level metal loading (monomer formation):



- for low level metal loading (dimer formation):



TOPO is a neutral donor. It is synthesized by substituting three hydroxyls in the chemical structure of the *orthophosphoric acid* by three organic radicals ($-\text{C}_8\text{H}_{17}$). Terbium is extracted by TOPO through the coordination with the oxygen of the phosphoryl group ($\text{P}=\text{O}$) in the structure. TOPO does not release any hydrogen ions as a result of dissociation; TOPO has been used as an auxiliary ligand in a synergistic extraction system containing D2EHPA as the primary ligand.

In this study, the use of the mixture of D₂EHPA and TOPO as a carrier for the extraction of terbium in a supported liquid membrane has not been reported in the literature. In the present work, the extraction of Tb from a nitrate solution through a supported liquid membrane impregnated with the mixture of D₂EHPA and TOPO was studied. Various parameters, such as the feed phase *pH*, molar feed ratio, and initial concentration of terbium, membrane thickness, time effect, ionic strengths and cycle number were studied.

MATERIALS AND METHODS

UV-Visible spectrometer was used for the analysis of the results (SPECORD 210 plus). Consort C 831 *pH* meter with combined glass electrode was used for *pH* measurements (Adwa). The membrane support was a microporous polyvinylidene difluoride (PVDF) film with nominal porosity of 70 %, an average pore size of 0.1 μm and a total thickness of 125 μm (VVHP04700), was procured from Millipore, Germany. Terbium (III) nitrate pentahydrate and Arsenazo (III) were procured from Sigma-Aldrich. Nitric acid was used for adjusting *pH* of terbium (III) solutions. TOPO and D2EHPA were procured from (Sigma Aldrich). Buffer at *pH* = 4.0 was procured from Prolabo.

The membrane extraction experiments were carried out a one compartment cell with mechanical stirring throughout the experiments, separated by a microporous membrane, one for feed solution and the other for stripping solution. Initial concentration of Tb in the feed phase was $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ in all the SLM studies. The liquid membrane phase was prepared by dissolving of D₂EHPA and TOPO in diethyl ether. The PVDF support was impregnated with the carrier solution for 24 h, SLMs needed more than 12 h [10], then

removed from the solution and wiped carefully with a tissue paper to remove the excess carrier after with water to remove the excess of the organic solvent from the surface of the membrane. After this, each membrane was leaved and dripped for 30 second before being placed in the transport cell (Figure 1), which consists of two identical compartments of 55 mL separated by the impregnated membrane. The effective membrane area was 11.2 cm². The extraction of the terbium ion was monitored by taking 100 μL from the compartment at different times for the spectrometer analysis after the addition of a buffer solution (pH = 4.0) and 150 μL 10⁻³ M of Arsenazo III. All experiments were performed at ambient temperature.

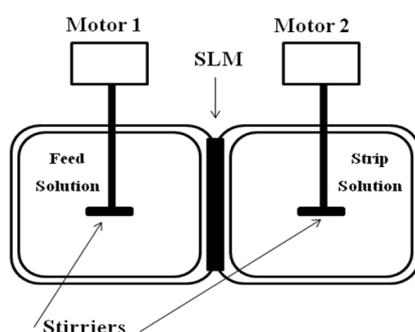


Figure 1. Experimental installation of supported liquid membrane

Calculations

The percent Tb (III) extraction, (%) was determined as in equation 3:

$$Yield(\%) = \frac{C_0 - C}{C_0} \cdot 100 \quad (3)$$

The adsorption amount was calculated as follows (equation 4):

$$q_t = \frac{V(C_0 - C) \cdot M}{w} \quad (4)$$

where: q_t is the adsorption amount (mg·g⁻¹), w the weight of the extractant (D₂EHPA/TOPO) impregnated, M molar mass (g·mol⁻¹), V the volume of solution (L), and C_0 and C are the concentrations (mol·L⁻¹) of terbium ions before and after adsorption, respectively.

Pseudo-first order model (PFO)

The PFO rate expression based on solid capacity is the most widely used rate equation for assigning the adsorption rate of an adsorbate from a liquid phase and is known as the Lagergren rate equation [17]. It is represented in equation 5:

$$\frac{dy}{dt} = k_f(q_e - q_t) \quad (5)$$

where: q_e (mg·g⁻¹) and q_t (mg·g⁻¹) are the adsorption capacity at equilibrium and time t respectively and k_f (min⁻¹) is the rate constant of the PFO adsorption reaction.

On integration and applying boundary conditions as $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$, equation (5) becomes:

$$\log(q_e - q_t) = \log q_e - k_f \cdot t / 2.303 \quad (6)$$

Pseudo- second order model (PSO)

The PSO kinetic expression describes the adsorption of metal ions onto adsorbent. The rate expression is represented as [17, 18]:

$$dq_t / dt = k_s (q_e - q_t)^2 \quad (7)$$

where: q_e and q_t ($\text{mg} \cdot \text{g}^{-1}$) are the adsorption capacities at equilibrium and time t respectively and k_s ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant for the PSO adsorption reaction.

The nonlinear form of PSO model in equation (7) can be rearranged into four different linear forms, of which the most popular one is:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \quad (8)$$

The product $k_s q_e^2$ ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) is the initial sorption rate (h).

Applying equation (8) for the analysis of kinetic data is usually based on the plotting of t/q_t versus t which should give a linear relationship; whereas, $1/q_e$ and $1/k_s q_e^2$ are the slope and the intercept of obtained line, respectively.

Experiment design

Preliminary experiments showed that, as expected, numerous factors can influence the yield extraction of terbium (III), but only some of them, namely the stirring rate; the concentration of the potassium nitrate and the contact time can be regarded as being the key parameters that govern the process efficiency. An adequate selection of the variable ranges is an essential requirement for establishing an accurate polynomial model that fully describes the investigated process. The limits of the variables ranges must take into account the results of the preliminary tests.

Table 1. Factor levels used in the 3^3 factorial experiment design at $T = 298.15 \text{ K}$

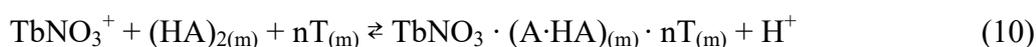
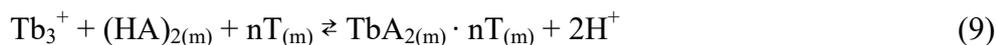
Factors	Symbol of coded variables	Low level (-1)	Medium level (0)	High level (+1)
Stirring rate, V [rpm]	X_1	180	540	900
Concentration of KNO_3 , S [M]	X_2	0.1	0.3	0.5
Contact time, t [min]	X_3	15	127.5	240

In our investigations, a series of 27 attempts were made according to a 3^3 experiment factorial design, by varying the stirring rate V [rpm] (X_1), the concentration of potassium nitrate S [M] (X_2) and contact time t [min] (X_3) in suitable parameter ranges. Three variation levels for each parameter were considered as summarized in Table 1.

RESULTS AND DISCUSSION

In order to study the kinetics of terbium (III) extraction with D₂EHPA/TOPO mixture at different times, a conventional solvent extraction system this is carried out in two steps, either, for separation or preconcentration of terbium (III) from its source solution. The extraction conditions indicated in the Figures 2 and 3 were selected considering that there are representative to characterize the carriers of the extraction process for the different study.

The extractions of terbium (III) with D2EHPA were represented by the following general equations [16]. With the addition of TOPO, the equations are in the form:



where (HA)₂ and T represent the dimeric form of D₂EHPA and TOPO, respectively.

The terbium species present in the feed phase before extraction have been quantified by the program Chemical Equilibrium in Aquatic System (CHEAQS).

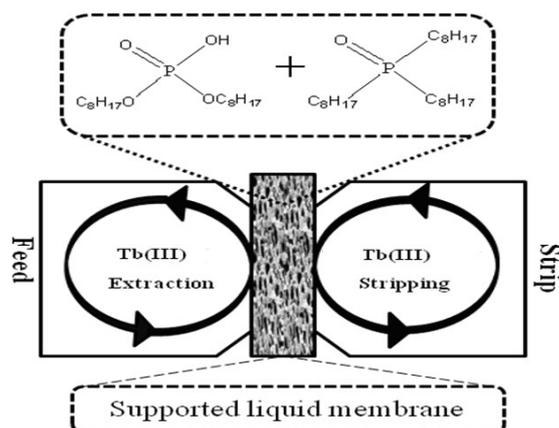


Figure 2. Metal ion transport illustration in SLM

Effect of stirring rate

The stirring rate was varied between 180 and 900 rpm. It was observed that terbium yield extraction increases with increasing stirring rate between 180 and 900 rpm. So it was assumed that stirring rates of 900 rpm, for further experiments were carried out with a stirring rate at 900 rpm. Similar results have been observed in the extraction with supported membrane liquid were used the same rate stirring [17, 18]. Time of experiment was 240 min.

Effect of initial pH

Based on mechanism of mass extraction process, the concentration difference between feed phase and removal phase is the driving power of mass extraction process. More H⁺ concentration decreases (pH increase) in the feed phase; the stronger the driving power of mass extraction process will be elevated [17, 18]. A stronger power will promote the

extraction of Tb (III). Equally, the greater the pH value in the feed phase is high; the extraction of Tb (III) is higher. The effect of pH in the feed phase on transport of Tb (III) was studied in the pH range of 2.0 to 8.0, adjusted with an HNO_3 or $NaOH$ solutions. Initial concentration of Tb (III) in the feed phase is $10^{-3} \text{ mol}\cdot\text{L}^{-1}$, volume of membrane solution in feed phase is 55 mL and molar ratio of D2EHPA/TOPO is 1/0.4. The yield extraction of Tb (III) decreased when the pH in the feed phase decreased from 5.3 to 2.0, and a maximum of yield extraction (64.2 %) was observed at pH 5.3 at 240 min. Above the pH of 5.3 in the feed phase, the yield extraction of Tb (III) decreased to $pH = 6.1$ (19.7 %), after increased to $pH = 8.0$ (53.4 %), but still remains lower than pH 5.3 (64.2 %), see Figure 5. When pH value was higher than 5.3, hydroxyl complex of Tb (III) was formed in the feed phase and the yield extraction of Tb (III) decreased (see Figure 5) [7]. It is large because the transport process is mainly governed by the driving power of mass transfer caused by the distribution equilibrium, when the renewal effect of the liquid membrane and the diffusion mobility of Tb (III) ions are determined under specific experimental conditions. Considering saving chemical agents as well as increasing transport rate, we chose pH of 5.3 as the optimum pH condition in the feed phase during the following experiments. From the Figure 6, it was observed that the yield extraction of Tb (III) ion decreases with the decrease in pH initial in the range 5.3 to 2, and then increases gradually. In the stripping compartment, 55 mL of HNO_3 1 M was put. In the discontinuous mode, the feed compartment is drain after membrane saturation. The results expressed in terms of permeability coefficient are shown in Figure 7. The maximum flux was obtained at $pH = 5.3$, shown in Figure 8.

Kinetics

In this study, batch sorption kinetics of Tb (II) ions at initial concentration, $10^{-3} \text{ mol}\cdot\text{L}^{-1}$, with the extraction $D_2EHPA/TOPO$ impregnated in the membrane has been studied. The different values of constants from the slopes and intercepts of linear plots of equations (6) and (8) are summarized in Table 2.

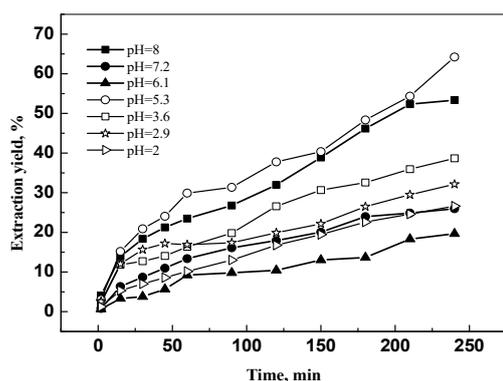


Figure 4. Effects of initial pH on the extraction yield of Tb^{3+} by SLM
Conditions: membrane thickness 125 μm ; stirring = 900 rpm; $T = 20 \pm 1 \text{ }^\circ\text{C}$; time of experiment 240 min; $[Tb(III)] = 10^{-3} \text{ M}$; $D_2EHPA/TOPO$ (molar ratio 1/0.4)

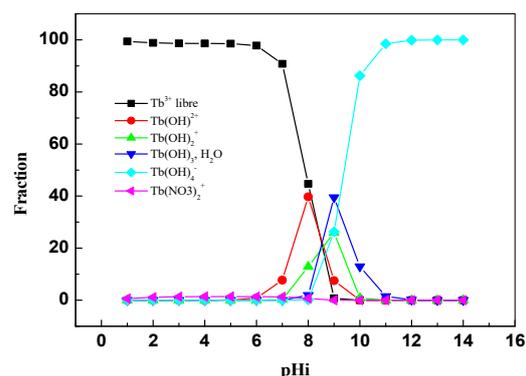


Figure 5. Diagram of the predominance of Tb species in aqueous phase given by CHEAQS $[Tb(NO_3)_3] = 10^{-3} \text{ M}$; $1 \leq pH \leq 14$

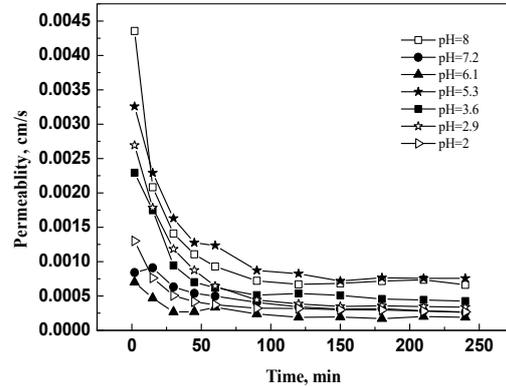
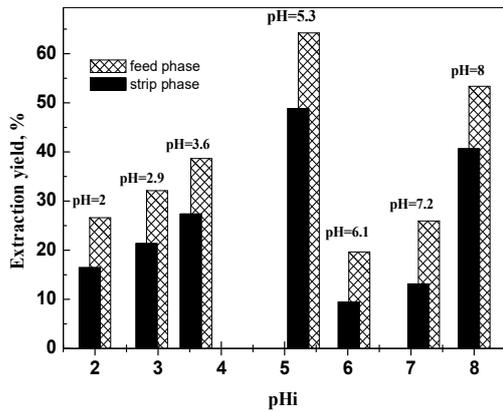


Figure 6. Effect of the strip flow system, on the extraction efficiency of various pH

Figure 7. Effect of initial pH on the permeability coefficient of Tb(III) by SLM

Conditions: membrane thickness 125 μm; stirring = 900 rpm; T = 20 ± 1 °C; time of experiment 240 min; [Tb (III)] = 10⁻³ M; D₂EHPA/ TOPO (molar ratio 1/0.4)

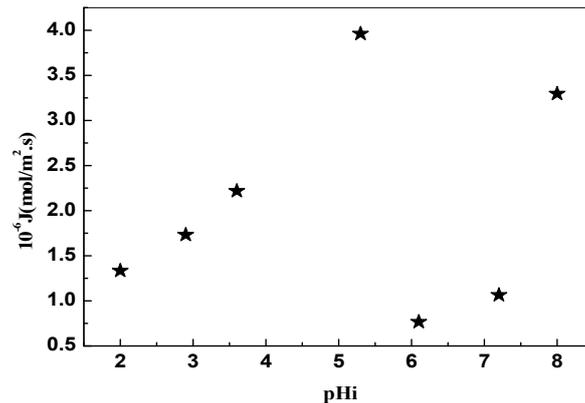


Figure 8. Variation of flux (J) with initial pH

Table 2. Kinetic parameters for adsorption of terbium by MLS

Models	Parameters	Attributions							
		pH _i	8.0	7.2	6.1	5.3	3.6	2.9	2.0
pseudo first order	k _f [min ⁻¹]		0.0027	0.0040	0.0016	0.0022	0.0018	0.0018	0.0015
	q _{cal} [mg·g ⁻¹]		101.68	53.01	58.90	143.83	99.35	65.37	72.61
	q _{exp} [mg·g ⁻¹]		121.11	58.91	44.60	145.79	87.76	72.92	60.41
	R ²		0.951	0.981	0.918	0.926	0.803	0.690	0.885
pseudo second order	10 ⁻⁴ k _s [g·mg ⁻¹ ·min ⁻¹]		4.82	2.78	4.19	2.93	3.93	3.93	15.92
	q _{cal} [mg·g ⁻¹]		81.69	60.49	36.68	103.41	68.77	48.66	48.22
	q _{exp} [mg·g ⁻¹]		121.11	58.91	44.60	145.79	87.76	72.92	60.41
	R ²		0.984	0.991	0.907	0.989	0.944	0.941	0.995

As shown in Table 2, the obtained coefficients values of the *pseudo-second-order* model (> 0.951) were better than those of the *first-order* model for the sorption of Tb (III) at the considered concentration for different pH initial, suggesting that the *pseudo-second-order* model was more suitable to describe the sorption kinetics of (D₂EHPA/TOPO) for Tb (III). This suggests that the rate limiting step may be a chemical process involving valence forces through sharing or exchange of electrons [17, 18].

Effect of PVDF membrane thickness

The effects of the membrane thickness were examined and the results are presented in Table 3 indicates that transport of Tb (III) across the membrane was inversely proportional to thickness of membrane. It decreased from 64.2 to 18.04 % with increase in membrane thickness from 125 μm to 375 μm . The results show on the Table 3 that the permeability of Tb (III) ions was nearby constant irrespective of the membrane thickness. This result implies that the permeation process through the SLM is dominated by membrane diffusion. Similar results for transport were obtained by “DNPPA+TOPO” [17].

Table 3. Permeability and recovery of Tb(III) as a function of the membrane thickness

Membrane thickness [μm]	Permeability [$\text{cm}\cdot\text{s}^{-1}$]	Recovery of Tb (III) [%]
125	7.57E-4	64.23
250	2.91E-4	28.48
375	1.72E-4	18.04

Factorial design study

In order to examine the interaction between the studied factors on the Tb (III) extraction, temperature was fixed at 298.15 K. The factorial 3^3 designs had been used, by varying three key variables, namely stirring rate V [rpm] (X_1), the concentration of potassium nitrate S [M] (X_2) and the time of extraction t [min] (X_3). These results are summarized in Table 4.

An adequate selection of these parameters is an essential requirement for establishing an accurate polynomial model equation (11). A wide range between low, medium and high levels was considered in order to observe clearly the effect of each factor on the yield. The design matrix of a 3^3 factorial design and their responses are shown in Table 4. The model calculations were achieved using non non-dimensional or reduced values of these variables, each of them being varied on three levels. The regression equation of matrices is represented by the following expression:

$$Y (\%) = 15.42 + 14.67 X_1 - 10.68 X_2 + 10.69 X_3 - 13.04 X_1 X_2 + 7.08 X_1 X_3 - 4.709 X_2 X_3 + 12.83 X_1^2 - 1.28 X_2^2 - 5.86 X_3^3 - 6.64 X_1 X_2 X_3 \quad (11)$$

The shape of the response surface was plotted three times by fixing successively the three parameters at the central values. The vicinity around these central values is supposed to include the optimum, and the resulting 3-D representations of the response function, as illustrated by Figure 9. For the sake of reproducibility, one must check

whether this model accurately describes the process investigated by determining which coefficients could be neglected, through Student's t test and Fisher's Test [17, 18].

Table 4. 3^3 factorial design matrices and the responses

No. experiment	Factors levels			Response function
	X ₁	X ₂	X ₃	Extraction yield [%]
1	-1	-1	-1	3.58
2	-1	-1	0	11.38
3	-1	-1	+1	15.63
4	-1	0	-1	3.98
5	-1	0	0	11.3
6	-1	0	+1	15.09
7	-1	+1	-1	0.613
8	-1	+1	0	6.31
9	-1	+1	+1	11.99
10	0	-1	-1	4.91
11	0	-1	0	13.36
12	0	-1	+1	17.85
13	0	0	-1	5.11
14	0	0	0	12.54
15	0	0	+1	18.57
16	0	+1	-1	1.99
17	0	+1	0	8.72
18	0	+1	+1	12.88
19	+1	-1	-1	24.41
20	+1	-1	0	82.17
21	+1	-1	+1	89.93
22	+1	0	-1	8.05
23	+1	0	0	51.72
24	+1	0	+1	54.79
25	+1	+1	-1	5.05
26	+1	+1	0	10.56
27	+1	+1	+1	14.79
(28, 29, 30) ^a	0	0	0	13.99, 13.75, 13.66

^a Three additional tests at the central point (0, 0, 0) for the calculation of the Student's t test

The model adequacy strongly depends on the accuracy of the experiment. In the current experiment, the main errors arise from volume and weight measurements. For this purpose, three additional attempts at the central point (0, 0, 0) are required for estimating the average error in the value of each coefficient, on the basis of the random variance shown in Table 5. Thus, with a 95 % confidence (i.e., $\alpha = 0.05$), and for a 2 variance (i.e., for three attempts at central point), we assessed the value of $t_{v,1-\alpha/2}$ as being equal to 4.3. Therefore, at this $(1-\alpha)$ level, the confidence range for all the coefficients estimated using 27 runs, will be $\Delta a_i = \pm 0.1412$ at 95 % confidence.

From the Student's t tests, there is no negligible coefficient. Consequently, the resulting new model remains the same will be the following:

$$Y = 15.42 + 14,67X_1 - 10,68X_2 + 10,69X_3 - 13,04X_1X_2 + 7,08X_1X_3 - 4,709X_2X_3 + 12,83X_1X_1 - 1,28X_2X_2 - 5,86X_3X_3 - 6,64X_1X_2X_3 \quad (12)$$

The observations from mathematical model already allow making the following statements:

The individual effect of the stirring rate (X_1), KNO_3 concentration (X_2) and extraction time (X_3) have a positive effect on the yield of the extraction for SLM. The ionic strength effect is more important for SLM with one membrane. The interactions between two parameters were unfavorable between Stirring rate and KNO_3 concentration (X_1X_2), significant effect involved simultaneously between the three parameters ($X_1X_2X_3$).

Table 5. Model adequacy tests and variance analysis

Feature	Symbol	Value
Average yield at (0,0,0) point	y_0	13.8
Random variance	S^2	0.03
Square root of variance	S	0.17
Risk factor (chosen arbitrary)	A	0.05 (95 %)
Student's t test factor	T_v	4.3 ^a
Average error on the coefficient value	Δa_i	± 0.1412 at 95 %
Model response at (0, 0, 0)	$b_0 (y_{000})$	15.42
Discrepancy on average yield	D	1.62
Error on average yield discrepancy	Δd	± 0.45

^a Student Law with 2 degrees of freedom at a 95 % confidence ($t_2, 0.975$)

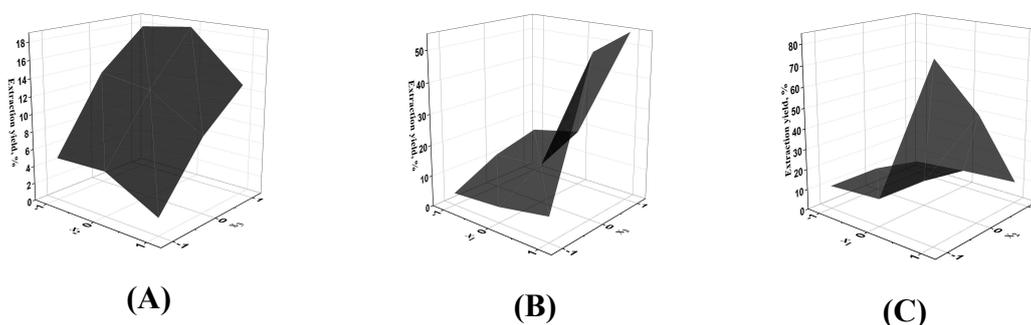


Figure 9. (A): 3D representation of the extraction of at fixed $X_1=0$. X_2 (-1 to +1), X_3 (-1 to +1); (B): 3D representation of the extraction of Tb^{3+} at fixed $X_2=0$. X_1 (-1 to +1), X_3 (-1 to +1); (C): 3D representation of the extraction of Tb^{3+} at fixed $X_3=0$. X_1 (-1 to +1), X_2 (-1 to +1)

Interpretation

The effect of individual variables and interactional effects can be estimated from the above equation. According to equation of the model, Stirring rate have a positive effect, Concentration of potassium nitrate and contact time has a negative effect, on the terbium separation, from equation, The stirring rate and contact time of extraction have a positive effect on terbium adsorption, by adsorption in the range of variation of each variable selected for the present study. A negative value for the effect indicates that the measured value of adsorbed metal amount decreased as the factor was changed from its first level to its second level.

The interaction between stirring rate and the concentration of potassium nitrate (X_1X_2) and the interaction between stirring rate and contact time (X_1X_3), of terbium plot in Figure 10 (A-B); respectively shows a higher separation of (X_1X_2) 10.02 and (X_1X_3) 11.97 at the (+1) and (+1) for each factor, a high separation of (X_1X_2) 6.54 and (X_1X_3) 10.05 at the (+1) stirring rate and (-1) concentration of potassium nitrate, As shown earlier, Figure 10 (C), for the interaction between the concentration of potassium nitrate and contact time (X_2X_3), the contact time is the most significant parameter with the interaction at the (+1) and (+1) for each factor, show a high separation of terbium 14.94 % .

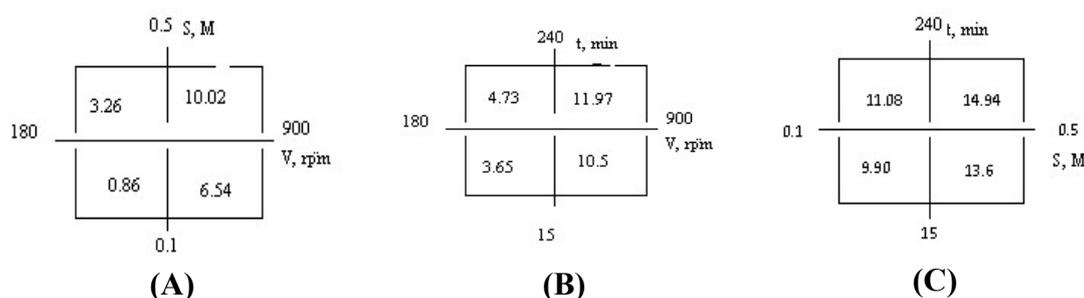


Figure 10. (A): Interaction factorial between stirring rate V , rpm and $[KNO_3]$ S , min (X_1X_2); (B): Interaction factorial between stirring rate V , rpm and the contact time t , min (X_1X_3); (C): Interaction factorial between $[KNO_3]$ S , M and the contact time t , min (X_2X_3)

CONCLUSIONS

The amount of Tb (III) extracted was $8.29 \text{ mg}\cdot\text{g}^{-1}$ for a concentration of Tb (III) = 10^{-3}M and a mass of 0.1054 g of D2EHPA/TOPO.

The optimal yield was obtained at 240 minutes. The extraction yield of Tb (III) by D2EHPA/TOPO on membrane (PVDF) took place at the initial pH of 5.3, with a flux value of $3.96 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and the initial terbium concentration equal to 10^{-3}M . A flux value of $6.82 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ was obtained at the same pH , with an initial terbium concentration of 10^{-4}M .

The extraction kinetics of Tb (III) by SLM followed the pseudo-second order kinetic model. Experiments with varying membrane thicknesses established that Tb (III) transport was limited by the internal diffusion through the membrane.

The transport of Tb (III) decreased as the membrane thickness increased. It was also found that the number of cycles was twelve. Based on the experimental results, it was decided to retain the molar ratio of D2EHPA/TOPO as equal to 1/0.4 for the extraction of Tb (III) from the aqueous solution. The mixture ratio of D2EHPA / TOPO (1/0.4) showed a synergistic effect.

A mathematical model based on the experimental data and representing the effect of three parameters, namely the ionic strength, stirring rate, extraction time and their impact on the yield, was established.

REFERENCES

1. León, G., Martínez, G., Guzmán, M.A., Moreno, J.I., Miguel, B., Fernández-López, J.A.: Increasing stability and transport efficiency of supported liquid membranes through a novel ultrasound-assisted preparation method: Its application to cobalt(II) removal, *Ultrasonics Sonochemistry*, **2013**, 20 (2), 650-654;
2. Jakubowska, N., Polkowska, Z., Namiesnik, J.: Analytical Applications of Membrane Extraction for Biomedical and Environmental Liquid Sample Preparation, *Analytical Chemistry*, **2005**, 35 (3), 217-235;
3. Zaheri, P., Abolghasemi, H., Maraghe, M.G., Mohammadi, T.: Intensification of Europium extraction through a supported liquid membrane using mixture of D2EHPA and Cyanex272 as carrier, *Chemical Engineering and Processing*, **2015**, 92, 18-24;
4. Singh, S.K., Misra, S.K., Tripathi, S.C., Singh, D.K.: Studies on permeation of uranium (VI) from phosphoric acid medium through supported liquid membrane comprising a binary mixture of PC88A and Cyanex 923 in *n*-dodecane as carrier, *Desalination*, **2010**, 250 (1), 19-25;
5. Ashraf, W., Mian, A.: Selective separation and preconcentration studies of chromium(VI) with Alamine 336 supported liquid membrane, *Toxicological Environmental Chemistry*, **2006**, 88 (2), 187-196;
6. Belkhouche, N.E., Didi, M.A., Romero, R., Jonsson, J.A., Villemin, D.: Study of new organophosphorous derivatives carriers on the selective recovery of M(II) and M(III) metals, using supported liquid membrane extraction, *Journal of Membrane Science*, **2006**, 284, 398-405;
7. Liang, P., Binghua, Y., Xinglong, F.: Study on transport of Dy(III) by dispersion supported liquid membrane, *Journal of Rare Earth*, **2009**, 27 (3), 447-456;
8. Liang, P., Liming, W., Guoqiang, Y.: Separation of Eu(III) with supported dispersion liquid membrane system containing D2EHPA as carrier and HNO₃ solution as stripping solution, *Journal of Rare Earth*, **2011**, 29 (1), 7-14;
9. Medjahed, B., Didi, M.A.: Removal of copper ions using aliquat 336/TBP based supported liquid membrane, *Scientific Study and Research*, **2013**, 14 (3), 163-172;
10. Vasylychko, V.O., Gryshchouk, G.V., Zakordonskiy, V.P., Patsay, I.O., Len'c, N.V., Vyviurska, O.A.: Sorption of terbium on Transcarpathian clinoptilolite, *Microporous and Mesoporous Materials*, **2013**, 167, 155-161;
11. Chen, Z., Ding, F., Hao, F., Bian, Z., Ding B., Zhu, Y., Chen, F., Huang, C.: A highly efficient OLED based on terbium complexes, *Organic Electronics*, **2009**, 10 (5), 939-947;
12. Kumar, B.N., Radhika, S., Kantama, M.L., Reddy, B.R.: Solid-liquid extraction of terbium from phosphoric acid solutions using solvent-impregnated resin containing TOPS 99, *Journal of Chemical Technology and Biotechnology*, **2011**, 86 (4), 562-569;
13. Vani, T.J.S., Rao, K.S.V.K.: Liquid-Liquid Extraction of Terbium (III) from Thiocyanate Solution by TPBD with some Synergistic Ligands (DOSO, TOPO, TPhPO), *Indian Journal of Advances in Chemical Science*, **2012**, 1, 10-16;
14. Huang, J., Hu, Y., Hu, Y., Li, G.: Disposable terbium (III) salicylate complex imprinted membrane using solid phase surface fluorescence method for fast separation and detection of salicylic acid in pharmaceuticals and human urine, *Talanta*, **2013**, 107, 49-54;
15. Girgin, S., Acarkan, N., Sirkeci, A.A.: The uranium (VI) extraction mechanism of D2EHPA-TOPO from a wet process phosphoric acid, *Journal of Radioanalytical and Nuclear Chemistry*, **2002**, 251 (2), 263-271;
16. Meena, A.K., Kadirvelu, K., Mishra, G.K., Rajagopal, C., Nagar, P.N.: Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*), *Journal of Hazardous Materials*, **2008**, 150 (3), 604-611;
17. Belkhouche, N.E., Didi, M.A., Villemin, D.: Separation of nickel and copper by solvent extraction using Di-2 ethylhexylphosphoric acid-based synergistic mixture, *Solvent Extraction & Ion Exchange*, **2005**, 23, 677-693;
18. Belyouci, O., Didi, M.A.: Sorption and separation study of Praseodymium and Cadmium by Magnetic bentonite. Factorial design optimization, *Desalination and Water Treatment*, **2017**, 68, 199-210.