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Extraction of cerium(III) ions from dilute aqueous solutions by emulsion liquid membrane: effects of operating conditions, salts and natural water matrices

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ABSTRACT

This work communicates an exploration for investigating the extraction of cerium(III) ions from dilute aqueous feed solutions by emulsion liquid membrane (ELM). The ELM contains di(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant, Span 80 as surfactant and kerosene as diluent. Nitric acid was used as internal stripping aqueous phase. Influence of operating parameters that affect the permeation of Ce(III) such as surfactant concentration, carrier concentration, external phase pH, internal phase concentration, type of internal phase, stirring speed, volume ratio of internal phase to membrane phase, treatment ratio, diluent type and Ce(III) concentration was examined. Additionally, the effect of salts (Na_2SO_4 and NaCl) concentration on the extraction of Ce(III) was studied. The obtained results show that it was possible to completely extract the Ce(III) ions from the external feed solution under the most favorable conditions. Best experimental parameters for higher extraction efficiency are: emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; surfactant concentration: 3% (w/w); D2EHPA concentration: 0.4% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of water-in-oil emulsion to external phase: 20/250; internal stripping phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene. Both the rate and efficiency of Ce(III) extraction were not meaningfully affected by the augmentation in NaCl concentration in the interval 0.5–5 g L^{-1} and the increase of Na_2SO_4 concentration in the range 0.1–20 g L^{-1}. Besides, the effectiveness of the ELM method to remove Ce(III) from real environmental matrices such as natural mineral water (Zamzam) and seawater was proven. ELM process is a promising alternative to conventional methods and should increase awareness of the potential for recovery of Ce(III) ions from dilute aqueous solutions.

Keywords: Extraction; Cerium; Emulsion liquid membrane; Operating parameters; Salts; Natural water matrices

1. Introduction

Rare earth elements (REE) are of increasing economic importance owing to their unique physical and chemical properties they were widely used in a growing number of applications and had become indispensable for a large variety of emerging technologies [1–5]. Additionally, they are used in many fields such as chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high-temperature superconductors, secondary batteries and catalysis, etc. [4–6]. REEs are mainly composed of 17 elements subdivided into two groups: light and

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heavy REEs [4]. Among the REEs, cerium is of commercial interest. The importance of cerium has intensely increased because it is most commonly used in strategic sectors such as rechargeable batteries, metal alloys, glass-fiber, glass polishing powders, fluorescent powders, permanent magnets, catalysts, pigments, solar panels, light-emitting diodes and biomedical applications [7–9].

Numerous processes are used to recover Ce(III) from aqueous media including chemical precipitation, adsorption, solvent extraction and ion exchange [7–9]. Conventional solvent extraction is usually used for the separation and concentration of Ce(III) [5]. However, solvent extraction processes are difficult for the separation and purification of Ce(III) at very low concentrations because of the low driving force, a large inventory of extractants, third phase formation, a large amount of solvent requirement, phase entrainment and a large number of extraction steps to obtain a purified product. In recent years, liquid membranes are gaining importance and are emerging as the most attractive substitutes for the solvent extraction process that combines the characteristics of solvent extraction with membrane separation. In particular, emulsion liquid membrane (ELM) is an excellent system for the extraction of Ce(III) at a low concentration from aqueous solutions.

ELM systems are those including a selective liquid membrane phase in which simultaneous extraction/stripping occurs. An ELM can be considered as a double emulsion consisting of three phases: the external, membrane and internal phases. Separation is achieved by permeation of solute through this liquid phase from a feed external phase to a receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. An aqueous internal (stripping) phase is stabilized by a surfactant and dispersed, using high-speed agitation or ultrasound, as very fine droplets inside a membrane (organic) phase [10]. The resulting liquid membrane, or water-in-oil (W/O) emulsion, is then dispersed as emulsion globules in the external feed phase (a second aqueous phase) with constant agitation. Target solute in the external feed phase is transferred across the membrane phase into the internal aqueous phase during an extraction process. In this water-in-oil-in-water (W/O/W) ELM, the organic phase serves a dual purpose of permitting selective transfer of one or more components through it from external phase to internal droplets and vice versa and functions as a barrier by preventing mixing of external and internal phases [11].

Though some works have been conducted on the separation of Ce(III) ions from aqueous solutions by liquid membranes [12–16], comprehensive studies on the influence of process conditions are yet to be carried out. However, to the best of our knowledge, no work has been reported in the literature on the removal of Ce(III) by ELM from real water matrices. Therefore, the main aim of the present work concerned the pertraction of Ce(III) ions from aqueous solutions by ELM using di(2-ethylhexyl)phosphoric acid as extractant carrier, Span 80 as surfactant and kerosene as diluent. The effects of experimental parameters such as surfactant concentration, carrier concentration, external phase pH, internal phase concentration, type of internal phase, stirring speed, volume ratio of internal phase to membrane phase, treatment ratio, diluent type and solute concentration on the extraction of Ce(III) by ELM were examined. The influence of salts (NaCl and Na_2SO_4) on the pertraction of Ce(III) was evaluated. The extraction of cerium by ELM technique from real environmental matrices such as natural mineral water (Zamzam) and seawater was investigated.

2. Experimental

2.1. Materials

Cerium(III) nitrate stock solutions were prepared by dissolving cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) 99.9%, purchased from Sigma-Aldrich (USA), in ultrapure water. Ce(III) feed solutions from a known amount of Ce(III) stock solution was diluted with ultrapure water to a given concentration.

Di(2-ethylhexyl)phosphoric acid (D2EHPA) was an analytical grade product (Fluka, USA) and was employed as received. A non-ionic surfactant sorbitan monooleate, Span 80 (Sigma-Aldrich), was used as an emulsifier.

All other chemicals used in this work were of analytical grade and were purchased from Sigma-Aldrich.

2.2. Procedures

The extraction of Ce(III) using liquid emulsion membrane includes three steps: preparation of liquid membrane emulsion, extraction of Ce(III) from feed by contacting the emulsion and separation of liquid emulsion from the external phase by settling.

Internal aqueous solutions were prepared by taking the required amount of acid solution (HNO_3, H_2SO_4, HCl or $HClO_4$) in ultrapure water. The organic membrane phase was prepared by dissolving the appropriate amount of Span 80 as a surfactant and the adequate quantity of D2EHPA as an extractant in a diluent (kerosene, n-hexane, n-heptane, xylene or trichloroethylene) under gentle mixing by a magnetic stirrer.

The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a high-speed disperser (Ultra-Turrax IKA T18) for a fixed mixing time. The volume ratio of the internal aqueous phase to the organic phase was changed from 1/2 to 2/1.

A volume of the prepared W/O emulsion was added to a fixed volume of an external aqueous solution, containing Ce(III), in a cylindrical thermostated vessel that was attached to an overhead mechanical stirrer. The agitator used was a 45° pitch four blades down-pumping impeller (diameter 5 cm). The content of the vessel was stirred in order to disperse the W/O emulsion in the external phase to make the W/O/W double emulsions. The external phase solution was periodically sampled at various time intervals. The concentration of Ce(III) in the solutions was determined by the Arsenazo-III method [17] using a Biochrom WPA Lightwave II spectrophotometer. Each experiment was repeated at least two times in order to verify the reproducibility. The maximum standard deviation was 2%–3%.

The operating parameters influencing the extraction of Ce(III) such as surfactant concentration (1%–9% (w/w)), extractant concentration (0.2%–0.8% (w/w)), external phase pH (1–6), internal phase (HNO_3) concentration (0.05–0.8 N), type of internal phase (HNO_3, H_2SO_4, HCl or $HClO_4$), stirring speed (100–400 rpm), volume ratio of internal phase to membrane phase (1/2–2/1), treatment ratio (5/300–60/300), diluent type (kerosene, n-hexane, n-heptane, xylene or trichloroethylene), Ce(III) initial concentration (25–400 mg L^{-1}) and salts (Na_2SO_4 and NaCl) concentration in the feed phase (0.5–40 g L^{-1}) were examined.

3. Results and discussion

The permeation mechanism of Ce(III) by ELM can be divided into six stages:

- In an acidic medium (pH 1–6), Ce(III) is predominantly presented in the form of Ce^{3+};
- Ce^{3+} ion diffuses at the external interface between feed phase and membrane phase;
- A cation exchange mechanism occurred between the extractant (D2EHPA) and Ce^{3+} cation. The oxygen atom of the phosphoryl group P=O ensures coordination with the extracted ion by forming a chelating product. D2EHPA forms a dimmer according to the reaction:

$$2\mathrm{HR} \rightarrow (\mathrm{HR})_2 \tag{1}$$

Ce^{3+} cation reacts with the carrier $(HR)_2$, dimerized D2EHPA, at the external interface to form $Ce(HR_2)_3$ complex and hydrogen ion (H^+):

$$\mathrm{Ce}^{3+} + 3(\mathrm{HR})_2 \leftrightarrow \mathrm{Ce}(\mathrm{HR}_2)_3 + 3\mathrm{H}^+ \tag{2}$$

- The $Ce(HR_2)_3$ complex then diffuses through the membrane phase to the internal interface;
- Cerium cation is released from the $Ce(HR_2)_3$ complex into the internal phase by the stripping reaction at the internal interface and the carrier reacts with H^+ ion provided by nitric acid solution:

$$\mathrm{Ce}(\mathrm{HR}_2)_3 + 3\mathrm{HNO}_3 \rightarrow \mathrm{Ce}(\mathrm{NO}_3)_3 + 3(\mathrm{HR})_2 \tag{3}$$

- Ce^{3+} is, finally, in the receiving phase and the extractant is ready for another cycle.

3.1. Effect of surfactant concentration

In the ELM process, surfactant concentration plays a major role in the formation of stable emulsion and solute extraction [18]. Too little surfactant renders the membrane weak, while an increase in surfactant concentration leads to larger diffusional resistance. Therefore, the effect of Span 80 (surfactant) concentration in membrane phase on the extraction of Ce(III) from aqueous solution was studied in the concentration range of 1%–9% (w/w) and the obtained results are exhibited in Fig. 1. It was observed that the extraction of cerium increases by increasing the surfactant concentration to 3% (w/w) and gradually decreases thereafter. At low surfactant concentration (1% (w/w)), the removal efficiency was reduced because the coverage of the membrane interface is incomplete caused by insufficient surfactant. A surfactant concentration of 3% (w/w) caused complete

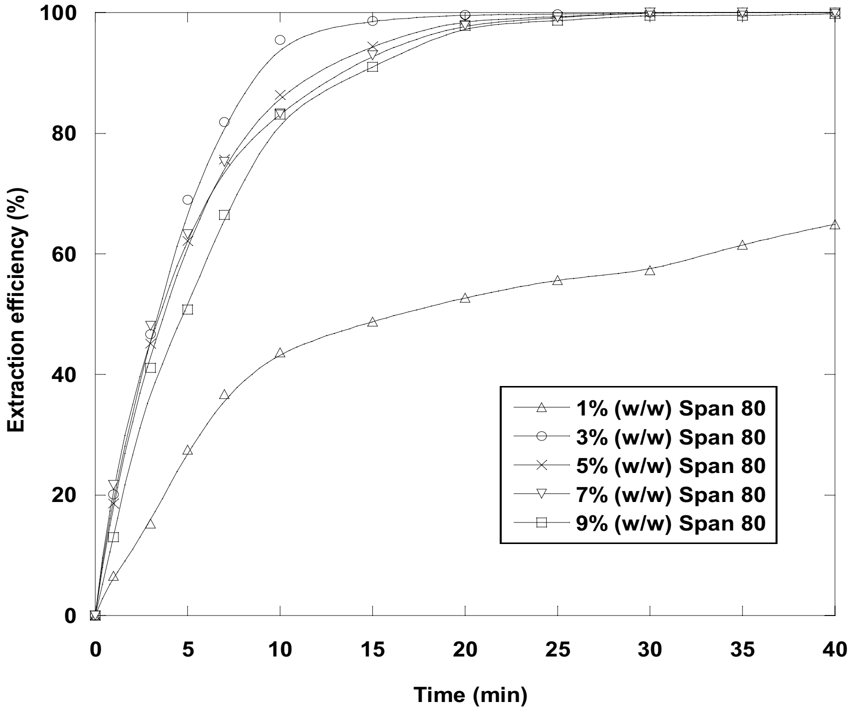

Fig. 1. Effect of surfactant concentration on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

extraction of Ce(III) from the external solution (extraction efficiency was 100%) after 20 min. The increment of surfactant concentration lowered the membrane's surface tension and yielded smaller globules, which led to a higher contact area [18,19]. An extraction percentage of 100% was obtained after 30 min for a Span 80 concentration of 5% (w/w) due to higher mass transfer resistance. An excessive amount of surfactant (beyond 5% (w/w)) slightly decreases the extraction extent. This was probably due to an increase in the liquid membrane thickness of the emulsion globule, which lead to an increase in interfacial viscosity and a decrease in movement of inner droplets within the emulsion globule [19–21]. Consequently, it was decided to maintain a 3% (w/w) surfactant concentration in all subsequent experiments.

3.2. Effect of carrier concentration

Carrier concentration in the membrane phase plays a significant role in the overall extraction behavior of ELM systems [22]. ELM extraction studies were conducted by preparing emulsions containing varying D2EHPA concentrations in the range of 0.2%–0.8% (w/w) and the results of Ce(III) extraction are shown in Fig. 2. It was observed that as the D2EHPA concentration increased from 0.2% to 0.4% (w/w), the extraction of Ce(III) increased from 76.8% to 100%. With the increase of carrier concentration from 0.4 to 0.8 (w/w), the extraction kinetics increased and the extraction percentage of Ce(III) remained equal to 100%. D2EHPA forms a complex with Ce(III) at the external interface between the feed and the membrane phases. The concentration gradient of the complex across the membrane enhances the flux of Ce(III) through the membrane. Consequently, the degree of extraction of Ce(III) increased with an increase in D2EHPA concentration. Thus, 0.4% (w/w) D2EHPA was considered as optimum concentration and used for further experimental purposes.

3.3. Effect of external phase pH

The pH of the feed phase is an important factor for consideration in the extraction of Ce(III) by ELM [23]. The influence of external solution pH was studied by varying the pH in the range of 1.0–6.0. It can be seen from Fig. 3 that the extraction efficiency is strongly dependent on the pH of the feed phase solution. The transport rate of Ce(III) increased when the pH in the external phase increased from 1.0 to 4.0, and a complete extraction percentage (100%) was observed at pH 3 after 35 min, at pH 4 after 20 min and at pH 5.1 (natural) after 20 min. However, with a feed solution pH of 6.0, the extraction rate declined slightly due to the equilibrium reaction at the feed-liquid membrane interface [1]. Thus, a feed solution pH of 5.1 (natural) as the optimum pH condition was chosen during the following experiments.

3.4. Effect of internal phase concentration

Internal phase concentration plays a vital role in the extraction of solute from feed solution to stripping phase through ELM [24]. Consequently, the influence of HNO_3 concentration in the stripping solution on the extraction

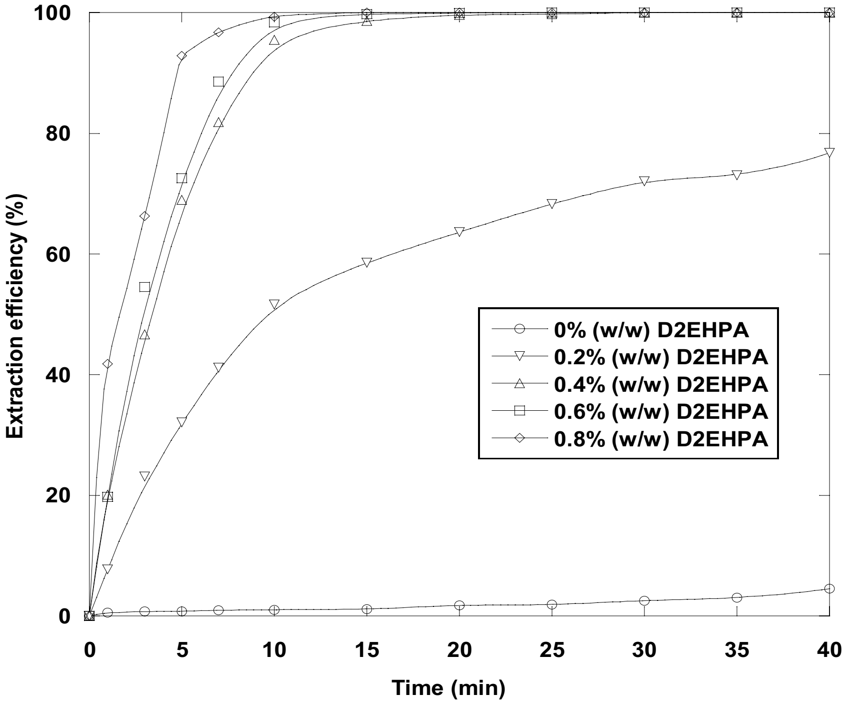

Fig. 2. Effect of carrier concentration on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

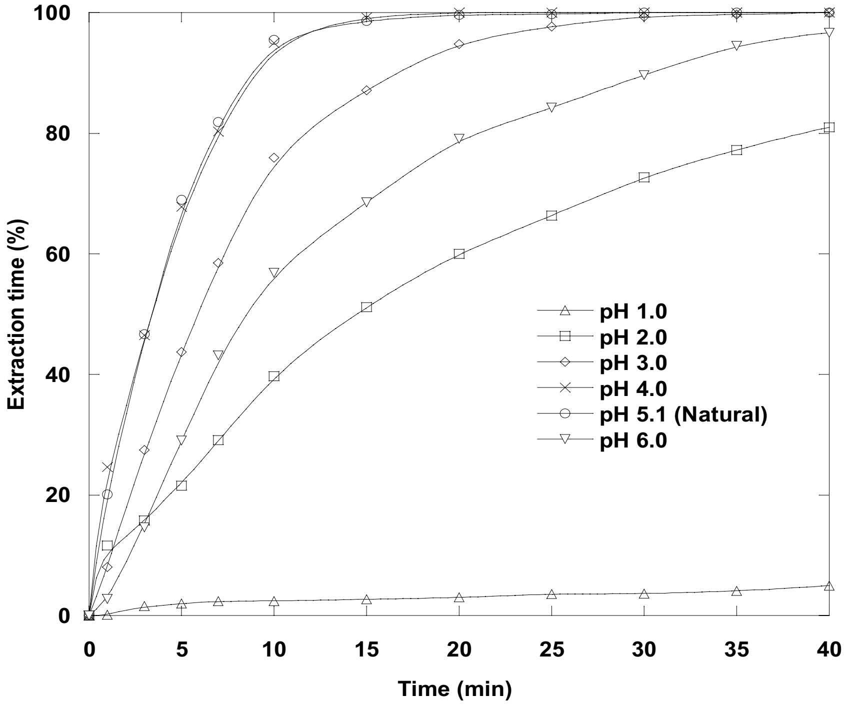

Fig. 3. Effect of external feed phase pH on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; diluent: kerosene).

of Ce(III) was investigated at different concentration levels from 0.05 to 0.8 N. The obtained results are shown in Fig. 4. The extraction rate increased with the increase of HNO_3 concentration in the internal phase up to 0.2 N. At lower HNO_3 concentration (below 0.2 N), there was insufficient reactant to remove the Ce(III) ions from the membrane phase resulting in lower extraction efficiency. The stripping process was slowed down and the saturation of Ce(III) on the membrane occurred. Maximum extraction and transport of Ce(III) were obtained in the concentration range of 0.2–0.8 N. This can be attributed to the more efficient stripping of the Ce(III) ion into the internal phase rendering the regeneration of the extractant molecules at a faster rate, which can lead to faster mass transfer reactions at the external phase – membrane interface [25]. It was expected that increasing the amount of HNO_3 in the internal stripping phase decreased the difference of densities and increased the emulsion viscosity. The increase of emulsion viscosity is reflected in an increase in the size of droplets [19,26]. Hence, the HNO_3 concentration of 0.2 N was chosen as the best internal phase concentration.

3.5. Effect of type of internal phase

The stripping reaction at the membrane-stripping solution interface plays a vital role in the extraction of solute from the feed solution to the stripping solution in the ELM process [27]. The selection of a suitable internal aqueous phase is considered to be one of the key factors for an effective ELM system. Though in the preliminary experiments HNO_3 solution was employed as the internal aqueous phase, other acids were also tested. The effects of 0.2 N of different stripping agents, namely HNO_3, H_2SO_4, HCl and $HClO_4$, in the internal phase on the extraction rate and efficiency of Ce(III) is shown in Fig. 5. It was observed that HNO_3 solution as internal aqueous phase gives higher extraction kinetics and efficiency of Ce(III) ions from feed phase. The nature of the stripping solution depends on the physicochemical properties of D2EHPA and the mode of extraction [28]. Therefore, the HNO_3 solution was selected as the best internal aqueous phase.

3.6. Effect of stirring speed

The stirring speed in the dispersion step is a paramount operating parameter in the ELM process [25]. Higher stirring rates lead to the formation of smaller-sized globules, thereby increasing the interfacial area between the continuous phase and the membrane phase, leading to an increase in the rates of mass transfer. Higher stirring speeds can also lead to more swelling and globule rupture. The effect of mixing speed on the extraction of Ce(III) was studied in the range of 100–400 rpm and the obtained results are shown in Fig. 6. For the lower stirring speed (100 rpm), the extraction rate and percentage were low because of the formation of larger emulsion globules involving a decrease of the area for mass transfer. Increasing the stirring speed from 100 to 200 rpm increased the rate of extraction. This might be because the size of droplets and the membrane thickness are both reduced by increasing the stirring speed.

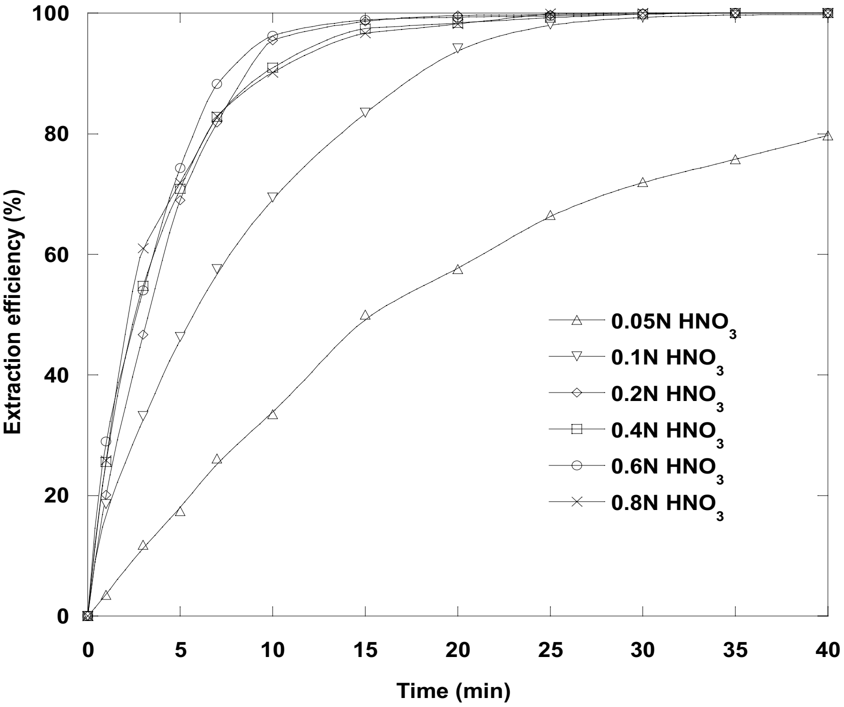

Fig. 4. Effect of internal phase concentration on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; pH of the feed phase: 5.1 (natural); diluent: kerosene).

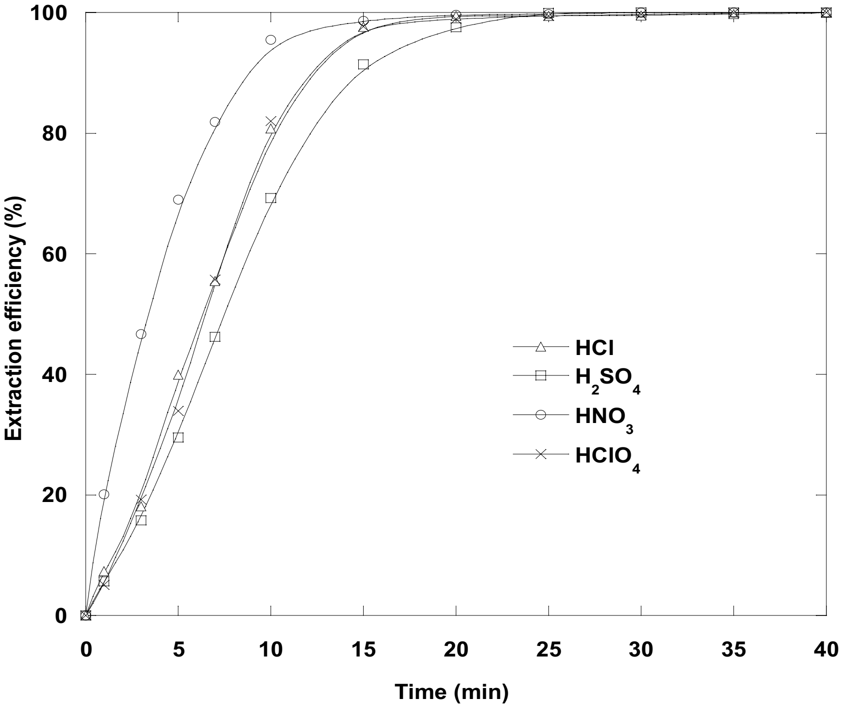

Fig. 5. Effect of internal phase type on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration: 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

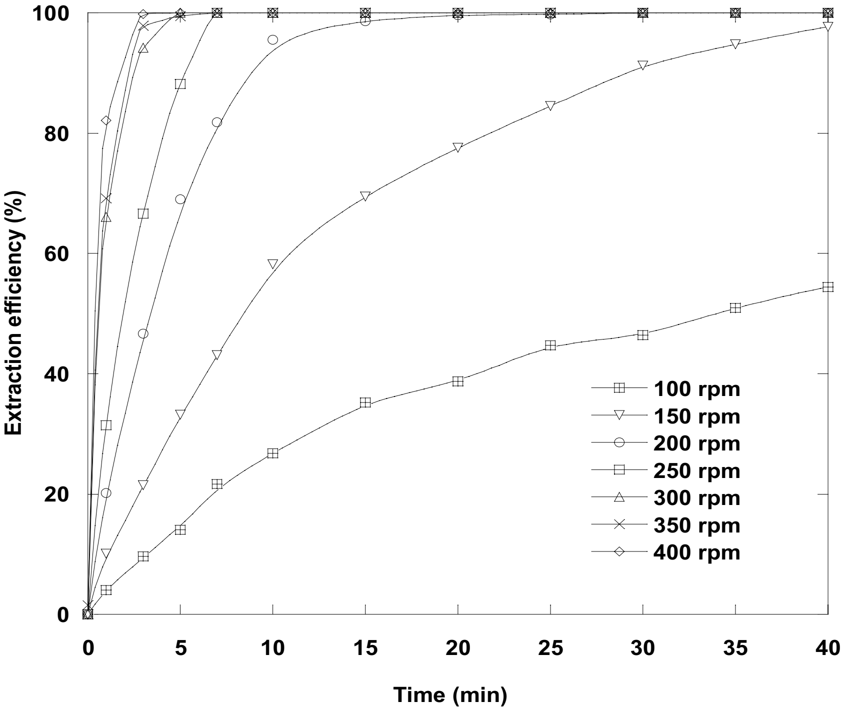

Fig. 6. Effect of stirring speed on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

Emulsion liquid droplets with smaller sizes led to better dispersion. At the same time, the more interfacial surface area is available between the external phase and the membrane phase, hence the extraction efficiency and transfer rate are higher. Further increase in speed of mixing from 200 to 400 rpm resulted in an improvement of both the rate of transport and the extent of extraction during the first few minutes. However, increasing the stirring speed above the critical value affects the stability of the emulsion and makes the emulsion unstable. Consequently, 200 rpm was recommended as the most appropriate stirring speed.

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

The volume ratio of the aqueous internal phase to the organic membrane phase plays a very important role in determining the effectiveness of the ELM system [11]. Change in the internal phase volume fraction not only leads to a change in the emulsion properties but also results in an increase in the capacity of the emulsion to extract the solute. The influence of volume ratios of the internal stripping solution to membrane phase in the range of 1/2–2/1, on the extraction of Ce(III), by maintaining membrane volume constant, is depicted in Fig. 7. It was observed that extraction efficiency increased with increasing of the phase ratio from 1/2 to 1/1. At a low volume ratio, membrane thickness and viscosity of the emulsion phase are high due to the relatively high organic content. In addition, a low volume ratio means less stripping agents are available for solute stripping. An increase in the internal phase volume fraction shifts the internal drop size distribution toward a larger size and decreases the thickness of the membrane phase resulting in enhanced mass transfer. This results in an increase in the capacity of the membrane for enhanced permeation of the solute. Beyond the ratio of 1/1, a further increase in the volume of the internal aqueous solution decreases both the rate and efficiency of extraction. This may be due to an increase in the emulsion viscosity and also an increase in the diameter of internal droplets [21]. The increase of droplets diameter decreases the interfacial contact area between the emulsion and feed solution and thereby decreases the extraction efficiency. Additionally, for higher volume ratios, the volume of membrane solution is not enough for enclosing all the stripping solutions [29]. Thus, the volume ratio of the internal aqueous phase to the membrane phase of 1/1 was selected as the best volume ratio.

3.8. Effect of treatment ratio

The treatment ratio, that is, the volume ratio of the emulsion phase to the feed aqueous phase is one of the important parameters on the extraction of Ce(III) ion and has great relevance in the actual application as effective extraction at a higher phase ratio means an increase in throughput. The results of Ce(III) extraction by ELM at varying phase ratios in the range of 5/250–60/250 are presented in Fig. 8. The increase of volume ratio of emulsion to the external aqueous solution resulted in an increase in both the rate and percentage of Ce(III) extraction. The phase

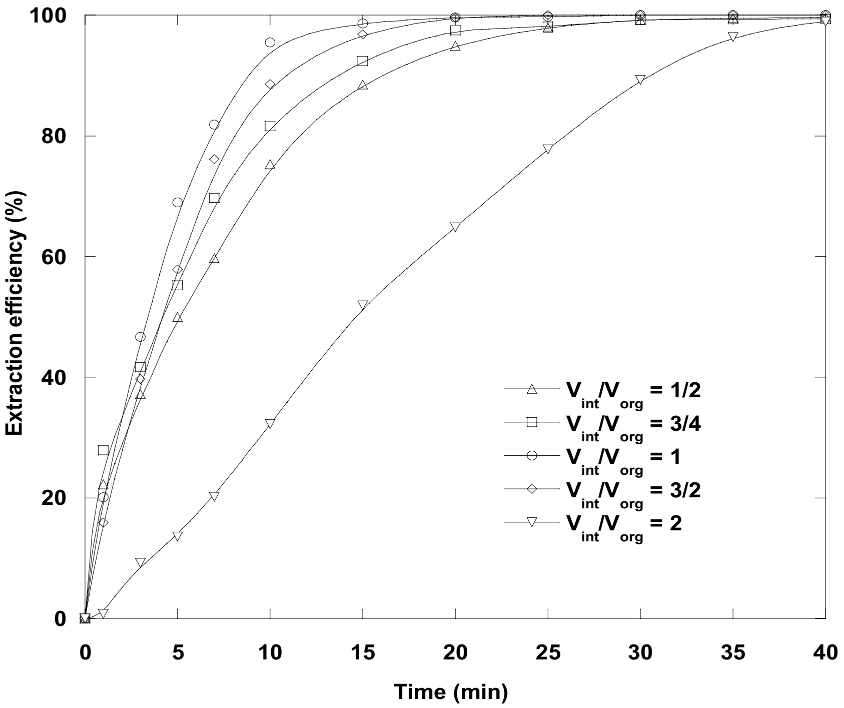

Fig. 7. Effect of volume ratio of internal phase to membrane phase on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

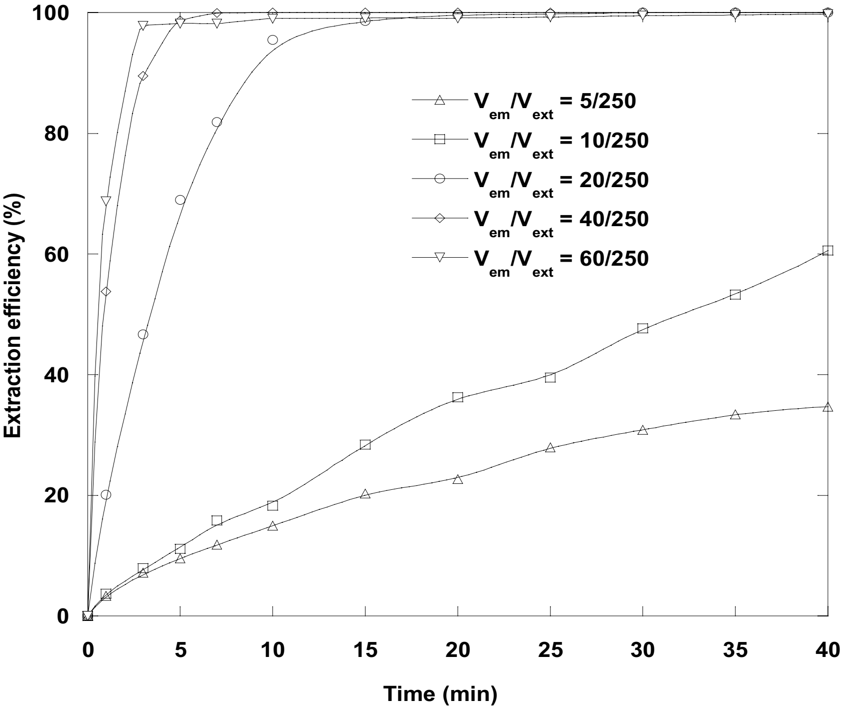

Fig. 8. Effect of treatment ratio on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 5–60 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

ratio controls the interfacial mass transfer across the emulsion liquid membrane and a decrease in the ratio improves the dispersion of emulsion molecules in the aqueous phase leads to an increase in the mass transfer through the interface. In general, a larger treatment ratio value interprets to a larger contact area of ELM with the aqueous solution to be treated, resulting in a greater mass transfer ratio, but at the expense of higher emulsion volume. The lower treatment ratio means less emulsion is required to extract the Ce(III) ion, which is desirable from a processing point of view to ensure maximum enrichment with respect to the feed aqueous phase. Consequently, the volume ratio of emulsion to an external feed solution of 20/250 was selected as the ideal treatment ratio.

3.9. Effect of diluent type

Various diluents were tested in the preparation of the emulsion liquid membrane, namely, kerosene, n-hexane, n-heptane, xylene and trichloroethylene. The mechanism of solute transfer through liquid membrane combines several mass transfer resistances, in which transfer of solute through the membrane phase might be considered as an important parameter. Therefore, the type of diluent may have a controlling effect on the efficiency of the ELM system. The permeation behavior of Ce(III) using kerosene, n-hexane, n-heptane, xylene and trichloroethylene as diluents is presented in Fig. 9. Extraction yields of Ce(III) from the aqueous feed phase are higher by using kerosene. Further extraction studies of Ce(III) were conducted using kerosene as a diluent in the present ELM system.

3.10. Effect of cerium initial concentration

As the results presented above dealt with external phase solutions containing 100 mg L^{-1} Ce(III), it was of interest to study the extraction of Ce(III) ion by changing its concentration in the external feed phase in the range of 20–400 mg L^{-1}. The obtained results are shown in Fig. 10. With the increase of initial concentration of Ce(III) in the external feed phase, the transport rate of Ce(III) decreased during the same time. This is because the number of D2EHPA molecules is definite through the membrane when the interface between the feed phase and the membrane phase is definite. That is to say, the number of Ce(III) ions transported is definite in this transport process. Complete extraction (100%) was obtained for Ce(III) concentrations in the range of 10–200 mg L^{-1}. This is because most of the solutes in the peripheral region of the emulsion globule were stripped by the internal aqueous phase droplets. The necessary time for extraction increases by increasing the external phase concentration. When the Ce(III) concentrations were 300 and 400 mg L^{-1}, the extraction efficiencies after 40 min were 74.2% and 49.8%, respectively. The saturation of the

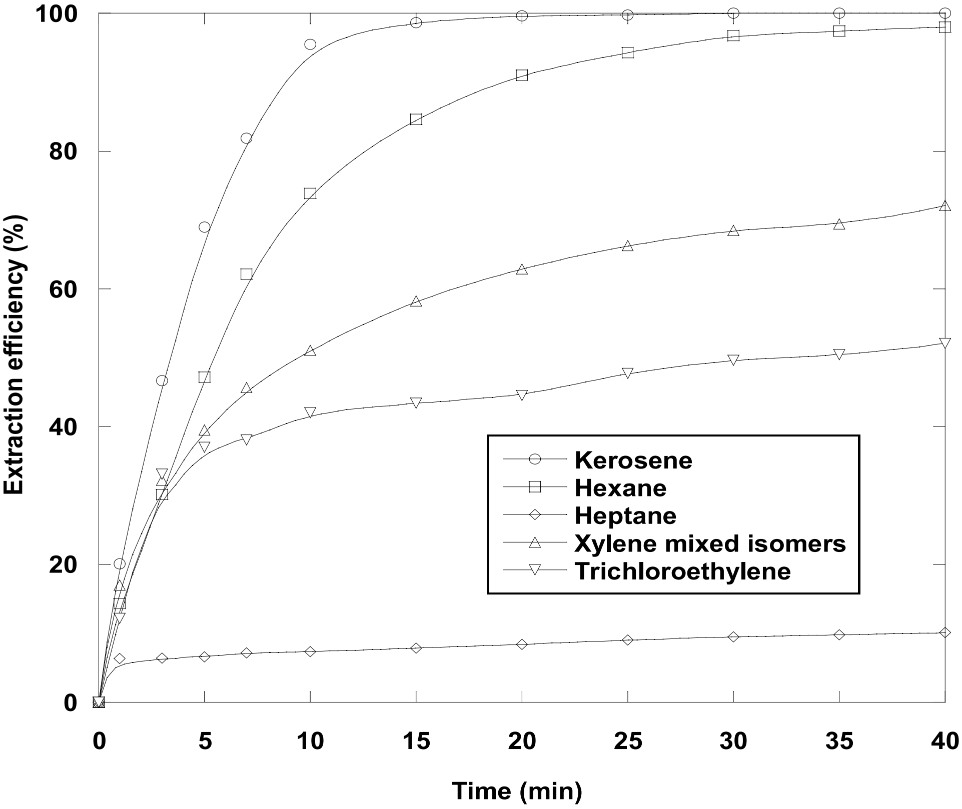

Fig. 9. Effect of diluent type on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural)).

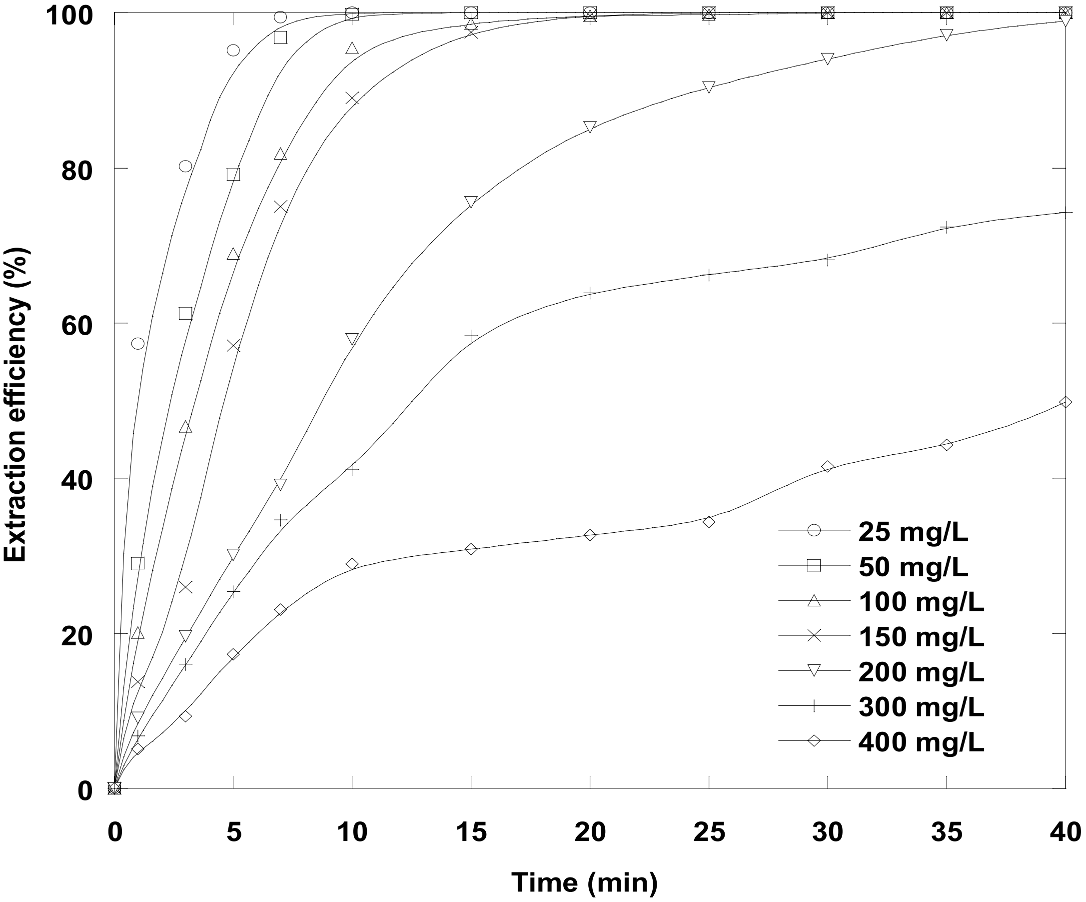

Fig. 10. Effect of cerium initial concentration on its extraction by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

internal droplets in the peripheral region of the emulsion is attained more rapidly for high Ce(III) concentrations in the external phase. When the solute concentration is high, the peripheral droplets are rapidly exhausted, requiring the solute to permeate deeper within the globule prior to being stripped. Therefore, an increase in initial Ce(III) concentration also corresponds to an increase in diffusional path lengths. This suggests that the mass transfer resistance in the emulsion globule becomes important at a higher concentration of Ce(III) complex, decreasing the rate of stripping and the extraction yield of Ce(III) [19].

3.11. Effect of salts

In order to investigate the influence of salts (NaCl and Na_2SO_4) on the extraction process, an aqueous external feed solution with different concentrations of salts was prepared and tested. The effect of salts in the external aqueous solution on the extraction kinetics of Ce(III) was analyzed over salts concentration in the range of 0.1–40 g L^{-1}. Fig. 11a and b illustrate the influence of NaCl and Na_2SO_4 concentration on the extraction of Ce(III) by ELM. Both the rate and efficiency of Ce(III) extraction were not significantly affected by the increase in NaCl concentration in the range 0.5–5 g L^{-1} and the augmentation of Na_2SO_4 concentration in the interval 0.1–20 g L^{-1}. At higher salts concentrations (5–40 g L^{-1} for NaCl and 40 g L^{-1} for Na_2SO_4), the extraction rate and efficiency were conspicuously affected. For higher salts concentrations, emulsion globules have a larger size and cannot be well dispersed in the entire volume of the external aqueous solution, which decreases the interfacial area and, consequently, diminishes the extraction yield. An improvement of extraction rate was observed for a concentration of 0.1 N NaCl, which was not the case for Na_2SO_4.

3.12. Effect of water matrices

The extraction of cerium was studied by dissolving the rare earth in a natural mineral water (Zamzam) and in seawater. The main characteristics of Zamzam water were: pH = 7.5, Ca^{2+} = 92 mg L^{-1}, Mg^{2+} = 18 mg L^{-1}, Na^+ = 129.5 mg L^{-1}, K^+ = 44.5 mg L^{-1}, Cl^- = 164.5 mg L^{-1}, SO_4^{2-} = 123.6 mg L^{-1}, HCO_3^- = 172 mg L^{-1}. The seawater (pH ~8.4), collected in the region of Annaba, Algeria, has a high salinity (~35 g L^{-1}) mainly formed of Na^+ ≈ 11 g L^{-1}, Mg^{2+} = 1.3 g L^{-1}, Ca^{2+} ≈ 0.4 g L^{-1}, Cl^- ≈ 20 g L^{-1}, SO_4^{2-} = 3 g L^{-1}. The obtained

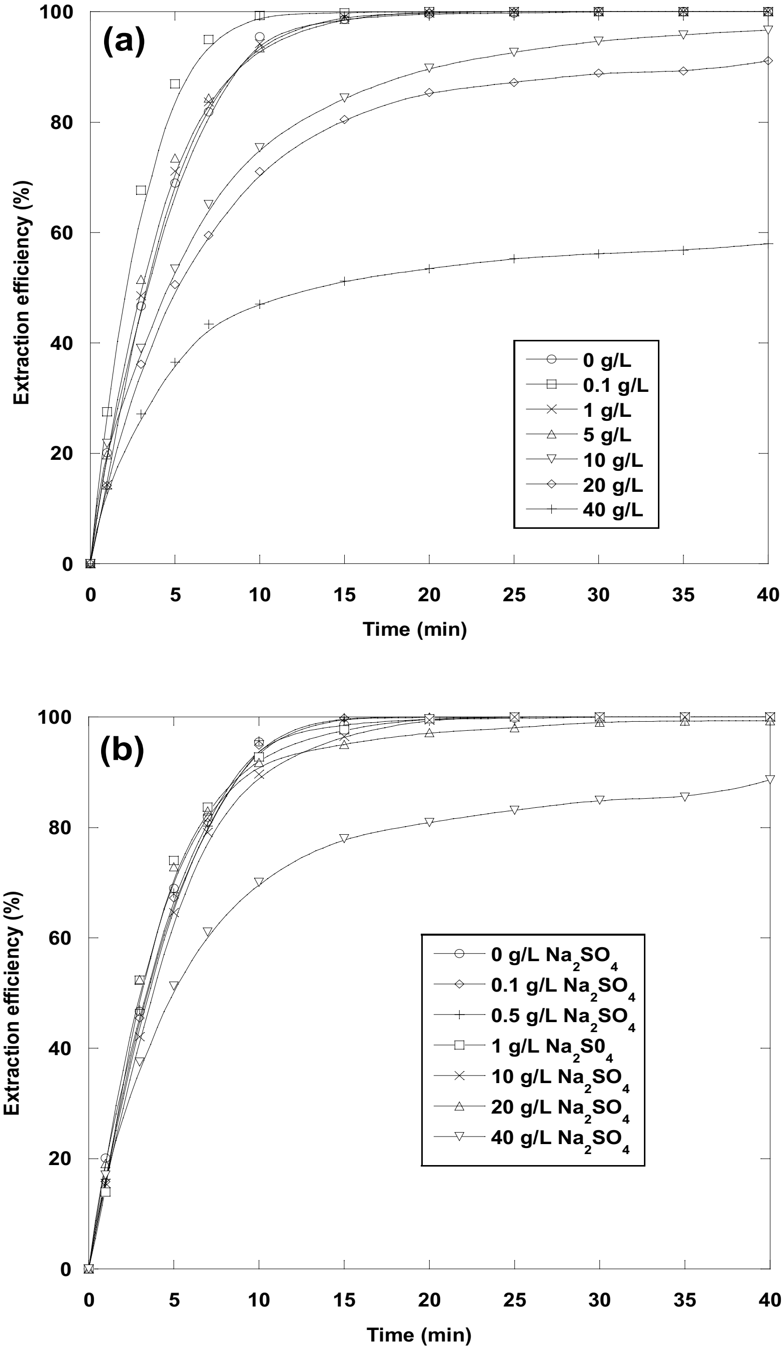

Fig. 11. Effect of salts (NaCl: (a)) and Na_2SO_4: (b)) concentration on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene).

results compared with those determined using ultrapure water are shown in Fig. 12. The extraction kinetics of Ce(III) in Zamzam water was very fast and 100% removal was obtained after only 7 min. The removal efficiency in seawater was 96.5% after 40 min. The above results show that the ELM treatment technique represents a very interesting separation process for the removal of Ce(III) in complex media such as natural water and seawater.

4. Conclusion

An emulsion liquid membrane was developed to extract and concentrate Ce(III) from dilute aqueous solutions using D2EHPA as extractant and Span 80 as surfactant. The influence of operating parameters on the extraction of Ce(III) was examined. Optimal experimental conditions for higher extraction rate and efficiency are: emulsion volume: 20 mL;

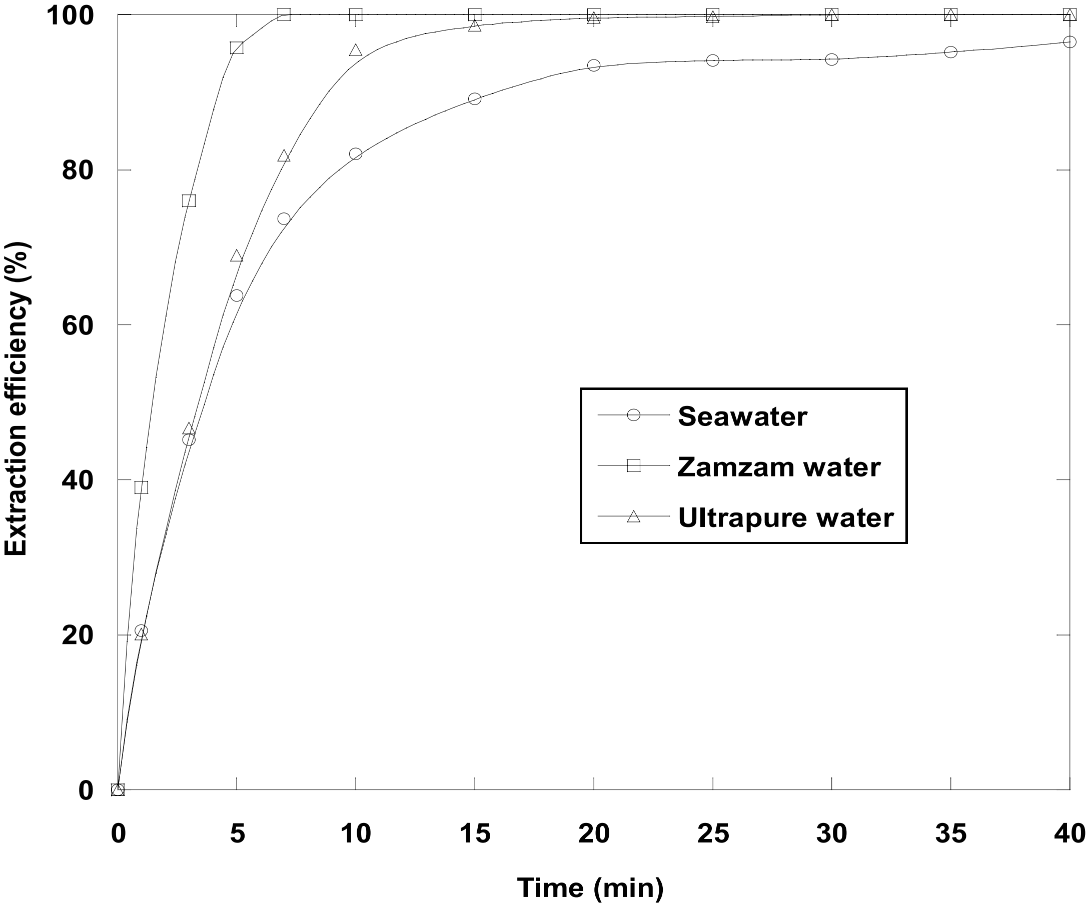

Fig. 12. Effect of water matrices on the extraction of Ce(III) (100 mg L^{-1}) by ELM (experimental conditions – emulsion volume: 20 mL; external phase (Ce(III) solution) volume: 250 mL; D2EHPA concentration: 0.4% (w/w); Span 80 concentration: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal phase concentration (HNO_3): 0.2 N; diluent: kerosene).

external phase (Ce(III) solution) volume: 250 mL; surfactant concentration: 3% (w/w); D2EHPA concentration: 0.4% (w/w); volume ratio of internal phase to organic phase: 1/1; stirring speed: 200 rpm; volume ratio of W/O emulsion to external phase: 20/250; internal stripping phase concentration (HNO_3): 0.2 N; pH of the feed phase: 5.1 (natural); diluent: kerosene. By using the best operating parameters, it was possible to wholly extract all of Ce(III) ions from the external feed solution within 20 min. Under the best-operating conditions, the extraction of Ce(III) was not affected in the presence of Na_2SO_4 and NaCl up to 20 and 5 g L^{-1}, respectively. At a higher salt concentration (40 g L^{-1} for Na_2SO_4 and 10–40 g L^{-1} for NaCl), the extraction efficiency decreased. The removal of Ce(III) was very fast in Zamzam water and decreased by only 4.5% in seawater, making the ELM process a highly promising technique for removing Ce(III) from natural contaminated waters.

The results obtained in the present paper show that it was possible to entirely extract the Ce(III) ions from the external feed solution under the most favorable conditions. Although comparisons for Ce(III) extraction by liquid membranes have only a relative meaning because of different testing conditions and methods, the extraction efficiency obtained in the present work is among the highest compared to that obtained in the literature.

ELM treatment process represents an efficient advanced separation technique for the extraction and concentration of Ce(III) ions from dilute aqueous solutions even in real environmental matrices.

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