



Removal of Europium(III) from water by emulsion liquid membrane using Cyanex 302 as a carrier

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ABSTRACT

The present paper introduces a technical feasibility study of one of the most advanced extraction techniques (AETs); emulsion liquid membrane (ELM) on the removal of Europium(III) from aqueous solutions. The study aims to give a comprehensive account of various parameters that affected the ELM formation and stability for increasing the removal of Europium(III). The organic membrane phase of ELM consists of Span 80 as a surfactant, Cyanex 302 as a carrier, kerosene as a diluent and sulfuric acid solution as an internal aqueous phase. At the optimum conditions, the main variables studied which influenced the ELM stability and extraction of Europium(III) were the concentration of surfactant (3%), carrier (0.3%), internal phase (0.5 N H₂SO₄), types of internal phase (H₂SO₄ sulfuric acid), diluent (Kerosene), stirring speed (200 rpm), and the effect of volume ratios of the internal phase to the organic phase 1:1 (A/O) and of the emulsion to the feed solution 20/200 (Vem/Vext). Under most favorable conditions, all the Eu(III) molecules presented in the feed phase were extracted within 30 min in a manner that makes more than 92% of the Eu(III) molecules extracted within the first 10 min. The findings revealed that ELM treatment process represents a very interesting advanced separation process for the removal of Eu(III) from aqueous solutions.

Keywords: Emulsion liquid membrane; Stability; Rare earth elements; Eu(III)

1. Introduction

Rare earths are a group of metals with neighboring properties including scandium, yttrium, and fifteen lanthanides [1]. In its elemental form, rare earths have a metallic appearance and are fairly soft, malleable and ductile. These elements are chemically quite reactive, especially at high temperatures or when finely divided. Rare earth elements (REEs) are mainly used in high technology even in new green technology products [1]. For the time being, people pay attention to rare earth metals which are applied in more and more developed technologies that allow new processes of production and impact our lives in a variety of ways. However, it's worth note that extreme extraction, resources waste of resources, smigling and environmental destruction are real problems that adversely affect the exploitation of rare earths.

Europium(III), which is one of the 15 lanthanides, is the most expensive and critical REEs [1,2] where it plays an important role in various fields for instance, Europium salts are used for newer phosphorescent paints and powders. In nuclear reactors, Europium(III) is used in control rods as a very good neutron absorber. For powerful street lighting [1], a little Europium(III) is added to mercury vapour lamps to give a more natural light. Else, Europium phosphors [1] are used in television tubes to give a bright red colour and as an activator for yttrium-based phosphors. Indeed, Europium(III) is an important raw material used in audio video electronic industry.

But nevertheless, Europium(III) is considered to be mildly toxic by ingestion in which body fluids can be contaminated and cause various diseases and accordingly results in excessive damage to the human body.

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A threshold value of 6 mg/L has been reported for Europium(III) in the literature [3]. However, as a result of their usage continuous exposure at its low concentrations (<6 mg/L) of Europium(III) can also cause serious adverse health effects because of its bioaccumulation along the food chains [4]. To solve this issue, it has therefore been essential to develop effective methods for the separation and recovery of Europium(III).

In the literature [5], several conventional methods, such as chemical precipitation, reverse osmosis, adsorption, ion exchange, and solvent extraction have been developed for these purposes, and have encountered various difficulties.

But, as a matter of fact, much attention has been attracted to the issue of liquid membrane (LM) techniques due to their specific characteristics. Indeed, the liquid membrane process has several characteristics as the simple operation with great efficiency and selectivity. For industrial applications, LM also used for the separation of ions in diluted solutions due to its efficiency [6]. In addition, one of the major advantages of membrane technology is their low energy consumption [7]; this technique seems to be useful in the hydrometallurgical treatment of rare earth ores [6].

Recently, a novel separation technique using supported liquid membranes (SLM) [5,8,9] or emulsion liquid membranes (ELM) [10–13], also named surfactant liquid membrane, has been noted as an efficient method for separating and concentrating the rare earth elements (REEs).

In this paper, we explore the possibility of studying one type of liquid membrane which is the emulsion liquid membrane (ELM). In fact, the technique of extraction by the emulsion liquid membrane (ELM) is a recent technique. This technology gained a big importance among other conventional separation methods and since its invention by Norman Li in 1968 for the separation of hydrocarbons [14]. The use of this method has attracted the attention of many researchers for the recovery of heavy metals: extraction of copper [15], cobalt and lead [16], uranium (iv) [17], cadmium [18], organic acids [19–22] and phenols : 4-nitrophenol [23], 4-chlorophenol [24] and phenol compounds [25–29].

ELM has many advantages such as; high selectivity, economical cost of operation [28], extraction along with purification (stripping) [23] and absence of saturation of the extractant and therefore their is a possibility of using much lower concentrations than in conventional liquid-liquid extraction.

The study of extraction by ELM is complicated because it depends on several factors [20]. ELM techniques compose of three steps; the first is the emulsion preparation in which the inner phase (the receiving phase) is emulsified at high speed using an emulsifier with an organic phase containing a surfactant (to stabilize the emulsion), a carrier and a diluent (to obtain very fine droplets [0.1–5 µm in diameter]). In a second step, the emulsion is dispersed in the form of globules [0.1 to 2 mm in diameter], within the feed phase (external phase) which contains the solute to be extracted, with a moderate speed. Besides, the transfer was from outside to inside (external feed phase to the internal stripping phase). In the third step, the emulsion and the continuous phase are separated in

a settling step which makes it possible to separate, on the one hand, the emulsion whose internal aqueous phase is loaded with solute and, on the other hand, the aqueous solution which constitutes the external phase; depleted of solute. The final step, however, consists in “breaking the emulsion” in order to recover on the one hand the internal aqueous phase that contains the concentrated solute and on the other hand the organic phase which is recycled to the emulsification stage.

The ELM process, used in this study for the elimination of Eu(III) has been schematically illustrated in Fig. 1.

A few works were done to study the transport of Eu(III) through an ELM from the prior literature [30,31]. However, enough works on the transport of Eu(III) through SLM were cited in [9,32–34].

The main novelty and importance of this work are concentrated on the evaluation of technical feasibility of ELM process and on the investigation of the influence of various parameters that can affect the ELM formation and its stability during the extraction of Eu(III) from aqueous solutions by the use of Cyanex 302 as a carrier.

2. Materials and methods

2.1. Materials

Analytical reagent grade chemicals were used throughout this study. A typical ELM composition and experimental conditions are:

Analytically Europium(III) supplied by Sigma was used in this study. Stock solutions of Europium(III) were prepared by dissolving appropriate amount of compound Europium Acetate in distilled water. In this work, Cyanex 302 was used as an extractant and procured from Sigma-Aldrich. Sorbitan Monooleate which is a product of Fluka, commercially known as Span 80, was used as surfactant (for stabilizing the emulsion). These reagents were properly diluted with kerosene (Flucka), hexane and heptane (VWR). The inorganic acids: Hydrochloric acid, Sulfuric acid, Nitric acid and all other chemicals were purchased from Sigma and used directly as received from the manufacturer. Arsenazo(III) [3,6-bis [(2-arsonophenyl)-azo]-4,5-dihydroxy-2,7-naphthalenedisulphonic acid] is used as complexant agent. The sensitivity of Arsenazo(III) is great for determination thorium, zirconium, uranium and rare-earth elements (REEs) [35].

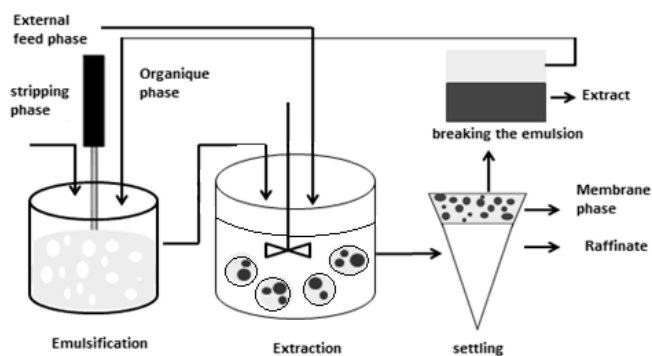


Fig. 1. The ELM process.

2.2. Membrane preparation

This membrane is made up of:

- An organic phase : used during the extraction which is made up of an extractant “Cyanex 302” and of a surfactant “Span80” solubilized in a diluent “Kerosene” under an agitation moderated using a magnetic bar.
- The aqueous internal phase: is an acid solution (sulfuric acid H_2SO_4).

In the experiments, the W/O emulsion was obtained by emulsifying a volume of the organic phase with a volume of the internal aqueous phase using the homogenizer (Ultra-Turrax IKA T18) for a fixed time in order to generate a stable emulsion. The volume ratio of the inner aqueous phase and the organic phase was varied from 1/2 to 2/1. The total volume of the emulsion produced is always kept constant and equal to 20 ml. After the addition of the internal aqueous phase to the beaker, the emulsifier head has been therefore immersed and accordingly a speed of about 20000 rpm has been exerted for various emulsification times (1–9 min).

For the preparation of water-in-oil (W/O/W) double emulsions, 20 ml of W/O emulsion is brought into contact with 200 ml of the external solution (Eu(III) solution). The W/O emulsion is dispersed in external phase using a mechanical stirrer. Additionally, samples are taken as a function of time in order to measure the decrease in the pollutant concentration within the external aqueous solution. However, the volume of the sample remains negligible compared to the total volume of the external phase.

2.3. Recommended procedure

For the spectrophotometric analysis of solutions, place an appropriate volume of treated sample (100 μ L) containing Eu(III) of aliquots into the external phase at different times; then, add a buffer solution (mixing of diluted hydrochloric acid and solution of sodium chloride at pH = 2.6) [36], and (100 μ L) 10^{-3} M of Arsenazo(III) solution. After that, measure the absorbance of this solution against the reagent blank at the wavelength ($\lambda_{max} = 653$ nm).

In order to select the optimal wavelength for analysing the given compound sample, the spectra that representing the absorbance values of the solution as a function of the wavelength is determined as can be seen from Fig. 2a shown below.

Obtain the europium quantity from a calibration curve, which has been prepared with known amounts (12–92 mg/L) of Eu(III). Note that the coefficient of determination R^2 was equal to 0.998 (Fig. 2b).

2.3. Membrane stability

To measure the rupture rate of the membrane, an emulsion was dispersed in distilled water free of Eu(III) and with a particular neutral pH. However, any change in the pH (The leakage of H^+ ions) of the distilled water may reflect the breakdown (rupture) of the emulsion due to the expulsion of H_2SO_4 from the internal phase to the external phase.

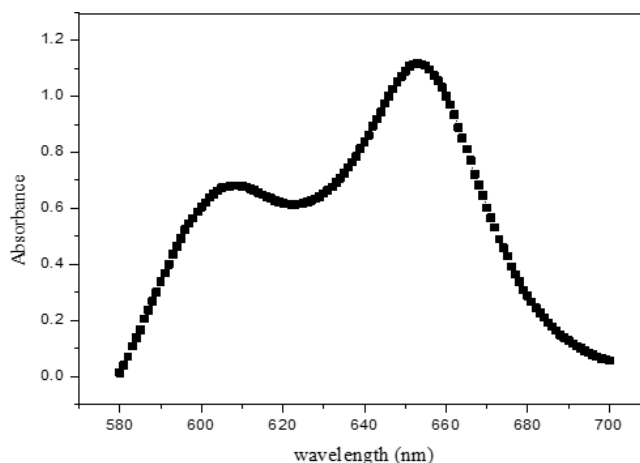


Fig. 2a. Absorption spectra of Eu(III)-Arsenazo(III) complex at pH 2.6 value of solution.

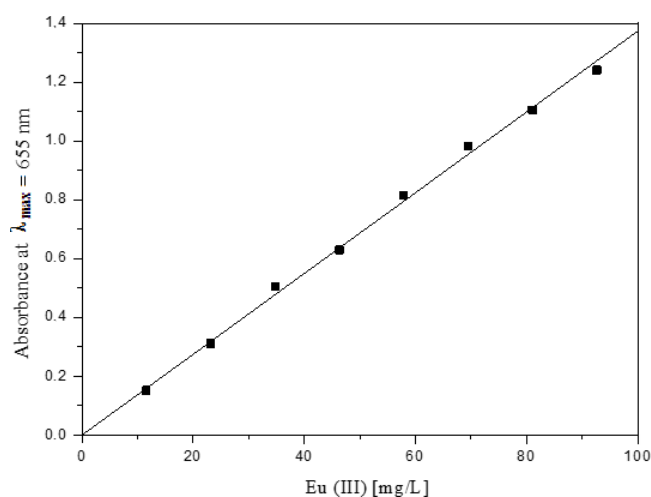


Fig. 2b. Absorbance of Eu(III)-Arsenazo(III) complex as a function of Europium mass concentration.

A tracer method is used to determine the stability of the liquid membrane, the percentage of emulsion breakage (ϵ) was calculated using the following equation:

$$\epsilon \% = \frac{V_s}{V_{int}} \times 100 \quad (1)$$

The emulsion breakage represents the ratio in percentage of the volume of internal phase leaked into the external phase by splitting (V_s) to the initial volume of the internal aqueous phase (V_{int}). The volume V_s is calculated by mass balance.

2.4. Extraction

The transport mechanism of Eu(III) by ELM using Cyanex 302: Bis (2, 4, 4 trimethyl) pentylthio phosphinic acid) as a carrier is shown in Fig. 3.

In this case, a reactive compound (Cyanex 302) is incorporated in the membrane phase; it is completely soluble in the membrane phase and completely insoluble in the adjacent phases (external feed phase and receiving

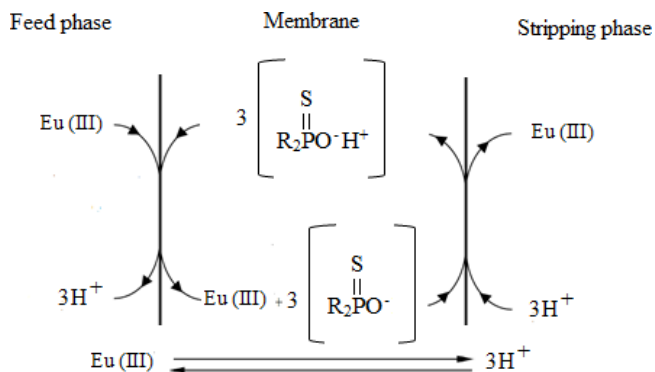


Fig. 3. Mechanism of the extraction of Eu(III) by emulsion liquid membrane.

phase). At the outer phase/membrane phase interface, Cyanex 302 forms selectively and reversibly with the solute (Eu(III)); a complex (Cyanex 302-Eu(III)) soluble, in the membrane (Fig. 3).

By taking advantage of the concentration gradient, the complex (Cyanex302- Eu(III)) diffuses through the membrane towards the membrane/internal phase/interface. At this interface, the complex (Cyanex302- Eu(III)) then reacts with the stripping agent (H₂SO₄) contained in the internal phase to form a complex with the transported solute (Eu(III)) which is more stable than the complex formed with the transporter (Cyanex 302). As a result of this reaction, the Cyanex 302-Eu(III) complex destruction is favored and the solute Eu(III) is irreversibly bound to this agent (H₂SO₄), while the carrier (Cyanex302) is regenerated and returned through the membrane to the first membrane/external phase/interface to transport again the remainder of the solute.

Extraction efficiency was calculated using the following equation:

$$\text{Extraction efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of Eu(III) in the external phase (mg/L) and C is the concentration of Eu(III) in the external phase at any time (mg/L).

3. Results and discussion

3.1. Membrane stability

The stability of the ELMs is very important and must be optimized before their use. Membrane break-up causes a decrease in the separation efficiency due to the leakage of the separated solute from the internal aqueous phase to the external aqueous phase [37]. In fact, a good stability according to the composition of the membrane has been reported in different studies [38,39].

In this study, the influence of surfactant concentration 1–9% (w/w); emulsification time 1–9 min; emulsification speed 11000–24000 rpm; and volume ratio of internal aqueous phase to organic phase 1/2–2/1 based on the stability of the prepared W/O emulsion were investigated. In addition,

experiments were conducted for the initial studies of the emulsion liquid membrane system by the use of the following experimental conditions — Internal phase concentration: 1 N H₂SO₄; stirring speed: 200 rpm; external phase (distilled water); volume ratio of emulsion to external phase: 20/200; and contact time: 30 min.

Unless otherwise indicated in this section, parameters and their associated levels listed in Table 1 are being used. The results show that breakage obtained is lower than 3% in almost all the experimental conditions.

For further studies that were conducted, the operational parameters used were identical to that used previously

Table 1
Emulsion breakage obtained in different experimental conditions

Parameter	Value	ε (%)
Emulsification time (min)	1	0.4
	3	0.29
	5	0.26
	7	0.34
	9	0.38
Surfactant (Span 80) concentration (% w/w)	1	0.33
	3	0.26
	5	0.22
	7	0.23
	9	0.15
Carrier (Cyanex 302) concentration (% w/w)	0.1	0.23
	0.3	0.26
	0.5	0.4
	0.7	0.42
	0.9	0.53
Volume ratio of internal phase to membrane phase (A/O)	1/2	0.33
	3/4	0.28
	1	0.26
	3/2	0.09
	2/1	0.06
Stirring speed (rpm)	100	0.15
	150	0.19
	200	0.26
	300	0.50
	400	1.28
Diluent	Hexane	1.4
	Kerosene	0.26
	Heptane	3.1
Emulsification speed (rpm)	11000	1.89
	15500	0.98
	20000	0.26
	24000	1.26

— surfactant concentration: 3% (w/w); stirring speed: 200 rpm; carrier concentration: 0.3%; external phase (distilled water); emulsification time: 5 min; and volume ratios of organic phase to internal phase: 1/1 and of emulsion to the external phase: 20/200.

As follows from Table 1 shown above, it was observed that:

- An increase in emulsification time up to 5 min increases the stability; the lower emulsion breakage was obtained for an emulsification time of 5 min, which was selected for further studies in this work;
- The stability of the W/O emulsion increases with the evolution of the Span 80 concentration in the organic phase. However, the considerable increase in the concentration of surfactant has two major drawbacks; A greater difficulty to break the emulsion at the end of the operation and a significant resistance to Europium transfer [40]. For this reason, we choose an optimal concentration of surfactant equal to 3%;
- Rupture increases with increasing concentration of Cyanex 302. The instability of emulsions results in the expulsion of the internal phase to the external phase (leakage) [41]. Therefore, it was decided to maintain 0.3% (w/w) of carrier concentration in all other experiments;
- The stability of the emulsion is conserved and improved with the increase of the volume ratio. For high volume ratios of the internal phase in the organic phase, the globules of the emulsion remain very large and can not disperse in the external phase. Else, the volume of the organic phase is insufficient to enclose all the dispersed phase [42]. Thus, the volume ratio of internal phase to membrane phase of 1/1 it was selected as optimum ratio in all other experiments;
- For high stirring speeds, the rupture percentage is important since it is affecting the stability of the W/O emulsions. Thus, the effect of stirring speed was studied in the range of 200 rpm and accordingly this value was selected as an optimum stirring speed;
- Kerosene gives the system a better stability compared to other hydrocarbon mixtures; heptane and hexane. In the present paper, a break of 0.26% for kerosene was obtained and hence, kerosene was chosen as a diluent for the preparation of stable W/O emulsions; and
- An insufficient emulsification time causes a relatively high percentage of breakage due to the large size of the droplets, which leads to coalescence. For an emulsification rate equal to 24000, the breakage increases again. It's worth noting that, the results obtained were relevant and in conformity with those achieved by Chaouchi et al. [23]; for an emulsification speed 20000 rpm, emulsion was stable. Thus, the used speed value not only considered as beneficial for the extraction of pollutants but as optimum in all other experiments as well.

3.2. Extraction

3.2.1. Effect of external phase concentration

Trivalent europium, Eu(III), can be found in wastewater at different concentrations. Extraction in the ELM process is directly related to the concentration gradient which is the driving force between the inner and outer phases. It is expected that the change in metal concentration in the outer phase may influence the percentage of mass transfer via the emulsion liquid membrane. The effect of the initial concentration of Eu(III) in the external phase was studied. The tests were performed for Eu(III) concentrations ranged from 2 to 231 mg/L. The results of these tests are shown in Fig. 4.

It is observed that, for concentrations between 2 and 92 mg/L, the extraction efficiency of Eu(III) increase with the decrease of the initial concentration of Eu(III) in the external phase [43]. In this concentration range, the efficiency is accurate due to an increase in the driving force (the concentration gradient between the external and internal phases) resulting in an improvement in the transfer of mass. In contrast, for Eu(III) concentrations above 92 mg/L, the extraction efficiency decreases. It is significant to note that this decrease is attributed to the saturation of the droplets of the inner phase by Eu(III) where the mass transfer resistance in the globules of the emulsion is important. Also, it is evident to note that the increase of the amount of time required Eu(III) extraction is associated with an increase in the solute concentration. Similar results have been reported in [45]. It is revealed that, for the concentration range studied (2–92 mg/L), the extraction efficiency reached a high degree ($\geq 99\%$).

3.2.2. Effect of internal phase concentration

The operating parameters used are identical to those used previously. Experiments were conducted for sulfuric

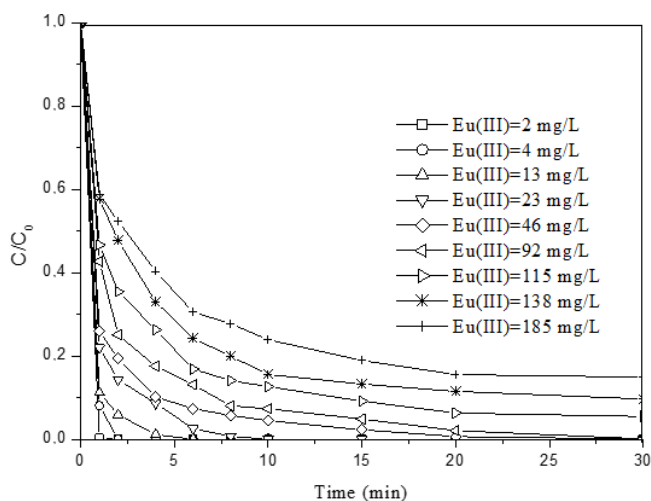


Fig. 4. Effect of Eu(III) concentration on the extraction efficiency. (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3% (w/w); volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: Kerosene).

acid concentrations ranging from 0.05 to 1 N in order to study the effect of the concentration in the inner phase on Eu(III) removal.

Fig. 5 shows the influence of the concentration of sulfuric acid in the internal phase on the Eu(III) extraction efficiency. It should be pointed out that the extraction increases with corresponding increases in the concentration in the internal phase from 0.05 to 0.5 N. Notwithstanding the fact that the efficiency of extraction above a concentration of 0.5 N of acid in the internal phase, decreases due to the instability of the emulsion.

Increasing the acid concentration in the internal phase between 0.1 and 0.5 N implies a decrease in the diameter of the globules of the emulsion. Moreover, the extraction efficiency increase in the range of H_2SO_4 concentration referred attributing that to the increase in the capacity of the receiving phase. The differences in chemical potential of the hydrogen ion between the two aqueous phases are the main driving force in the emulsion liquid membrane process.

When the concentration of H_2SO_4 is varied from 0.7 to 1 N, the extraction efficacy decreases due to both; the increase in viscosity and the reaction of H_2SO_4 with Span 80, leading to an instability of the emulsion. In fact, it is possible that this is due to the hydrolysis of Span 80, which induces a partial loss of its emulsifier properties as indicated by Chaouchi et al. in [23]. Hence, a concentration of 0.5 N in sulfuric acid was used in the internal phase in the rest of the study experiments.

3.2.3. Effect of type of internal phase

The influence of different types of acid in the internal phase on Eu(III) extraction was studied. However, choosing the appropriate treatment solution is one of the most important factors and the essential key factor in the

effectiveness of the ELM system. Indeed, several types of stripping reagent solutions can be used in an emulsified (E/H/E) system. Fig. 6 shows the effect of the type of acid in the internal phase on Eu(III) extraction.

It is noted that Eu(III) solution is more purified with sulfuric acid in the internal phase than with any other types of acids. This result affirms the initial choice of sulfuric acid as the receiving phase since the nature of sulfate ion makes the transfer very fast. These results, therefore, are in agreement with the findings obtained by Othman et al. in [46] who they have revealed that sulfuric acid was more preferable in making acidic thiourea solution than HCl because it makes the emulsion almost stable during the extraction operation of silver. For this reason, 0.5 N sulfuric acid was chosen as the best stripping agent.

3.2.4. Effect of surfactant concentration

The amount of surfactant in the liquid membrane has a decisive importance for any ELM system. Although it ensures the stability of the W/O emulsion during extraction, it also changes the viscosity of the emulsion and thus the resistance to transfer of mass. It acts as a protective barrier between the external phase and the internal phase, preventing emulsion leakage [23]. It should be, therefore, pointed out that low amounts of surfactant can make the emulsion fragile, notwithstanding the fact that an increase may conduce to a greater diffusion resistance. In this concern, five various concentrations of Span 80 were tested (1–9% w/w).

As shown in Fig. 7, the increasing concentration of Span 80 from 1 to 3% improves the stability of the emulsion and the percentage of Eu(III) extraction. This improvement is attributed to an increase in the thickness of the interfacial film between both; the external and the internal

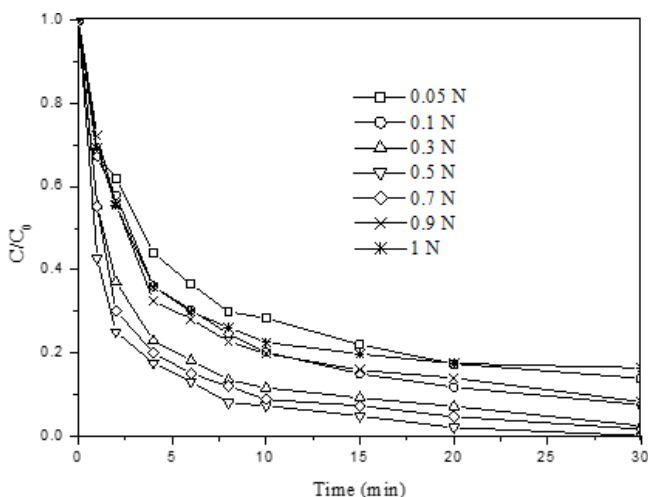


Fig. 5. Effect of internal phase concentration on the extraction of Eu(III) by ELM (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3% (w/w); volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

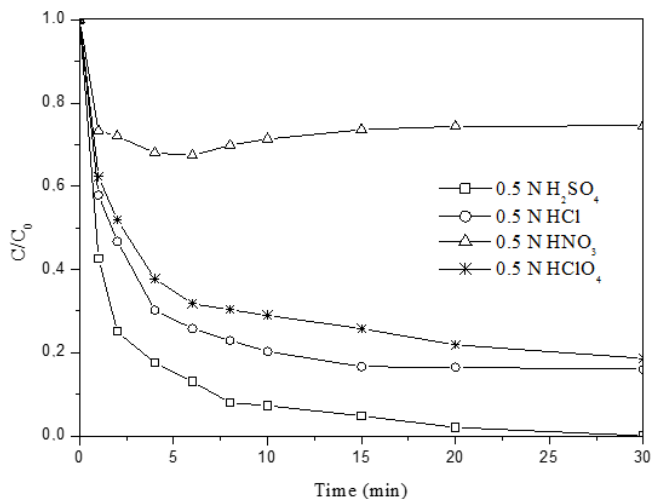


Fig. 6. Effect of acid type in external phase on the extraction of Eu(III) by ELM (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3% (w/w); volume ratio of W/O emulsion to external phase: 20/200; diluent: kerosene).

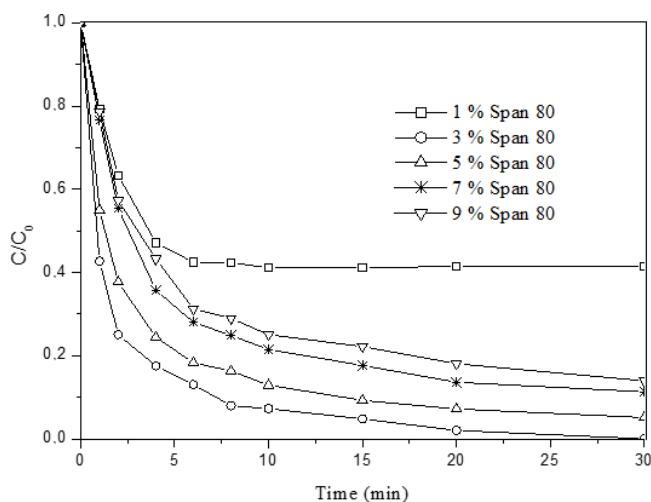


Fig. 7. Effect of surfactant concentration on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III)) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; carrier concentration: 0.3% (w/w); stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

aqueous phases which therefore leads to an increase in the size of the globules. In addition, the extraction efficiency decreases for concentrations above 3%. Further, the excess of surfactant (5–9%) tends to decrease the transfer rate on the one hand and increase the viscosity and thickness of the liquid membrane on the other hand, which will in turn result in an augmentation of mass-transfer resistance of Eu(III) molecules to internal phase as reported by Bourenane et al. [16], Sabry et al. [47], Juang et al. [48] and Li et al. [49].

A surfactant concentration of 3% (w/w) caused the highest removal efficiency of Eu(III) (99.7%) and the lowest emulsion breakage (Table 1). It is recognized that the mass percentage of the surfactant in the liquid membrane must be maintained at a level of 3% in all the other experiments.

3.2.5. Effect of carrier concentration

Several studies often use organophosphorus compounds to separate actinides and lanthanides [50–52].

To study the effect of carrier concentration, Eu(III) ion was extracted using various concentrations of Cyanex 302. The Cyanex 302 concentrations were varied from 0.05–0.9% (w/w). The results obtained are shown in Fig. 8.

Increasing the amount of Cyanex 302 to 0.3% by weight in the organic phase improves the Eu(III) transport, where the extraction capacity increases. The extractant forms a complex with Eu(III) at the interface between the feed phase and the membrane. The concentration gradient of the Cyanex 302–Eu(III) complex increases the solute transfer flux across the membrane and therefore, the extraction efficiency. Beyond this extractant concentration, the extraction yielded decreases due to a decrease in the stripping reaction rate. The Eu(III) remains unstripped in the complex form in membrane phase and thereby significantly reducing the final recovery. Similar results have been reported by Davoodi [53].

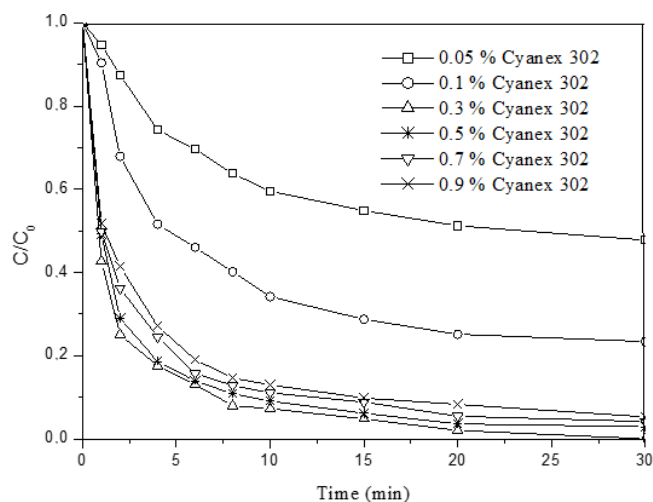


Fig. 8. Effect of carrier concentration on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III)) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; Span 80 concentration: 3% (w/w); stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

In addition, the higher concentrations of the carrier affect the stability of the liquid membrane and the emulsion becomes viscous on account of the opposite behaviour of surfactants and carriers as well as their interfacial properties as referred to by Sabry et al. and Bourenane [16,47]. Furthermore, higher concentrations of the carrier promote the membrane swelling and thereby, diluting the stripping phase.

It is evident from Fig. 8 that the carrier concentration has a significant effect on the recovery of Eu(III) from aqueous solution. Thus, the optimal carrier concentration has proven to be in the range of 0.3% in order to achieve a complete removal of Eu(III).

3.2.6. Effect of stirring speed

In the ELM separation process, stirring speed is an essential and beneficial factor for extraction. In order to study the influence of the stirring rate on Eu(III) extraction, experiments were carried out under the optimized operating conditions. The effect of agitation rate on Eu(III) extraction is shown in Fig. 9.

By increasing the stirring speed from 100 to 200 rpm, the extraction efficiency is significantly improved due to the increase in the mass transfer coefficient across the external interface. For low stirring speed, the size of the globules is large and, therefore, the interfacial contact area and the mass transfer have been decreased. However, increasing stirring speed above a critical value (200 rpm) not only decreases slightly the extraction efficiency but also affects the stability of the emulsion which may lead to an instability and thus, causes a breakage in the emulsion droplet as it is illustrated by Davoodi et al. in [53].

By increasing the agitation speed, the shear force which acts on the emulsion globules is increased in which it makes the globules smaller and accordingly increases the area for mass transfer. Else, the excessive stirring speed over an

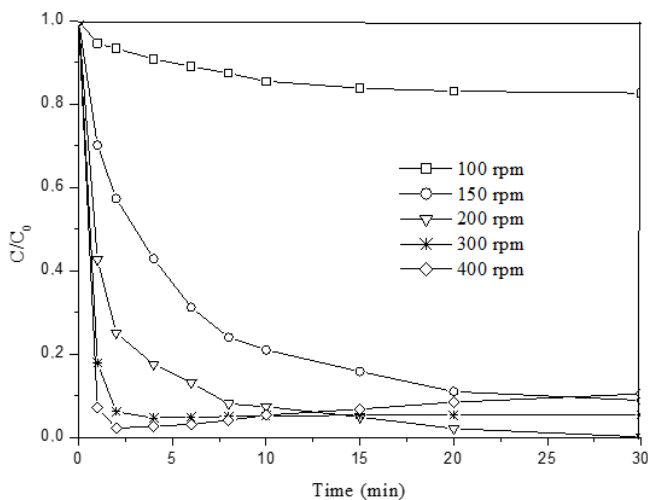


Fig. 9. Effect of stirring speed on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; Span 80 concentration: 3% (w/w); carrier concentration: 0.3%; volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

optimum value leads to the membrane phase destruction due to the presence of high turbulence at the interfaces and the consequent partial separations of membrane phase. Similar results have been also reported by P. Venkateswarin through working on copper in [54].

Although some researchers [38,55] have reported that osmotic swelling of the membrane increases with the increasing agitation speed this behavior was not observed, however, in our study. Thus, 200 rpm was chosen as the

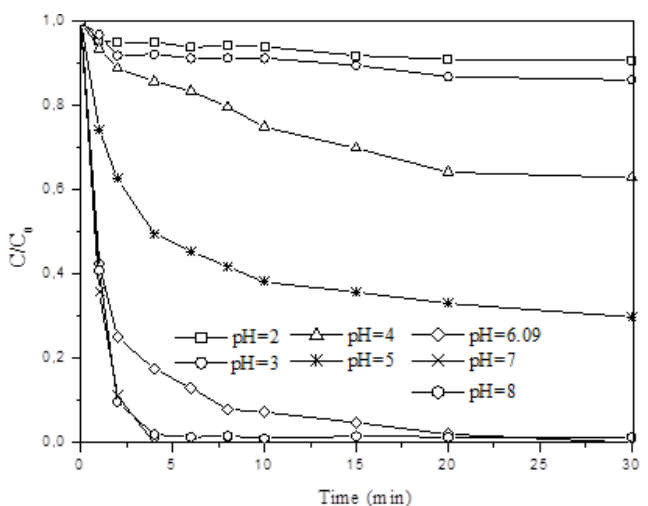


Fig. 10. Influence of feed phase pH on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed 200 rpm; Span 80 concentration 3% (w/w); carrier concentration 0.3%; volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4) 0.5 N; diluent: kerosene).

optimal stirring speed because it leads to a good emulsion stability and an excellent Eu(III) extraction efficiency.

3.2.7. Effect of initial pH of the feed phase

pH is an important parameter in the transport of ions by ELM. When Eu(III) ions are carried from the feed phase to the stripping phase, protons are transported in the other direction (Fig. 3) where the gradient in proton concentration is considered the driving force for the Eu(III) transport. The dependence of the percentage of Eu(III) extraction on the feed phase pH is shown in Fig. 10.

As observed, the percentage of extraction increases with the increasing pH value of the feed phase. When H^+ concentration decreases, the more metal ions are extracted (no competition of H^+ ions with the solute). However, this phenomenon is supported by Zaheri et al. [34] who found that the increase of pH is significantly affect on extraction efficiency. Subsequently, for pH values greater than 6.09, the formation of a white precipitate which is due to the Europium hydroxide form ($Eu(OH)_3$) is observed. Thus, we concluded that the best transport is obtained at natural pH of Eu(III) solution (pH = 6.09).

3.2.8. Effect of volume ratio of internal phase to membrane phase

ELM processes allow very high mass transfer rates due to the large surface area within the emulsion globules and internal droplets [38].

The variation in the volume of the internal phase affects the properties of the emulsion and the extraction efficiency. This ratio must be chosen correctly in order to obtain a stable and well-dispersed emulsion in the external aqueous phase. To investigate the effect of the volume ratio of internal phase to membrane phase on the extraction of Eu(III) by ELM, this ratio was varied at 1/2, 3/4, 1/1, 3/2, and 2/1. The obtained results are shown in Fig. 11.

It is observed that the removal efficiency of lead increases from 95.6% to 99.9% as A/O ratio increases till 1. This is related to the fact that the viscosity of the emulsion sharply increases at A/O ratio less than 1 as shown in Fig. 13, which prevents Eu(III) ions permeation through the membrane as reported by Sabry et al. [47].

For volume ratios higher than 1, an increase in the volume of the internal aqueous phase reduces the extraction efficiency due to the increase in the viscosity of the emulsion and the diameter of the globules. Besides, an increase in the size of the globules reduces the interfacial area of mass transfer and thus reduces the overall efficiency of extraction. Additionally, Djenouhat et al. [42] showed that for $A/O > 1$ the volume of organic phase was not enough for surrounding all the internal aqueous phase and the dispersion of the W/O emulsion was more difficult. A volume ratio of the inner aqueous phase on the membrane phase of 1 was selected as the best volume ratio.

3.2.9. Effect of treatment ratio

The treatment ratio defined as the volume ratio of the external phase to the emulsion plays a major role in deter-

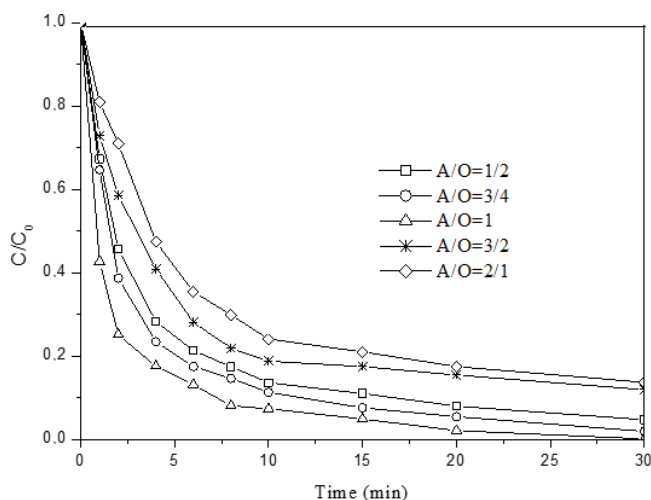


Fig. 11. Effect of volume ratio of internal phase to organic phase on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—emulsion volume: 20 mL; external phase (Eu(III) solution) volume: 200 mL; emulsification time: 5 min; Span 80 concentration: 3% (w/w); carrier concentration: 0.3%; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/200; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

mining the efficiency of ELM process [53]. Experiments were carried out to study the effect of the treatment volume ratio (emulsion/external) for the following values: 5/200; 10/200; 20/200; 40/200 and 60/200. The results of Eu(III) extraction kinetics are shown in Fig. 12.

Results obtained show that the increase in the treatment ratio improves the efficiency of the extraction and its rate which is decreased with a lower ratio as reported

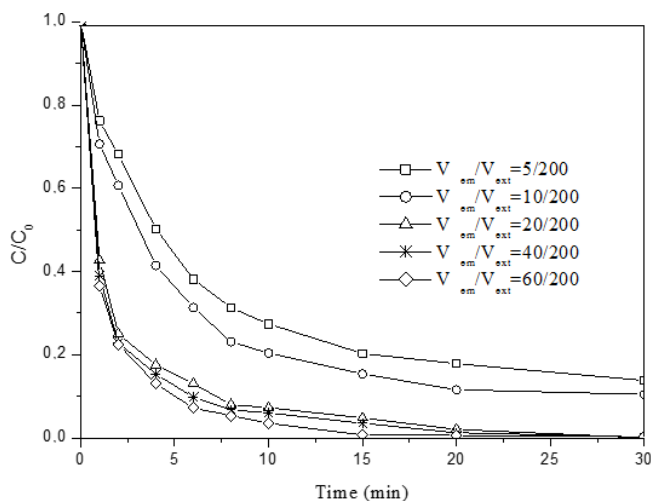


Fig. 12. Effect of volume ratio of emulsion to external phase on the extraction of Eu(III) by ELM (92 mg/L) by ELM (experimental conditions—external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3%; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

by Zhang et al. [12]. The present findings further explicate that the more volume of emulsion increases, the more the quantity of carrier is big which can contribute to the progress of the transport of Eu(III). In addition, a big volume of emulsion favors the formation of a huge number of globules, by offering a large exchange surface, and hence a better transfer. As a result, in order to ensure an excellent dispersion and distribution of the emulsion in the external phase, a treatment ratio of 20/200 was chosen as the best treatment ratio.

3.2.10. Effect of emulsification time

The emulsification time influences the formation of the segregation droplets dispersed in the emulsion globule, during the preparation of the emulsified phase. For this, experiments were carried out under the same operating conditions as previously reported by utilising the 0.5 N sulfuric acid solution in the internal phase, and varying the emulsification time from 1 to 9 min. The results obtained are shown in Fig. 13.

This figure shows that kinetics and extraction efficiency increase with increasing emulsification time up to 5 min, and they decrease beyond the time limit. Since the low emulsification times (<5 min), the formation of large droplets will take place, which will promote their coagulation (coalescence) and thus destabilising the emulsion. In the contrary, the high duration of emulsification leads to high shear, which affects the stability of the membrane and decreases the extraction efficiency. These results, in fact are in agreement with the findings obtained by Dâas et al. [37].

An emulsification time equal to 5 min gives better kinetics and extraction efficiency. For this reason, we chose this time limit in the rest of the study experiments.

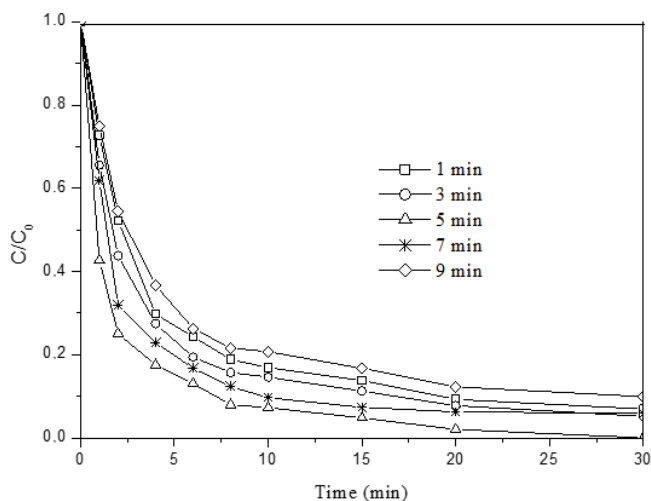


Fig. 13. Effect of emulsification time on the extraction of Eu(III) by ELM (92 mg/L) by ELM (experimental conditions—external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; volume ratio of W/O emulsion to external phase: 20/200; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3%; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

3.2.11. Extraction of Eu(III) from real waters

The removal efficiency of Eu(III) was examined by dissolving the pollutant in a natural mineral water, seawater and distilled water. Experiments were carried out using an initial Eu(III) concentration of 92 mg/L and shown in Fig. 14.

The efficiency of Eu(III) elimination in distilled water is high compared to those obtained in natural water and seawater. The concentration of Eu(III) in the phase treated is reduced from 92 to 0 mg/L in distilled water, 4.34 mg/L in natural mineral water and 7.58 mg/L in seawater. A 99.9% yield is recorded in distilled water, 95.3% in mineral water and 91.81% in sea water. Thus, ELM treatment process represents an efficient advanced separation technique for the removal of Eu(III) from real water.

3.2.12. Effect of diluent type

The viscosity and density of the diluents are the main parameters that ensure the thickness and permeability of the membrane for the metal ion.

Experiments were conducted under the same conditions as mentioned previously, by taking into account the optimized parameters. The extraction of Eu(III) was studied using different solvents dissolved with Cyanex 302 as a carrier: hexane, kerosene, and heptane.

Fig. 15 shows the effect of diluents on the extraction of the Eu(III) by ELM. The extraction performance of Eu(III) decreased according to the following order: kerosene > heptane > hexane.

This Figure shows that kerosene is better than other diluents, taking into account the stability of the emulsion. Kerosene with high viscosity organic phase produces higher emulsion stability which allows better extraction performance. A similar observations are also reported by

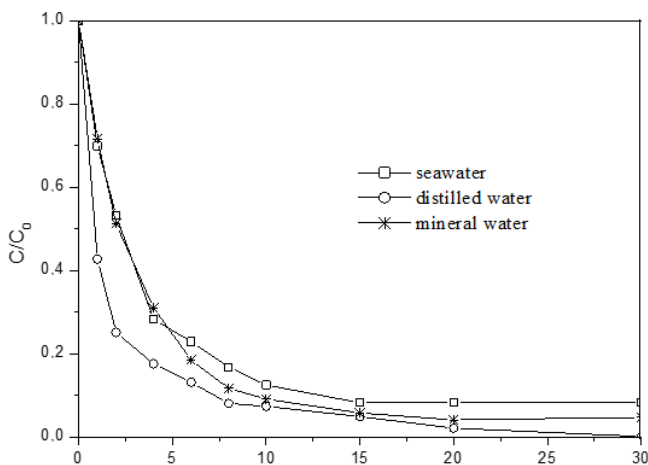


Fig. 14. Effect of real waters on the extraction of Eu(III) (92 mg/L) by ELM (experimental conditions—external phase (Eu(III) solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; volume ratio of W/O emulsion to external phase: 20/200; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3%; internal phase concentration (H_2SO_4): 0.5 N; diluent: kerosene).

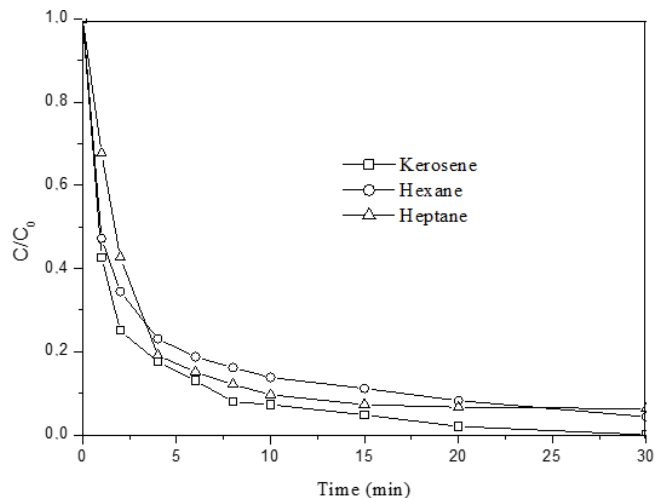


Fig. 15. Effect of diluent type on the extraction of Eu^{3+} (92 mg/L) by ELM (experimental conditions—external phase (Eu^{3+} solution) volume: 200 mL; volume ratio of internal phase to organic phase: 1/1; volume ratio of W/O emulsion to external phase: 20/200; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); carrier concentration: 0.3%; internal phase concentration (H_2SO_4): 0.5 N).

Othman et al. [46]. Thus, kerosene was chosen as a diluent for further study.

4. Conclusion

Extraction processes using emulsion liquid membrane (ELM) have received major attention due to their potential as an effective and advanced technique for the treatment of industrial liquid wastes. However, the membrane must be very stable to successfully apply ELM on an industrial scale. An emulsion organophosphorus liquid membrane was prepared using Cyanex 302 as organophosphorus extractant and Span 80 as a non-ionic surfactant for the Eu(III) recovery, from sulfat medium. The best parameters values for meta-stable W/O emulsion and higher extraction efficiency, such as the concentrations of surfactant, carrier, and stripping solution, the natures of diluents and stripping solution, stirring speed, and volume ratios of internal phase to organic phase and of W/O emulsion to external phase, were selected.

Summing up the results, it can be concluded that the extraction of Eu(III) by ELM showed that the elimination efficiency is very rapid because the extraction efficiency is 74.9% after 2 min of contact time. Most of the Eu(III) cations are eliminated in the first 10 min (92.68%). The results demonstrated that the ELM with Cyanex 302 as a carrier had a high selectivity for Eu(III).

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Symbols

Eu(III)	—	Europium(III)
AETs	—	Advanced extraction techniques
REEs	—	Rare earths elements
ELM	—	Emulsion liquid membrane
SLM	—	Supported liquid membranes
ε	—	Percentage of emulsion breakage
V_s	—	Percentage of the volume of internal phase leaked into the external phase by splitting.
V_{int}	—	The initial volume of the internal aqueous phase.
C_0	—	The initial concentration of Eu(III) in the external phase (mg/L).
C	—	The concentration of Eu(III) in the external phase at any time (mg/L).
W/O	—	Water/Oil.
A/O	—	Volume ratio of internal phase to membrane phase.
V_{em}/V_{ext}	—	The treatment volume ratio (emulsion / external).

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