

Optimization Extraction of Terbium by Supported Liquid Membrane Using D2EHPA and TOPO

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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 Hydrophobic Polyvinylidene Fluoride (PVDF) membrane was used as solid support. The sorption process followed pseudo-second-order kinetics. The quantity of 8.29 mg/g was extracted using a Supported Liquid Membrane (SLM). 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 was used to show the relative importance of the extraction process parameters.*

KEYWORDS: *Extraction; Analysis; Supported liquid membrane; Rare earth, D₂EHPA; 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. *Leon et al.* [1] in their paper show that this is largely due to concerns increasingly higher environmental issues related to energy savings and optimization of industrial extraction. In these extraction techniques, use was made of the properties of the membrane which is a thin layer and serves as a barrier capable of preferential/selective transfer of the components of the mixture. 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 LM processes is becoming increasingly important in

the separation and recovery of toxic 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 in the literature [5-7]. 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 [8]. In SLM 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

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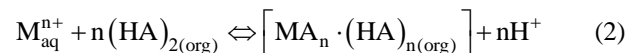
forms; then, it is back-extracted into the strip phase due to the proton gradient between the strip and the feed phases. Belkhouche in his work [9] has shown that this is the driving force for mass transfer. The removal of Rare Earth Elements (REEs) can be achieved by the supported liquid membrane extraction process [10,11]. Several membrane supports, such as polypropylene (PP), polypropylene (PP) [1], polyvinylidene difluoride (PVDF) [12] and polytetrafluoroethylene (PTFE) [13-17], were reported in various publications and have been used in LM processes. 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 for a good understanding of these methods. 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. This is an important member of the rare earth family, widely used in cathode ray tubes, optical magnets, computer memories and magnetostrictive alloys [14, 15]. Primarily use of this rare element is in phosphors, particularly in fluorescent lamps, and high-intensity green emitters used in projection televisions. 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. 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]. Its separation 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 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, synthesized by substituting three hydroxyls in the chemical structure of the orthophosphoric acid by three organic radicals ($-\text{C}_8\text{H}_{17}$). Terbium (III) was 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, has been used as an auxiliary ligand in a synergistic extraction system containing D2EHPA as the primary ligand.

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 as a carrier 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.

EXPERIMENTAL SECTION

Materials

UV-Visible spectrometer was used for the analysis of the results (SPECORD 210 plus) of the Tlemcen University (Algeria). Consort C 831 pH meter with combined glass electrode was used for pH measurements (Adwa) of the Tlemcen University (Algeria). 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), 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 solution pH = 4.0 was procured from Prolabo.

Methods

The membrane extraction experiments were carried out in a one compartment cell with mechanical stirring

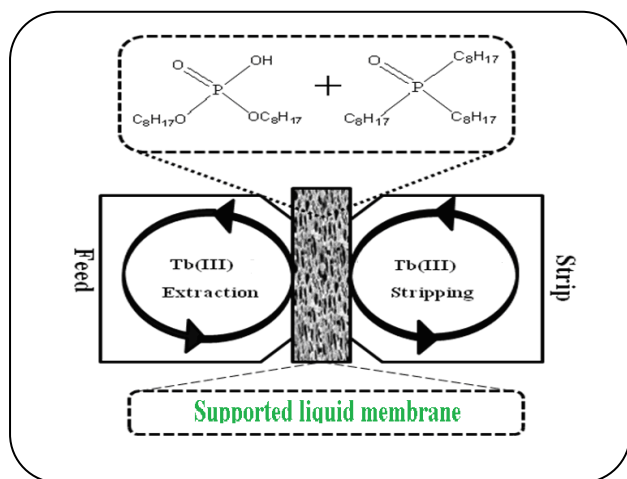


Fig. 1: Metal ion transport illustration in SLM.

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} mol/L in all the SLM studies, as described in Fig. 1. 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, 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 μ L from the compartment at different times for the spectrometer analysis after the addition in the cell (2mL) of a buffer solution (pH = 4.0; 1.7 mL) and 150 μ L 10^{-3} M of Arsenazo III as complexing agent [18]. All experiments were performed at ambient temperature.

Calculations

The percent Tb (III) extraction, (%) was determined as follows:

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

where C_0 and C are the concentrations (mol/L) of terbium ions before and after adsorption, respectively.

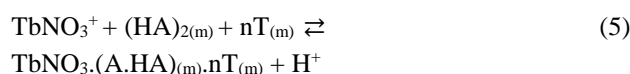
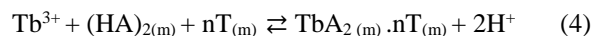
Experiment design

Preliminary experiments showed that, as expected, numerous factors can influence the yield extraction of Terbium (III), but only three 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.

In our investigations, a series of 27 attempts were made according to a 3^3 experiment factorial design (statgraphics 18.1.06), 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

The extractions of Terbium (III) by D₂EHPA with the addition of TOPO were represented by the following equations [19]:



Where: $(\text{HA})_2$ and T represent the dimeric form of D₂EHPA and TOPO, respectively.

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 high [20, 21]. A stronger power will promote the extraction of Tb (III). 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} mol/L, 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

Table 1: Factor levels used in the 3³ factorial experiment designs at ambient temperature.

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

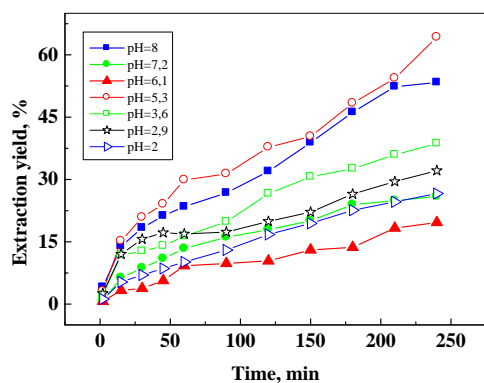


Fig. 2: Effects of initial pH on the extraction yield of Tb³⁺ by SLM; Conditions: membrane thickness 125 μm; Stirring = 900 rpm; [Tb (III)] = 10⁻³M; D₂EHPA/ TOPO (molar ratio 1/0.4).

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 = 5.3, the extraction yield of Tb (III) decreases to pH = 6.1 (19.7%), then increases to pH = 8.0 (53.4%). The optimum yield is at pH = 5.3 (64.2%), as described in Fig. 2. 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 Fig. 2, 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

Factorial design study

In order to examine the interaction between the studied factors on the Tb (III) extraction; the factorial 3³ designs had been used, by varying three key variables, stirring rate V, rpm (X₁), the concentration of potassium

nitrate S, M (X₂) and the time of extraction t, min (X₃). These results are summarized in Table 2.

An adequate selection of these parameters is an essential requirement for establishing an accurate polynomial model Eq. (6). 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 3³ 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:

$$Y (\%) = 15.42 + 14.67 X_1 - 10.68 X_2 + 10.69 X_3 - 13.04 X_1 X_2 + 7.08 X_1 X_3 - 4.709 X_2 X_3 + 12.83 X_1^2 - 1.28 X_2^2 - 5.86 X_3^3 - 6.64 X_1 X_2 X_3 \quad (6)$$

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 Fig. 3. 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 [20, 21].

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 3. Thus, with a 95% confidence (i.e., α=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-α) level, the confidence range for all the coefficients estimated using 27 runs, will be Δa_i = ± 0.1412 at 95% confidence.

Table 2: 3^3 factorial design matrices and the responses.

Experiment no.	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

Table 3: 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
Variability of the experimental data	R^2	0.997

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

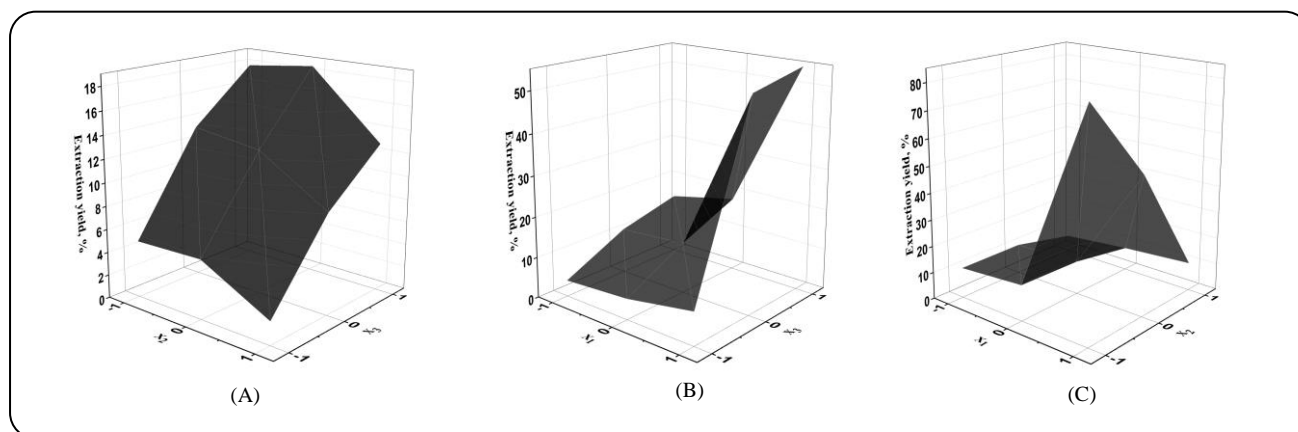


Fig. 3: (A):3D representation of the extraction of at fixed $X_1=0$. $X_2 (-1 \text{ to } +1)$, $X_3 (-1 \text{ to } +1)$. (B): 3D representation of the extraction of Tb^{3+} at fixed $X_2=0$. $X_1 (-1 \text{ to } +1)$, $X_3 (-1 \text{ to } +1)$. (C): 3D representation of the extraction of Tb^{3+} at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

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

$$Y = 15.42 + 14.67X_1 - 10.68X_2 + 10.69X_3 - 13.04X_1X_2 + 7.08X_1X_3 - 4.709X_2X_3 + 12.83X_1X_1 - 1.28X_2X_2 - 5.86X_3X_3 - 6.64X_1X_2X_3 \quad (7)$$

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 ($X_1X_2X_3$).

Interpretation

The effect of individual variables and interaction 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

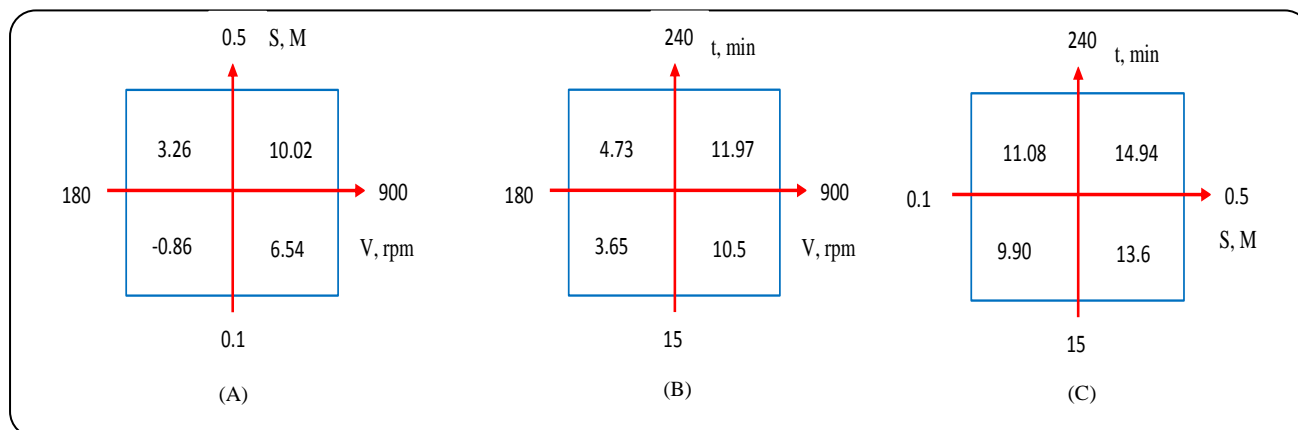


Fig. 4: (A): Interaction factorial between stirring rate V , rpm and $[KNO_3]$ S , min (X_1X_2). (B): Interaction factorial between stirring rate V , rpm and the contact time t , min (X_1X_3). (C): Interaction factorial between $[KNO_3]$ S , M and the contact time t , min (X_2X_3).

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 are plotted in Fig. 4 (A-B). Also, show 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 can be seen in Fig. 4 (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 % .

CONCLUSIONS

The environment is polluted by different chemical compounds. Terbium, together with substances in the lanthanide class and other chemicals, can pollute the environment, being residues from different industries. Extraction of Terbium is significant in terms of pollution reduction, and to be recycled into other possible applications. In this article, the separation of this element is shown by means of extraction of a dilute liquid phase and the liquid phase being passed into another, in order to concentrate it. In the experiments an advanced technique was used: the selective membrane technique, using a liquid membrane supported on a porous material. The D2EHPA / TOPO mixture was used as the transmissive

liquid membrane, and PVDF was used as support. In the extraction process of Terbium (III), an important role has its working pH. Following our experiments, it has been found that a maximum extraction yield is obtained by working at a pH of 5.3 pH units. To determine the influence of all the key factors on the extraction process (expressed in terms of yield) and the optimal experimental work, we have recourse to the use of the factorial program (3^3). Following the 27 experiments, it was found that the 67.7% extraction efficiency can be achieved under the following working conditions: Initial pollutant concentration (Tb) - 10^{-3} M, Temperature - 20°C , Time - 240 min, stirring - 900 rotations (rpm) per minute, and D2EHPA / TOPO molar ratio (1 / 0.4). In conclusion, the technique of extraction with supported liquid membranes used by us in this study has definite advantages in separating and concentrating this element: Terbium. This technique requires few chemicals, flows in one step, shows little energy and can be optimized relatively easily. The results obtained at the laboratory level are promising and we therefore believe that it can be extended at the industrial level.

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