

Selective and Efficient Ligandless Water-in-Oil Emulsion Liquid Membrane Transport of Thorium(IV) Ions

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ABSTRACT: *The present paper concerns on the selective and very efficient transport of thorium(IV) ions from aqueous solutions through an emulsion liquid membranes composed by paraffin and a surfactant, without carrier requirement. The influence of pH of the external aqueous phase, the surfactant concentration in the membrane phase, the type and concentration of the acid used in the receiving phase, the emulsification and mixing speed on the process efficiency were examined and discussed. The optimized conditions were: liquid paraffin as diluent, 5% surfactant (non-ionic polyamine surfactant span-80), emulsification rate 5250 rpm, 15 min of stirring at 750 rpm in the extraction step, pH 5, oil/aqueous ratio of 3 in emulsions and using 0.3 M solution of sulfuric acid as stripping phase. Under optimized experimental conditions, thorium ions were selectively and quantitatively transported from its mixture solution with lanthanides La(III), Sm(III), Eu(III) and Er(III). The concentration of thorium ions, in single component transport experiment, was measured spectrophotometrically using ArsenazoIII as indicator at 655 nm, and the analysis of metal ions in competitive experiments was performed by an ICP-OES instrument under recommended conditions provided by the instrument's manufacturer.*

KEYWORDS: *Emulsion liquid membrane; Ligandless transport; Thorium; Lanthanides; Separation.*

INTRODUCTION

Although solvent extraction and ion-exchange processes are known as efficacious techniques for management of various industrial wastes [1], they suffer from some disadvantages. Ion-exchange processes are relatively slow and are limited to be used for very dilute solutions. Solvent extraction processes need to use volatile organic diluents and organic extractants which lead to large volumes of secondary wastes.

Separation methods based on liquid membranes have been found to be promising as they lower the consumption

of organic extractant as well as organic diluents [2–5]. Separation techniques based on liquid membranes include two main groups, i.e. methods without phase dispersion and those with phase dispersion [2]. The latter methods comprise those in which one or two of the three liquids are dispersed in drops.

Emulsion (surfactant) Liquid Membrane (ELM) is a triple dispersion system [6]. The membrane in this method is formed by a diluent, an emulsion stabilizer (surfactant) and a carrier in most cases in the facilitated

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1021-9986/2016/4/125

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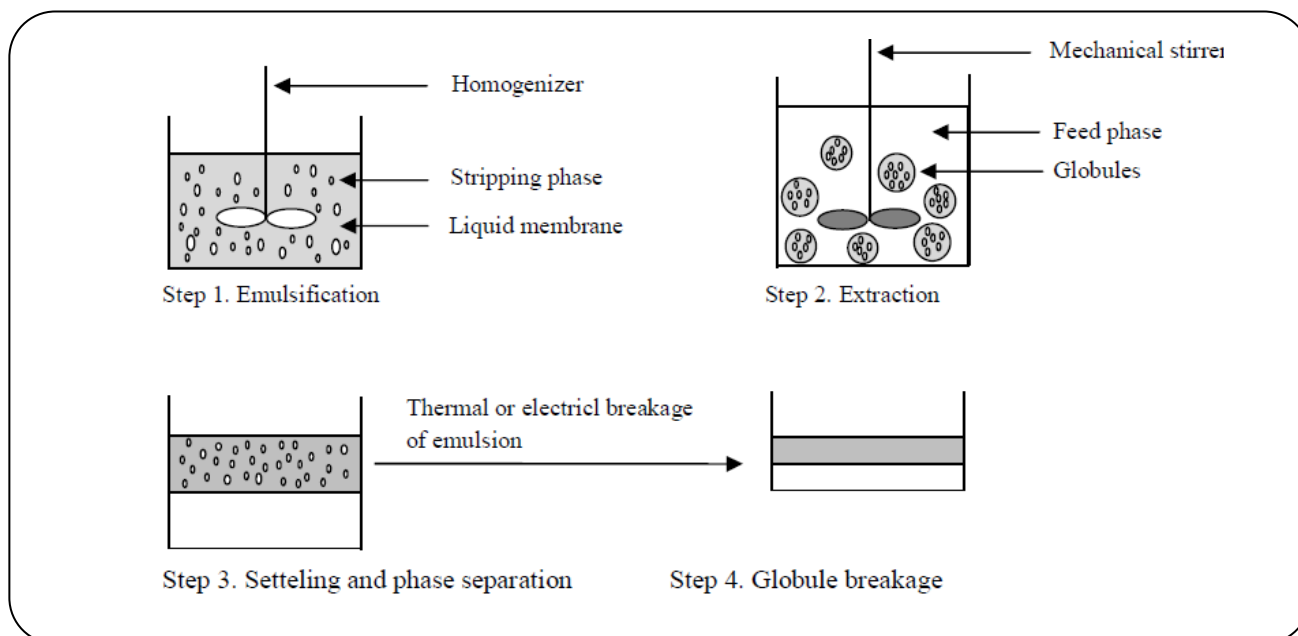


Fig. 1: Schematic representation of the steps involving in an ELM process.

transport process. By contacting feed phase and emulsion globules, solute is transported through the membrane into the internal aqueous phase and is then concentrated. After permeation, the emulsions are separated from the feed phase and their breakage (demulsification) is usually performed by thermal or electrical methods. Heat treatment of the emulsion is an effective method of demulsification because it reduces the viscosity and density of the oil. As oils have a larger coefficient of expansion than water, their density decreases faster than that of aqueous phase. Elevated temperature also increases the solubility of the surfactants in both oil and water phases. It results weakening the interfacial film. The drawback of heat treatment alone is slow demulsification kinetics. For this reason, heat treatment in conjunction with some other technique which improves coalescence kinetics is required [7]. A schematic diagram of this method is presented in Fig. 1.

Due to some advantages associated with this technique, such as large mass transfer area, need to lower amount of carrier and ability to accumulate the analyte in the receiving phase with high concentration factor [2, 8, 9], the application of emulsion liquid membrane technique has been considered for separation and concentration of a variety of chemical species such as metal ions [10-12], organic [13-15] and biochemical compounds [16-18].

Thorium is a radioactive element that occurs naturally in low concentrations (~10 ppm) in the earth's crust. The most common source of thorium is monazite, a kind of rare earth phosphate mineral, which contains 6–7% thorium phosphate on average [19]. This element has wide applications in various arrays of products and processes such as the production of ceramics, carbon arc lamps, alloys and in mantles for lanterns. In addition, thorium is used as a representative element for tetravalent actinides in their separation studies [20-26]. Due to the wide spread use of these ions, and the importance of the separation of tetravalent and trivalent actinides from nuclear wastes [27, 28], the development and improvements of efficient techniques for separation of thorium ions are among the main subjects of actinides separation investigations.

Several strategies have been developed for the separation of thorium and rare earths [29-35]. Various extractants such as calixarenes [19, 24], oximes [26], phosphoric acids [36, 37], neutral phosphates [38, 39], amines [40], isoxazolones [41], crown ethers [42, 43] and ionic liquids [44] have been employed for the extraction of thorium and rare earths. Some of them have been employed for rare earths extraction by emulsion liquid membrane technique [45-49].

In this work we investigated transport of Th(IV) ions from aqueous solutions through emulsion liquid membranes

from feed phase into receiving phase. The studied membranes contains by a diluent and an emulsion stabilizer, without further carrier. The effects of various experimental parameters such as pH of the external aqueous phase, the surfactant concentration in the membrane phase, the type and concentration of the acid used in the receiving phase, the emulsification and mixing speeds on the process efficiency were investigated. The extraction of rare earths was also studied for the possible separation of thorium and rare earths.

EXPERIMENTAL SECTION

Materials and Apparatus

The liquid membrane solution is composed by a surfactant and a diluent. Solution of sulfuric acid (Merck, Germany) as stripping phase, liquid paraffin (Merck, Germany) as diluent, and non-ionic polyamine surfactant sorbitan monooleate commercially known as Span 80 (Merck, Germany), were used for emulsion preparation. Stock solutions of thorium ions was prepared by dissolving appropriate amount of $\text{Th}(\text{NO}_3)_4$ salts (Fluka, US) in deionized water containing 0.01 mol/L nitric acid. The stock solutions of La(III), Sm(III), Eu(III) and Er(III) ions were prepared by dissolving an appropriate amount of their oxides (Fluka, US) in concentrated nitric acid. Working solutions were prepared by dilution of the stock solution with deionized water. The pH values of these solutions were adjusted with diluted nitric acid or sodium hydroxide (Merck, Germany) solutions.

The transport vessel was a cylindrical glass container (65 mm diameter and 90 mm height) equipped with four round glass baffles (6 mm diameter). Emulsion preparation was performed using a rotor–stator type high speed rotational disperser (homogenizer) IKA Ultra Turrax T-18. A stainless steel probe bearing four pitched blades (45° angle, 25mm length and 9 mm wide), attached to a mechanical mixer (Heidolph RZR- 2021) with variable speed 40–2,000 rpm, was used for the extraction experiments. Separation of the phases was performed by a Heraeus centrifuge (Labofuge 300). The absorbance determinations were performed on a UV–Vis spectrometer Hach (DR5000). A Metrohm 780 pH meter was used for pH measurements.

Procedure

Emulsions were prepared by emulsifying sulfuric acid solution (internal phase) in an organic membrane phase

composed by liquid paraffin and the non-ionic polyamine surfactant Span 80. This was realized by 10 min. homogenizing of the mixture at 3500–7000 rpm with the disperser. Mixing continued for 5 minutes. Permeation was started by dispersing the freshly prepared emulsion in the external aqueous phase containing thorium ions adjusted at a given pH by using mixture of sodium hydroxide/nitric acid solutions. At a regular time intervals samples were taken from feed phase by disposable sanitary syringes and centrifuged to separate the emulsion phase from the external phase. The concentration of thorium ions remained in the feed phase was measured spectrophotometrically at 659 nm. The analysis of metal ions in the competitive experiments was done by ICP-OES. The mass balance confirmation was tested in few experiments by demulsification of the globules which was performed by adding 1.5 mL of dichloromethane to 5 mL of emulsion phase and magnetically stirring at about 80°C . The presence of dichloromethane decreases the viscosity of the membrane and improves demulsification kinetics. After one hour, the mixture was centrifuged and internal aqueous phase separated to determination of thorium concentration. Results show that more than 96% of thorium is transported through the membrane under the optimized experimental conditions.

RESULTS AND DISCUSSION

Preliminary liquid-liquid extraction of thorium ions into a dichloromethane solution of Span 80 confirms the role of this surfactant as phase transfer agent of thorium ions. However, negligible amount of La(III), Sm(III), Eu(III) and Er(III) ions was extracted into the same organic phase. These results provoke us to study the selective separation of thorium ions from lanthanides by using a ligandless emulsion liquid membrane. A variety of operating parameters such as emulsification speed, globule/feed phase mixing speed, surfactant concentration, the organic to aqueous phase volume ratio, kind and concentration of stripping agent, feed phase pH and treatment ratio affect transport efficiency in emulsion liquid membrane technique.

Emulsification speed

The purpose of this experiments was to determine how different emulsification processes especially homogenizer speed affect the extraction efficiency.

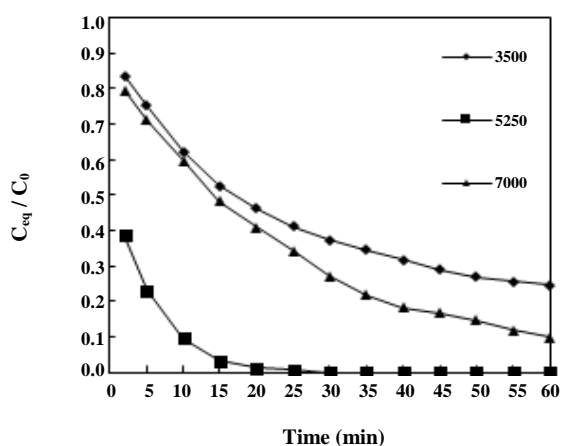


Fig. 2: Effect of emulsification speed on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 2.0×10^{-5} M, pH 5, receiving phase 0.5 M HNO_3 , surfactant 2 %v span 80, organic to aqueous ratio 3, treatment ratio 0.1, stirring rate of the extraction step 700 rpm.

Emulsion formation is usually achieved by a mechanical technique. Initially, the interface between the two phases is deformed to such an extent that large droplets are formed, and these large droplets are subsequently broken up into smaller ones. During emulsification, the interfacial area between two liquids increases, liquids tend to minimize the surface area and therefore, mechanical agitation is required for forming emulsion.

Fig. 2 shows the effect of emulsification speed on the extraction efficiency and stability of the emulsions. Three speed of homogenizer 3500, 5250 and 7000 rpm were tested in 15 minutes emulsification process. An increase in emulsification speed from 3500 to 5250 is accompanied with an increase in the extraction efficiency by forming the globules with thinner membrane. However, further increase to 7000 rpm decreases the process efficiency. This observation can be attributed to the breakage of the globules at high emulsification speeds. Thus, 5250 rpm was chosen as optimum emulsification speed for the following experiments.

Stirring speed in the extraction step

Mixing speed of the feed solution with emulsions in the extraction step affects the performance of ELM process to a great extent. This parameter speed was studied in the range of 400–800 rpm and the results were shown in Fig. 3. In the ELM process, fine emulsion

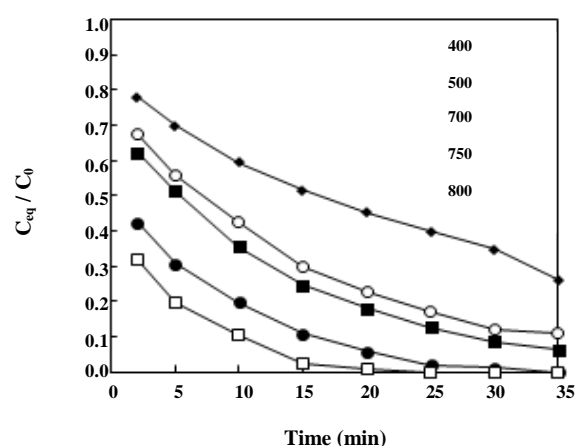


Fig. 3: Effect of mixing speed on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 2.0×10^{-5} M, pH 5, receiving phase 0.5 M HNO_3 , surfactant 2% (w/v) span 80, organic to aqueous ratio 3, treatment ratio 0.1, emulsification speed 5250 rpm.

droplets form globules in the feed solution. An increase in mixing speed would increase interfacial area and the mass transfer coefficient. The bigger globules may disintegrate to form smaller globules, thereby resulting in an increase in area, however further increase in speed is likely to break the emulsion droplets, thereby reducing overall enrichment and extraction [50].

It was observed that increasing the mixing speed from 400 to 750 rpm increased the rate of extraction. This is due to an increase in the mass transfer area in the aqueous feed solution (between the emulsion “globules” and aqueous solution), but further increase in the mixing speed from 750 to 800 rpm resulted in a decrease in the extent of extraction. This was attributed to the hydrodynamic instability of the emulsion at the higher speed. This breakage can be explained as follows: as the mixing speed increased, the co-transport of water was also increased. The emulsion phase swells, becomes highly unstable and breaks into the external phase. The other reason is that there is an increase in shear on the emulsion phase with the increase in the mixing speed. This also causes the breakage of the emulsion and finally results in the gradual reduction in extraction and enrichment efficiency as the mixing speed is increased further. Thus, there is a trade-off between decrease in external mass transfer resistance and stability of emulsion. Therefore, the mixing speed plays an important role [51].

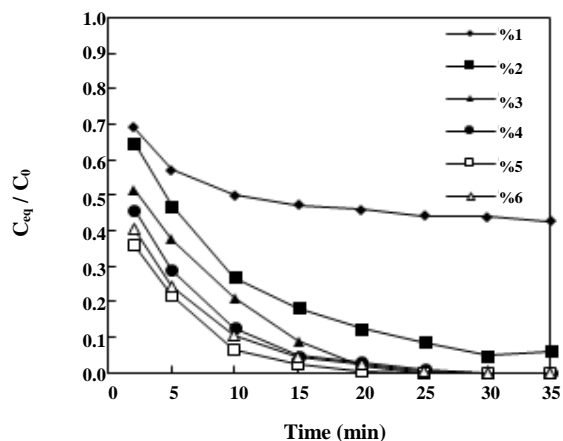


Fig. 4: Effect of surfactant concentration on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 2.0×10^{-5} M, pH 5, receiving phase 0.5 M HNO_3 , organic to aqueous ratio 3, treatment ratio 0.1, emulsification speed 5250 rpm, stirring speed 750 rpm.

Fig. 3 also shows that breakage is increased as the agitation speed increases and becomes higher after 750 rpm because of increase in shear stress. This investigation conducts selecting 750 rpm as optimum stirring speed in the extraction speed.

Surfactant concentration

Emulsion liquid membranes are normally unstable. To overcome this defect certain amounts of surfactant must be added through emulsion formation step. The surfactant avoids emulsion breakdown caused by the coalescence of dispersed drops [52]. In addition, the surfactant makes a decrease in the interfacial tension, contributing to stabilization of the emulsion by producing smaller droplets. Besides, it is known that the increase in the concentration of surfactant does not favor the kinetics of extraction [53]. The effect of surfactant concentration on thorium extraction is shown in Fig. 4. At the lowest concentration of surfactant, both extraction efficiency and the final volume of emulsion decreased. This confirms that emulsion stability is strongly dependent on the surfactant concentration. The emulsion stability was improved with the increase in surfactant concentration. By increasing the concentration of surfactant from 1 to 5% (w/v) the stability of the liquid membrane increases, which leads to an increase in the extraction efficiency. Excessive surfactant tends to increase the resistance at the interface and this can be attributed to the increase

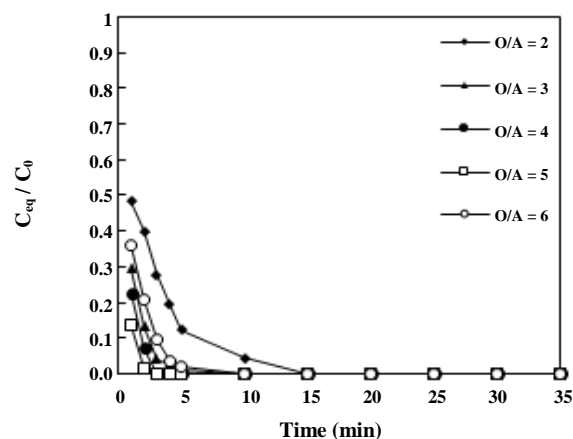


Fig. 5: Effect of O/A ratio on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 2.0×10^{-5} M, pH 5, receiving phase 0.5 M HNO_3 , surfactant 5% (w/v) span 80, organic to aqueous ratio 3, emulsification speed 5250 rpm, stirring speed 750 rpm.

in viscosity of the organic phase. Therefore, increasing surfactant concentration beyond 5% increased the emulsion stability but the mass transfer was adversely reduced. This indicates that internal diffusion of Th(IV) ions further affected by viscosity of the membrane phase [54]. A similar effect was observed by Reis & Carvalho [52] and Valenzuela *et al.* [55], in the recovery of zinc and copper ions. They found that the use of an unnecessarily high content of surfactant produces lower metal extraction due to the generation of higher interfacial resistance. Hence, a surfactant concentration of 5% was chosen as the best concentration for following the experiments.

Organic to aqueous phase volume ratio in the emulsion globules (O/A)

The effect of Organic membrane (O) to the internal Aqueous phase (A) volume ratio on the process was checked in the range 2 to 6 (Fig. 5). As it is shown, an increase in O/A volume ratio in the range 2-5 accompanies with an augmentation in the extraction efficiency and extraction rate. Beyond this range a decrease in the extraction rate is observed. To give an explanation for these observations one should consider two opposite effects. The first is the improvement of the membrane stability by increasing O/A volume ratio. In fact a higher volume of the organic phase results the globules with a thicker membrane. This advantage

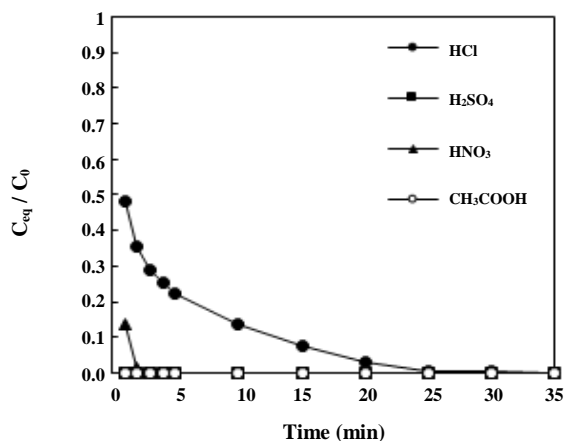


Fig. 6: Effect of the kind of acid used as stripping reagent phase on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 2.0×10^{-5} M, pH 5, surfactant 5% (w/v) span 80, organic to aqueous ratio 5, emulsification speed 5250 rpm, stirring speed 750 rpm.

is compensated with increasing the mass transfer resistance by the organic layer thickness. Based on these results the optimum O/A ratio of 5 was chosen for following the experiments.

Stripping reagent

As other liquid membrane techniques, in ELM separation techniques, extraction and simultaneous stripping of solute occurs on the external and internal interface of the membrane. Thus the type of the stripping solution used in the internal phase is an important parameter influencing the extraction efficiencies. To determine the suitable stripping reagent, solutions of sulfuric acid, hydrochloric acid, nitric acid and acetic acid (0.5 mol L^{-1}) were examined. The results shown in Fig. 6 reveal that the transport efficiency varies by the examined stripping reagent in the order of $\text{CH}_3\text{COOH} = \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$.

To investigate the influence of the sulfuric acid concentration on thorium extraction, a series of experiments was carried out by using 0.1 to 0.5 mol/L solutions of sulfuric acid as stripping reagent. The results (Fig. 7) shows that the efficiency increases by increasing the acid concentration in the internal phase from 0.1 to 0.3 mol/L, but further increase causes a decrease in the process efficiency which can be attributed to the destabilization of globules. It is noteworthy that in these experiments and following experiments, an initial

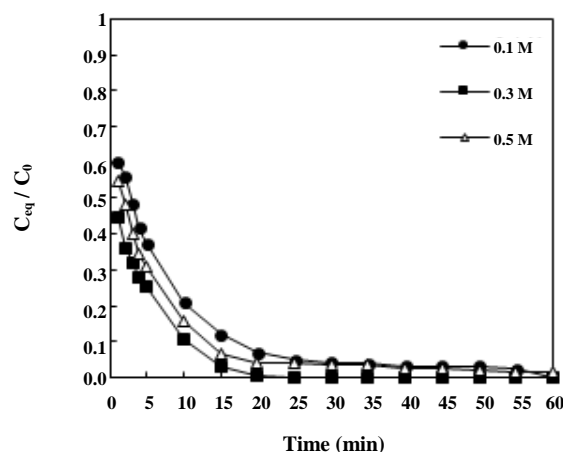


Fig. 7: Effect of sulfuric acid concentration, as internal phase, on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 8.0×10^{-5} M, pH 5, surfactant 5% (w/v) span 80, organic to aqueous ratio 5, treatment ratio 0.1, emulsification speed 5250 rpm, stirring speed 750 rpm.

concentration of 8.0×10^{-5} mol/L was used. According to these results, a solution 0.3 mol/L of sulfuric acid was used as appropriate stripping reagent.

Effect of the feed phase pH

The effect of feed phase pH on the extraction rate was studied in the range 2–8 (Fig. 8). As it is seen, at the pH values above 2 and up to 5 the extraction efficiency increases. It may be due to that high concentration of H^+ prevented the transfer of thorium in pH 2 and 3 and spans 80 more likely to be protonated. But at pH values up to 5, by decreasing the H^+ concentration, competition reduced and transfer of thorium will be taken place. Beyond pH 5, a decrease in the extraction efficiency can be attributed to the formation of metal hydroxide. According to these results, pH 5 was chosen as optimum value for the following study.

Effect of treatment ratio

The treatment ratio, defined as the volume ratio of the emulsion phase to the feed solution, plays an important role in determining the efficiency of ELMs [56, 57]. As the amount of emulsion in the feed solution increases, the number of available globules and interfacial surface area per unit volume of the feed solution increases and thus the flux of extracted thorium from the feed solution to emulsion, and extraction efficiency increases. It is noticeable that according to the literature, increasing of treatment

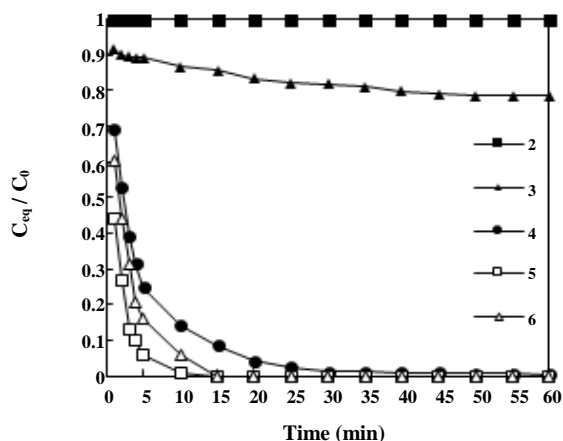


Fig. 8: Effect of feed phase pH on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 8.0×10^{-5} M, internal phase 0.3 mol/L sulfuric acid, surfactant 5% (w/v) span 80, organic to aqueous ratio 5, treatment ratio 0.1, emulsification speed 5250 rpm, stirring speed 750 rpm.

ratio may slightly increase the size of globules, which causes inversely a reduction in interfacial surface area. However, the increment in the size of globule is suppressed by that of increment in the number of globules [58].

Fig. 9 shows that the extraction efficiency is increased by increasing the emulsion to feed ratio from 1:16 to 1:4. For saving used chemicals and enough volume for sampling, treatment ratio 1:10 was used for this study.

Membrane selectivity

In order to examine the selectivity of the proposed method, competitive extraction experiments on mixtures of Th(IV) and four lanthanides i.e. La(III), Sm(III), Eu(III) and Er(III) ions were performed, under optimized experimental conditions. Although a quantitative transport of thorium ions was found, there was no detectable transport of the competing metal ions. The results approve an excellent selectivity behavior towards thorium of the proposed method. It is noteworthy that the concentrations of Thorium and Other metal ions in competitive transport experiments were measured by ICP-OES under recommended conditions provided by instrument's manufacturer.

CONCLUSIONS

The results of this study show the efficient extraction and transport of Th(IV) ions from aqueous solutions through emulsion liquid membranes. The proposed

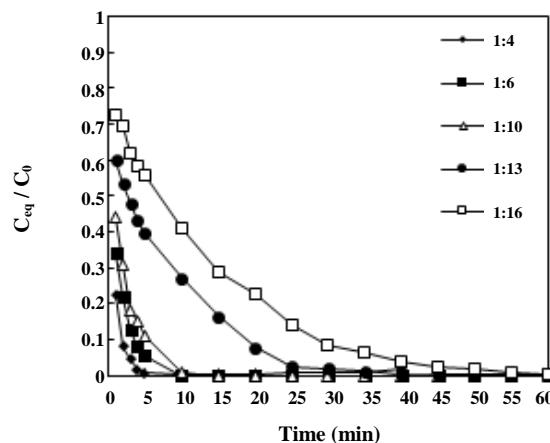


Fig. 9: Effect of treat ratio on the extraction efficiency. Experimental conditions: initial thorium ion concentration in the feed phase 8.0×10^{-5} M, internal phase 0.3 mol/L sulfuric acid, surfactant 5% (w/v) span 80, organic to aqueous ratio 5, emulsification speed 5250 rpm, stirring speed 750 rpm.

method is a simple and rapid method for separation of Thorium. It is found that the process does not need to any carrier for transport of thorium ions from feed phase into receiving phase. The influence of pH of the external aqueous phase, the surfactant concentration in the membrane, the type and concentration of the acid used in the receiving phase, the emulsification and mixing speeds on the process efficiency were examined and discussed. The optimized conditions were: liquid paraffin as diluent, 5% surfactant (non-ionic polyamine surfactant span-80), emulsification rate 5250 rpm, 15 min. stirring at 750 rpm in the extraction step, pH 5, oil/aqueous ratio of 5 in emulsions and using 0.3 mol/L solution of sulfuric acid as stripping phase. A quantitative and highly selective transport of Th(IV) ions (initial concentration 8×10^{-5} mol/L) with respect to four La(III), Sm(III), Eu(III) and Er(III), has been achieved, under optimized experimental conditions.

Received : Sep. 12, 2015 ; Accepted : Jan. 18, 2016

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