SUPPORTED LIQUID MEMBRANE EXTRACTION OF TERBIUM(III) BY CYTOS IL102/D_2EHPA (TRIHEXYLTETRADECYLPHOSPHONIUM BROMIDE/DI(2-ETHYLHEXYL) PHOSPHATE) EXTRACTANT MIXTURE

Mohamed A. Didi[a]* and Sid Ahmed Elhabiri[a]

Keywords: Terbium(III); trihexyltetradecylphosphonium di(2-ethylhexyl) phosphate (D_2EHPA); trihexyl (tetradecyl)phosphonium bromide(Cytos IL102); membrane extraction; ionic liquid.

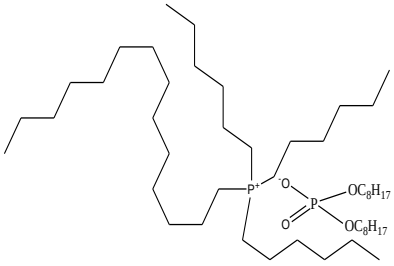
We have developed a membrane impregnated with ionic liquid Cytos IL102/D_2EHPA (trihexyltetradecylphosphonium bromide/di(2-ethylhexyl) phosphate) for the extraction of Tb(III) from aqueous solutions at different pH values. Various parameters such as the mixing effect Cytos IL102/D_2EHPA, the initial terbium concentration, the stirring speed and the extraction time have been studied. The amount of Tb(III) retained per gram of extractant (Cytos IL102/D2EHPA) is 4.37 mg g^{-1} for a concentration of Tb(III) of 10^{-3} M. The optimal yield was obtained at 240 min and stirring speed at 900 rpm.

* Corresponding Authors
Fax: +213552639237
E-Mail: madidi13@yahoo.fr (M.A. Didi)
[a] Laboratory of Separation and Purification Technologies, Department of Chemistry — Faculty of Sciences, Box 119, University of Tlemcen —13000, Algeria.

INTRODUCTION

The supported liquid membrane separation (LMS) technique is an advanced solvent extraction technique that provides a simple and effective method for extracting and separating metal ions.[1] The use of membranes 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 secondary waste.[2,3] Rare earth removal can be achieved by the supported liquid membrane extraction process.[4-8]

Terbium is used in alloys and in the production of electronic devices and other magneto mechanical devices. Terbium oxide is used in green phosphors in fluorescent in trichromatic lighting technology of lamps and colour TV tubes. In order to meet the fast-growing demand and to ensure sufficient supply of terbium, it is essential to develop an efficient Terbium recovery process from post-consumer terbium containing products.



Scheme 1. Trihexyltetradecylphosphonium di(2-ethylhexyl) phosphate (D2EHPA).

In the present work, the extraction of Tb(III) from a nitrate solution through a supported liquid membrane impregnated with the new ionic liquid D_2EHPA (Scheme 1)/Cytos IL102 (trihexyltetradecylphosphonium bromide) has been studied.

Various parameters have been studied, such as agitation speed, pH of the feed phase and the initial concentration of terbium. The use of the mixture of D_2EHPA and Cytos IL 102 as extractants for the extraction of terbium(III) on a supported liquid membrane has not been reported in the literature.

EXPERIMENTAL

Terbium solution at 10^{-2} M was prepared by dissolving of terbium(III) nitrate (3.025 g) in 1 L of distilled water (purchased from Sigma-Aldrich). The initial pH of the sample solutions were adjusted by using dil. HNO_3 or NaOH (from Sigma-Aldrich). $NaNO_3$ (from Merck) was used to study the salt effect. Arsenazo III 10^{-3} M (from Alfa-Aesar) was prepared by dissolving 0.0820 g in absolute ethanol. Cytos IL102 (trihexyl (tetradecyl)phosphonium bromide) was obtained from Cytec (www.cytec.com).

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 (Figures 1 and 2).

Samples containing Tb(III) were analyzed by spectrophotometer (Analytik Jena Specord 210 Plus), with Arsenazo III as ligand. The morphology of the hydrophobic support membrane at the surface and in the thickness was determined using a scanning electron microscope (SEM) Carl Zeiss EVO®40 EP. pH measurements were taken on a potentiometer Consort C831.

General extraction procedure

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} mol L^{-1} in all the SLM studies.

The liquid membrane phase was prepared by dissolving of D_2EHPA and Cytos IL102 (Scheme 1) in diethyl ether. The PVDF support was impregnated with the carrier solution for 24 h, SLMs needed more than 12 h, 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.

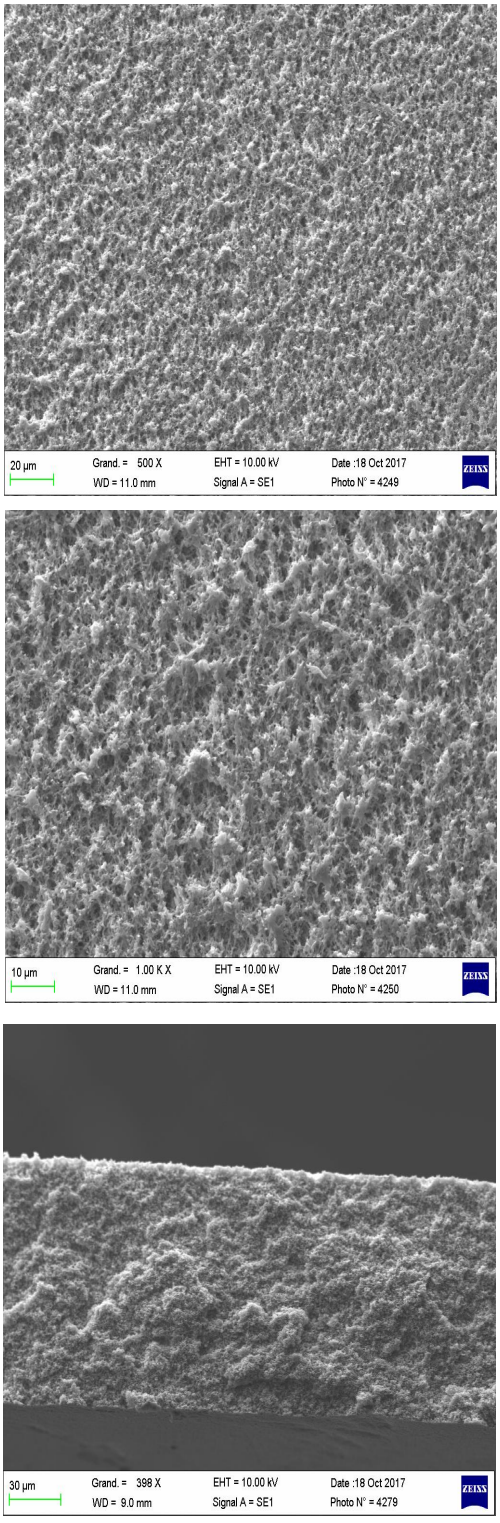


Figure 1. Surface SEM images of a PVDF hydrophobic support membrane and its thickness (Millipore VVHP04700).

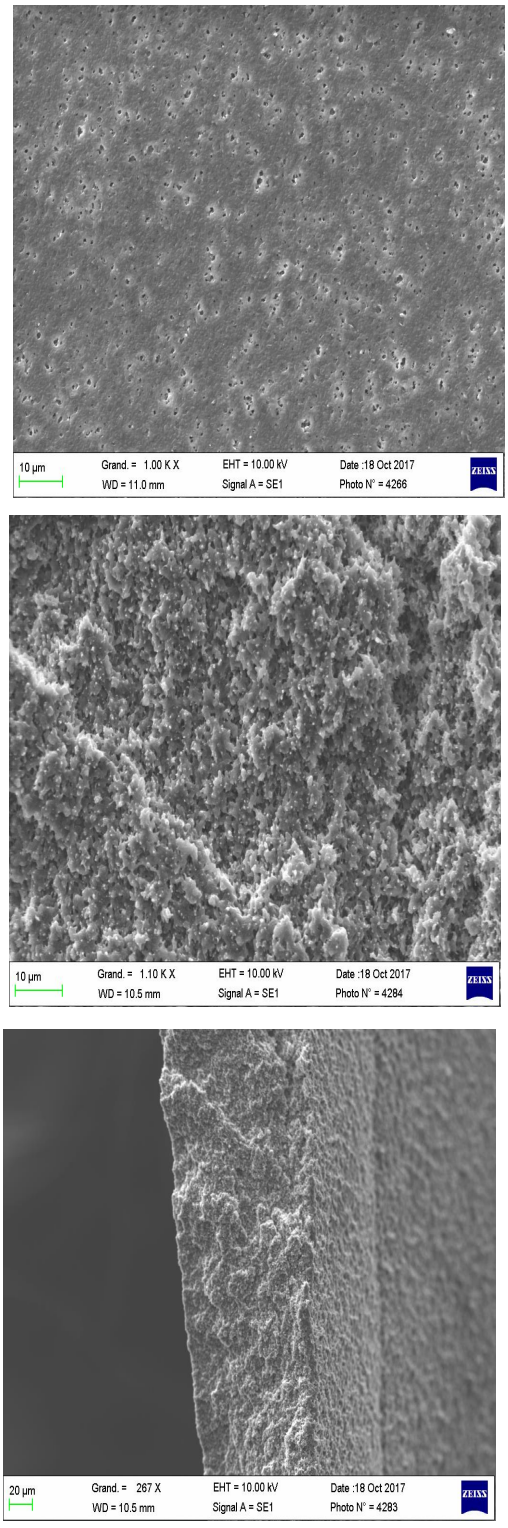
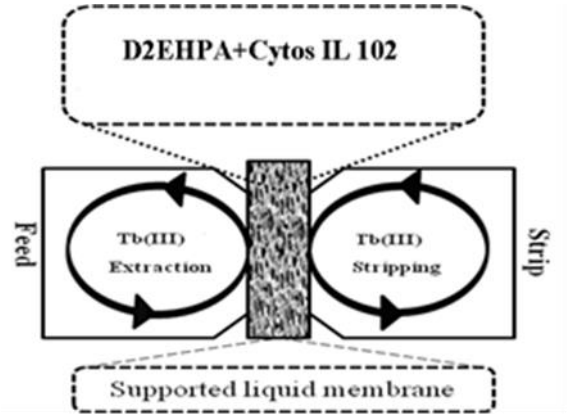


Figure 2. SEM image of the hydrophobic support membrane impregnated with D_2EHPA/Cytos IL102.

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 cm^2 (see Scheme 2). The extraction of Tb(III) 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 25°C.[9,10]



Scheme 2. Illustration of transport of terbium ion in SLM.

The reaction of Arzenazo III with Tb(III) is very fast to form a green complex, which absorbs in the visible range (λ_{max} = 654 nm).[11] Three concentrations of Tb(III) variants from 1.10^{-4} M to 10^{-3} M were prepared to plot the calibration. The percentage of Tb(III) that was extracted by MLS was determined using Eqn.(1).[12]

$$Extraction\ yield\,(\%) = \frac{c_i - c_t}{c_i} \times 100 \qquad (1)$$

The uptake rate of Tb, q_t (mg g^{-1}) was determined by Eqn. (2),

$$q(mg/g) = \frac{(C_0 - C_e)VM}{m} \qquad (2)$$

where

C_i, C_t and C_e were the initial, at time, *t*, and equilibrium Tb(III) concentration (mol L^{-1}), respectively;

V (55 mL) was the volume solution;

M molecular weight (g. mol^{-1}), and

m was the mass of extractant used.

The yields are obtained with an error of ± 0.01 %.

RESULTS AND DISCUSSION

In this study, we have used of the mixture of D_2EHPA and Cytos IL102 as extractants for the extraction of terbium on a supported liquid membrane. Cytos IL102 is a commercial phosphorous ionic liquid (trihexyl(tetradecyl)phosphonium bromide). In this study, the hydrophobic 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), was used for the extraction of Tb(III) from a solution of Terbium nitrate. A parametric study was conducted to optimize the extraction conditions.

Effect of stirring speed

One of the main resistances in the liquid membrane technique is the extraction of metal ions. To minimize this resistance, the solutions in the two compartments must be kept in agitation. Figure 1 represents the extraction yield of Tb(III) as a function of time by a hydrophobic membrane for two stirring speeds of 180 rpm and 900 rpm. It is observed that the extraction yield of Tb(III) increases with increasing stirring speed. The best yield was obtained for a stirring speed of 900 rpm. Thus, the stirring speed of 900 rpm was used for the other experiments to be carried out (see Figure 3).

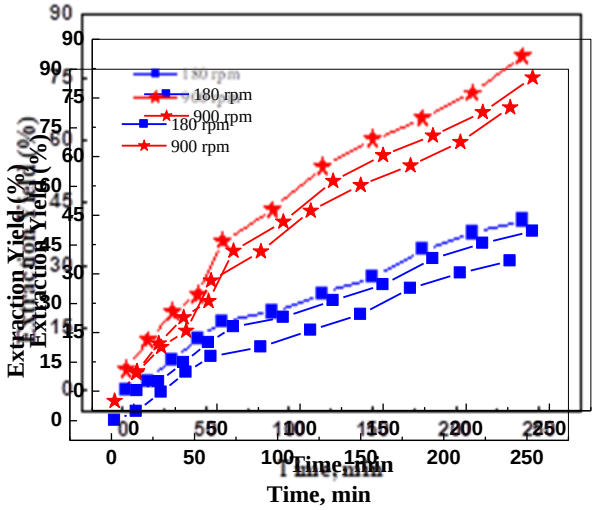


Figure 3. Kinetics of extraction of Tb(III) on MLS hydrophobic at different stirring speeds. [Tb(III)] = 10^{-3} M, molar ratio D_2EHPA/Cytos IL102 (1/1), *T* = 25 °C, pH_i = 5.3, membrane thickness = 125 µm.

Effect of initial pH

The effect of pH in the feeding phase on Tb(III) extraction was studied in a pH range of 2.0 to 5.3 where the predominant species is Tb(III). The solution was adjusted with HNO_3 solutions. The initial concentration of Tb(III) in the feeding phase is 10^{-3} M, the volume of the solution to be extracted in the feed phase is 55 mL and with a molar ratio of D_2EHPA/Cytos IL102 = 1. The results obtained are illustrated in Figure 4.

The curves in Figure 4 show that as the pH decreases from 5.3 to 2.0 in the feed phase, the extraction yield decreases; a maximum yield (80%) was observed at pH 5.3 and for 240 min.

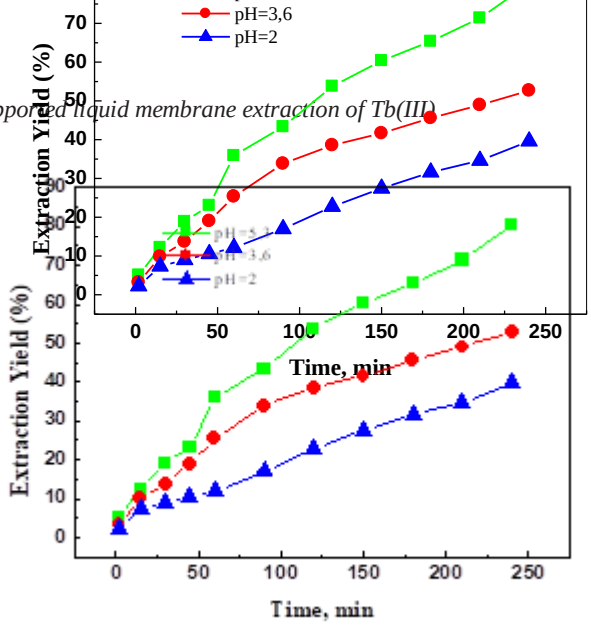


Figure 4. Tb(III) extraction kinetics on MLS hydrophobic at different initial pH. [Tb(III)] = 10^{-3} M, D_2EHPA/Cytos IL102 (1/1), *T*=25°C, pH_i = 5.3, membrane thickness = 125 µm.

Effect of initial concentration

The influences of the initial concentration of terbium(III) on the extraction yield were carried out in a concentration range between 10^{-3} and 10^{-4} M. The volume of the solution to be extracted was adjusted to 55 mL and the molar ratio of D_2EHPA/Cytos IL 02 was 1:1. The results obtained are presented in Figure 5.

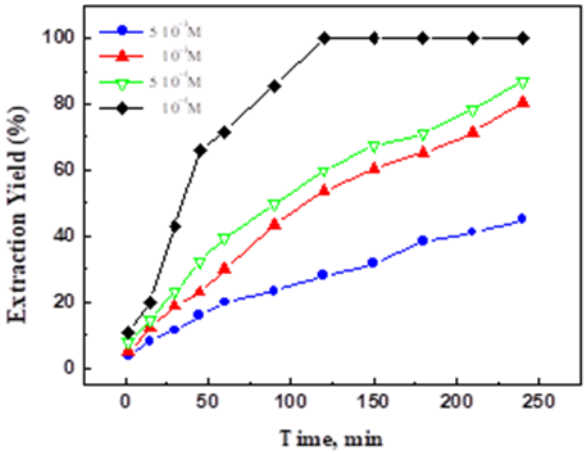


Figure 5. Tb(III) extraction kinetics on MLS hydrophobe at different initial concentrations. D_2EHPA/Cytos IL102 (1/1), *T*=25°C, stirring = 900 rpm, pH_i = 5.3, membrane thickness = 125 µm.

From Figure 5 it is observed that the extraction yield decreases with the increase in the initial concentration of terbium(III) in the feeding phase. In addition, a maximum yield of 100 % is obtained in 120 minutes of stirring, when the initial concentration of terbium(III) is 10^{-4} M.

CONCLUSION

Our work in this study focuses on the extraction of Tb(III) by a membrane impregnated with the ionic liquid D_2EHPA/Cytos IL102. Various parameters, such as the mixing effect D2EHPA/Cytos IL102, the initial terbium concentration, the stirring speed and the extraction time, have been studied. The amount of Tb(III) retained per gram of extractant (D_2EHPA/ Cytos IL102) was 4.37 mg g^{-1} for a concentration 10^{-3} M of Tb(III). The optimal yield was obtained at 240 min and stirring speed at 900 rpm.

REFERENCES

[1]Mulder, J., *Basic Principles of membrane Technology*, Springer Science and Business Media, Dordrecht, **2012**. DOI: 10.1007/978-94-009-1766-8

[2]Porter, M C., *Handbook of industrial membrane technology*, Noyes Publ., Park Ridge, USA, **1989**.

[3]Ishikawa, N., Upward Temperature Shift of the Intrinsic Phase Lag of the Magnetization of Bis (phthalocyaninato) terbium by Ligand Oxidation Creating an S=1/2 Spin, *Inorg. Chem.*, **2004**, *43*(*18*), 5498-5500. https://doi.org/10.1021/ic049348b

[4]Shimada, H., Pulmonary toxicity of systemic terbium chloride in mice, *J. Toxicol. Env. Health*, **2010**, *48*(*1*), 81-92. DOI: 10.1080/009841096161483

[5]Alonso, E., Sherman, A. M., Wallington, T. J., Everson, M. P., Field, F. R., Roth, R., Kirchain, R. E., Evaluating rare earth element availability: a case with revolutionary demand from clean technologies. *Environ. Sci. Technol*., **2012**, *46*, 3406-3414. DOI:10.1021/es203518d

[6]United States Environmental Protection Agency (2012) Rare earth Elements: a review of production, processing, recycling, and associated environmental issues, EPA 600/R-12/572**, 2012,** Cincinnati, Ohio, USA.

[7]Binnemans, K., Jones, P. T., Blanpain, B., Gerven, T. V., Yang, Y., Walton, A., Buchert, M., Recycling of rare earths: a critical review, *J. Clean. Prod.*, **2013**, *51*, 1. https://doi.org/10.1016/J.JCLEPRO.2012.12.037

[8]Graedel, T. E., Allwood, J., Birat, J. P., What do we know about metal recycling rates, *J. Ind. Ecol.*, **2011**, *15*, 355. https://doi.org/10.1111/*j*.1530-9290.2011.00342.x

[9]Belyouci, O., Didi, M A., Sorption and separation study of Praseodymium and Cadmium by Magnetic bentonite. Factorial design optimization, *Desalination Water Treat*., **2017**, *68*, 199–210. DOI:10.5004/dwt.2017.20321

[10]Didi, M. A., Abderrahim, O., Azzouz, A., Villemin, D., Liquid-liquid extraction of thorium (IV) by fatty acids. Comparative study, *J. Radioanal. Nucl. Chem*., **2014**, *299*(*3*), 1191-1198. https://doi.org/10.1007/s10967-013-2855-6

[11]Kadous, A., Didi, M. A., Villemin, D., Extraction of Uranium(VI) with D_2EHPA/TOPO using the Supported Liquid Membrane, *J. Radioanal. Nucl. Chem*., **2009**, *280*(*1*), 157-165. https://doi.org/10.1007/s10967-008-7435-9

[12]Didi, M. A., Kaid, M., Villemin, D., Dodecylhydroxydiphosphonic acid for solvent extraction, *Solvent Extr. Ion Exch*., **2008**, *26* (*2*), 113-127. https://doi.org/10.1080/07366290801904715

Received: 14.08.2019.
Accepted: 04.08.2019.