*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2020.25450

187 (2020) 333–344
May

# Neodymium pertraction through sunflower oil-based emulsion liquid membrane: stability and mass transfer investigation

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Received 27 April 2019; Accepted 8 January 2020

**ABSTRACT**

In this paper, the possibility of using sunflower oil as an environmentally friendly and sustainable solvent for pertraction of neodymium (Nd) from aqueous solution through an emulsion liquid membrane (ELM) was studied. The ELM contained sunflower oil as a green diluent, a mixture of mono-(2-etylhexyl) ester of phosphoric acid (M2EHPA) and bis-(2-etylhexyl) ester of phosphoric acid (D2EHPA) as carrier, and Span 80 as surfactant. The process parameters influencing the extraction efficiency such as external phase pH, stirring speed, carrier concentration, surfactant concentration, treatment ratio, and internal phase concentration have been investigated. The results indicate that nearly all of Nd present in the external aqueous phase was extracted under the optimum condition (external phase pH: 3.5, stirring speed: 370 rpm, carrier concentration: 2% (v/v), surfactant concentration: 1.5% (v/v), treatment ratio: 1/3, and internal stripping phase concentration (nitric acid): 1 M) during a period of less than 20 min. Furthermore, Nd extraction efficiency in ELM process using sunflower oil was compared with using the other organic diluents and the overall mass transfer coefficients were calculated. Finally, it was observed that sunflower oil is the most effective diluent for Nd pertraction.

*Keywords:* Emulsion liquid membrane (ELM); Neodymium (Nd); Sunflower oil; D2EHPA; M2EHPA

## 1. Introduction

The rare earth elements (REEs) have received considerable attention due to their extensive industrial applications in various fields, including metallurgy, catalysts, ceramic, nuclear fuel control, electronics, and magnesium alloying. In addition, they play essential roles in some modern technologies such as rechargeable batteries, permanent magnets, hydrogen storage, luminescence and laser materials [1,2].

Neodymium (Nd) is one of the most critical REEs, which is applied in medicine and as a basis for solid state lasers in material processing. It is also used in in welding goggles and as a colorant for glass [3,4]. Moreover, the Sm-Nd dating methods are applied to determine the age of rock [5]. Nowadays, the main industrial application of Nd is in the neodymium–iron–boron (Nd-Fe-B) permanent magnets production [6]. Due to the wide utilization of permanent magnets in different devices from cell phones, home electric appliances to hybrid vehicles, and wind turbines, the

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demand and thereby the price of Nd has been recently grown [4,7]. Furthermore, it is predicted that over the next 21 y the global demand for Nd will increase by 700% [3,4]. Therefore, extraction and purification of such a valuable metal are crucial. Several methods have been developed for extraction and separation of metal ions from the aqueous solutions such as precipitation [8], adsorption [9,10], ion exchange [11], and liquid-liquid extraction [12,13].

Recently, liquid membranes are of interest to a wide range of researchers as an emerging technique for the pertraction of phenolic compounds [14–16], different dyes [17–19], pharmaceutical compounds [20,21], and various metal ions [22–26] from aqueous solutions. Based on configuration, liquid membranes can be generally categorized into four types, including bulk liquid membrane, emulsion liquid membrane (ELM), supported liquid membrane (SLM), and polymer inclusion membranes [27]. ELM is a combined extraction/stripping process. In this method, a double emulsion is applied, which consist of an external phase, a membrane phase and an internal phase. The external continuous phase contains the substances to be transferred into the internal phase. An organic liquid form a membrane separating both internal and external aqueous phases. This oil layer (membrane) contains a surfactant to maintain emulsion stability and a carrier (extractant) is typically dispersed in it to accelerate the transport [27]. ELM offers a number of advantages such as high interface area for mass transfer due to the small size of the aqueous phase droplets, capability to treat a variety of elements and compounds with high selectivity, and consuming lower amounts of organic solvent and greater efficiency compared to solvent extraction. Thus, this technique has been given considerable attention by investigators [28].

Several papers deals with the Nd extraction by solvent extraction method [6,13,29–34]. However, there are few reports in the literature on Nd pertraction using liquid membranes, particularly ELM system. Wannachod et al. [35,36] studied the separation of Nd through the hollow fiber SLM. They employed 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) as a carrier in octane and also dinonyl phenyl phosphoric acid (DNPPA) as carrier in n-dodecane and investigated mass transfer analysis. Extraction of Nd reached 98% in both systems and it was found that the mass transfer due to extraction reaction is the controlling step. Anitha et al. [37] investigated Nd extraction through the SLM process by using tri-n-octylphosphine oxide (TOPO) and DNPPA as carrier in petrofin and their results showed that 97% of $3.47 \times 10^{-4}$ M Nd was transported after 6 h using 0.6 M DNPPA+0.13 M TOPO. They also employed DNPPA and TOPO mixture in an ELM system and more than 98% extraction efficiency under the optimum conditions was achieved. Their results showed that ELM is a much faster mass transfer method than the other liquid membrane techniques such as hollow fiber which required about 30 min for the extraction of the metal ion [1]. The present study was aimed at the pertraction of Nd from aqueous solutions by an ELM. The most appropriate extractants for cations extraction are acidic carriers, which form complexes salt with cations by proton exchange. Di-2-ethyl hexyl phosphoric acid (D2EHPA) is one of the most widely used acidic extractants in REEs separation industry. Higher metal ions extraction and synergistic effect of using a binary mixture of acidic extractants has been revealed by many researchers [17,30,38–40]. Tachimori et al. [41] reported that adding mono-2-ethyl hexyl phosphoric acid (M2EHPA) to DEHPA resulted in an enhancement of Nd extraction and using a mixture of DEHPA - MEHPA is a more powerful extractant for lanthanide extraction from nitric acid solutions than the individual extractants. Based on the above mentioned reasons, a mixture of DEHPA and MEHPA which was product of Fluka has been used in this work as the mobile carriers.

Nd belongs to the lanthanide series which are nearly always in the +3 oxidation state and Nd (III) ion is stable in water. Thus, Nd (III) extraction and purification has been reported in the published papers concerning extraction of rare-earth metals from monazite ore or waste recycling of permanent magnet scrap leach liquor to retrieve valuable metals such as Nd [5,30,31,42,43]. Hence, we have used a synthetic wastewater and selected Nd (III) for study in this paper.

Petroleum based diluents that have been commonly used in ELM formulations are flammable, volatile, non-renewable, non-biodegradable, and toxic. Hence, the use of less hazardous replacement for these diluents is necessary due to environmental concerns [17,44,45]. Recently, we have reported the successful pertraction of hexavalent chromium by vegetable oil ELM [24]. In the present study, we have used sunflower oil instead of regular organic solvents for Nd pertraction to take the opportunity of applying an environmentally-friendly diluent in in ELM process, since vegetable oils are low cost, non-hazardous, non-toxic, and easily available in comparison to petroleum-based solvents [17,44,46–50]. To determine the optimum operating condition, the effects of various parameters including effect of solvent type on the extraction efficiency of Nd through ELM process have been investigated.

The stability of the membrane is one of the key factors affecting the efficiency of the ELM. Membrane stability is mainly governed by membrane swelling and breakage phenomena. Swelling refers to the permeation of water from the external phase into the internal phase through the membrane phase. It could be caused by difference in the osmotic pressure between the phases or the entrainment of the external phase into the internal phase owing to the frequent coalescence and re-dispersion of emulsion globules during the pertraction time. The swelling dilute the strip phase which directly results in lower extraction efficiency. In addition, swelling ultimately leads to breaking of emulsion membrane. Breakage includes the rupture of the emulsion globule and the leakage of the internal agent and the previously extracted to the external phase. Thus, the pertraction efficiency decreases due to decreasing the volume of the internal stripping phase and driving force for mass transfer [51,52]. Under the light of above mentioned information, the membrane stability was considered in process parameters optimization. The main focus of this study is on the potential and possibility of using vegetable sunflower oil as a biodegradable diluent for Nd pertraction using ELM process. Hence, the novelty of this work is the application of sunflower oil- based ELM for efficient pertraction of Nd ions as well as the relevant optimization procedures in accordance with the pertraction and stability results of the membrane.

## 2. Experimental

### *2.1. Materials*

All chemicals and reagents used were analytical reagent grade. Neodymium (III) nitrate hexahydrate (Nd $(NO_3)_3$·$6H_2O$, 99.9% purity) was procured from Middle East Ferro Alloy Company (Iran). A mixture of DEHPA and MEHPA which was product of Fluka (Hannover, Germany) has been used in this work. The proportion of D2EHPA and M2EHPA in this product was at a fixed value (60:40).

The non-ionic surfactant selected as an emulsifier was Sorbitan monooleate ($C_{64}H_{124}O_{26}$, HLB = 4.5) that was a product of Sigma-Aldrich Company (Schnelldorf, Germany) (commercially also known as Span 80). Sunflower oil was used as diluent which was obtained from local supplier (NINA Oil Company, Tehran, Iran). The other diluents including toluene, butyl acetate, chloroform, and kerosene were product of Sigma (Schnelldorf, Germany). Nitric acid ($HNO_3$ (65%)) was also purchased from Merck (Darmstadt, Germany).

### *2.2. Procedure*

The operating parameters influencing the permeation of Nd such as the pH of the feed phase, stirring speed (the mixing speed to disperse the emulsion phase in the feed solution), carrier and surfactant concentration, treatment ratio, and internal phase concentration have been investigated to observe their effect on Nd extraction. In addition, the effect of internal phase concentration on the stripping efficiency has been studied. Finally, the effect of type of diluent has been investigated. The range of the studied operating parameters and conditions are given in Table 1.

Aqueous feed solution was prepared by dissolving certain amount of neodymium nitrate in distilled water to obtain a concentration of 50 mg $L^{-1}$ and the feed phase pH was adjusted before each run. To make liquid membrane, appropriate amounts of Span 80 and mixture of D2EHPA/M2EHPA were mixed in the diluent under a gentle agitation using a magnetic stirrer. Then, the emulsion was prepared by mixing the membrane phase and internal solution. The total volume of the emulsions was 60 mL and the emulsions were prepared by the equal volume of the membrane and stripping internal phase. In other words, the volume ratio of internal phase to the membrane was 1:1. According to the literature, this is the most convenient value for ELM process at laboratory scale [1,21,53–56].

The stability of emulsions with respect to time was estimated by visual observation. The emulsification was conducted under the continuous stirring for 10 min to produce a milky-white W/O emulsion and the applied emulsification speed was 6,000 rpm which is in the range reported by other investigators [57–60]. A high speed homogenizer (Ultra-Turrax IKA T18, Germany) was utilized to mix the internal aqueous solution with the organic membrane phase. It was found that the emulsions were stable up to 3 h by examining the phase separation or any change in their homogeneity and uniformity over time. In this work, the pertraction time was less than 30 min. Thus, it can be concluded that the primary emulsions were stable enough and the composition of the membrane was kept constant during the pertraction time.

In 400 mL beaker, the prepared W/O emulsion (membrane solution and internal solution) was dispersed in the acidic feed solution by using a variable speed mixer. The agitator used to make the W/O/W double emulsions was a 3-blade marine propeller (diameter 5 cm). The volume ratio of feed to emulsion was variable, whereas the volume of the W/O emulsions was fixed at 60 mL in all experiments.

Samples were taken at regular interval up to 20 min using syringes and then were kept motionless until the emulsion and the feed phase were separated. The clear solutions were filtered using a filter paper (Whatman, No.1, USA) and the final Nd concentration in the external phase was measured by ICP-AES (Thermo Jarrell Ash, Model Trace Scan, Canada). The volume and number of samples were kept to a minimum in order to minimize the change in feed and membrane volume. This sampling method is consistent with the method used in the previous literature where the effect of process parameters on ELM performance studied at different time intervals [59,61–67].

The stability of the membrane was examined by measuring the swelling and breakage ratio. Tracer method is the most widely used technique to measure swelling and membrane breakage simultaneously. Tracer must not be transported through the membrane. The tracer is added into the internal phase and then, by measuring its concentration in the external and internal phase, a mass balance for it in the operation of the ELM process, and considering the volume change of the internal phase the ratios of membrane

Table 1
Operational ranges of the experimental parameters

| Operating parameters | Range |
|---|---|
| Nd concentration in the feed phase (mg/L) | 50 |
| Feed phase pH | 0.5, 1.5, 2.5, 3.5, 4.5 |
| Surfactant concentration % (v/v) | 0.5, 1, 1.5, 2, 2.5 |
| Carrier concentration % (v/v) | 1, 1.5, 2, 2.5 |
| Stirring speed (rpm) | 270, 320, 370, 420 |
| Treatment ratio (v/v) | 1/5, 1/4, 1/3, 1/2, 1 |
| Concentration of stripping solution (M) | 0.25, 0.5, 1, 2 |
| Type of diluent | Sunflower oil, Kerosene, Toluene, Chloroform, Butyl acetate |

breakage and swelling can be easily calculated as completely discussed by Wan and Zhang [51]. In the present work, KCl was used as tracer in the internal phase and based on the mentioned method, swelling and breakage ratio defined as follows:

$$\%\text{ Swelling} = \left[\frac{\left(1-\frac{C_{e,I}}{C^0_{i,I}}\right)\left(\frac{C^0_{i,I}-C_{i,I}}{C_{i,I}-C_{e,I}}-\frac{C_{e,I}\left(1+R^0_{\text{oi}}\right)}{R^0_{\text{ew}}\left(C_{i,I}-C_{e,I}\right)}\right)+}{\frac{C_{e,I}\left(1+R^0_{\text{oi}}\right)}{R^0_{\text{ew}}C^0_{i,I}}}\right]\times 100 \quad (1)$$

$$\%\text{Breakage} = \frac{C_{e,I}}{C^0_{i,I}\left(C_{i,I}-C_{e,I}\right)}\left[\frac{1+R^0_{\text{oi}}+R^0_{\text{ew}}}{R^0_{\text{ew}}}C_{i,I}-C^0_{i,I}\right]\times 100 \quad (2)$$

where $C^0_{i,I}$, $C_{i,I}$, and $C_{e,I}$ are the initial concentration of the used tracer in the internal phase, and concentration of tracer in the internal and external phase at time *t* (the time of measurement), respectively. $R^0_{\text{oi}}$ and $R^0_{\text{ew}}$ are the initial volume ratio of the oil phase to the internal phase and the initial volume ratio of the external phase to the emulsion which are originally known.

Since the pertraction time was 20 min, the stripping and stability data were obtained at the end of 20 min of mixing. In fact, the mixture was stirred for 20 min and then the samples were taken and quickly introduced into a separation funnel. After that, the two layers of aqueous and emulsions were clearly separated. The bottom layer was the aqueous phase and emulsion at the upper layer used for analysis.

For stability study, the concentration of KCl in the bottom layer which was the external phase was measured by ICP-AES (Thermo Jarrell Ash, Model Trace Scan, Canada). Similarly, the concentration of KCl in the internal phase was measured after demulsification of the upper layer. In this study, demulsification was carried out by heating the emulsions to 80°C and centrifugation at 5,000 rpm in 3 min.

For enrichment factor and stripping efficiency calculation, the final Nd concentration in the external phase (bottom layer) was also measured using ICP-AES. Likewise, the final Nd concentration in the internal phase was also determined after demulsification of the upper layer. Stripping efficiency was calculated using below Eq. (3) which is determined by mass balance:

$$\text{Stripping}\left(\%\right) = \frac{C_i V_i}{C^0_e V^0_e - C_e V_e}\times 100 \quad (3)$$

where $C_i$ is the final concentration of Nd in the internal phase, $C^0_e$ is the initial concentration of Nd in the external phase, $C_e$ is the final concentration of Nd in the external phase, $V_i$ is the final volume of the internal phase, $V^0_e$ is the initial volume of the external phase, and $V_e$ is the final volume of the external phase.

The extent of Nd enrichment was calculated as follows:

$$\text{Enrichment} = \frac{C_i}{C^0_e} \quad (4)$$

where $C_i$ is the final concentration of Nd in the internal phase, and $C^0_e$ is the initial concentration of Nd in the external phase.

## 3. Results and discussion

### 3.1. Effect of the external phase pH

In order to investigate the important role being played by pH of the external phase in Nd permeation from the aqueous solution, the pH of the feed solution varied from 0.5 to 4.5, whereas other operating parameters including carrier concentration and Nd concentration in aqueous phase were kept constant. The effect of the pH of the external phase on the extraction efficiency of Nd is depicted in Fig. 1.

The results confirm that Nd forms a neutral ion pair complex with the carrier according to the equation below which is the common cation-exchange mechanism for extraction of trivalent REEs with cationic extractants such as D2EHPA and M2HEHPA [3,30,39,68]:

$$Nd^{3+}_{aq} + 3\left[RH_2\right]_{org} \leftrightarrow \left[Nd\left(R\cdot HR\right)\right]_{org} + 3H^+_{aq} \quad (5)$$

As shown in this equation, the extraction is an equilibrium that can proceed in either direction, depending on the [$H^+$]. Hence, the observed lower transport of metal ion in the acidic pH range is caused by decreasing the driving force of the process. In fact, the facilitated transfer of Nd ions in the presence of the carrier occurs when the pH value of the internal phase is lower in value than the external phase and increasing the pH in the feed side leads to an increase in the dye transport from donor to acceptor phase. It can be inferred from Fig. 1 that Nd transport rate increases with increasing the pH from 0.5 to 3.5 and the maximum extraction of 99% for Nd was achieved at pH 3.5.

According to the results, Nd extraction increases until 16 min and then decreases. It can be due to emulsion breakage by prolongation of the pertraction time. In other words, longer pertraction time causes membrane swelling, and

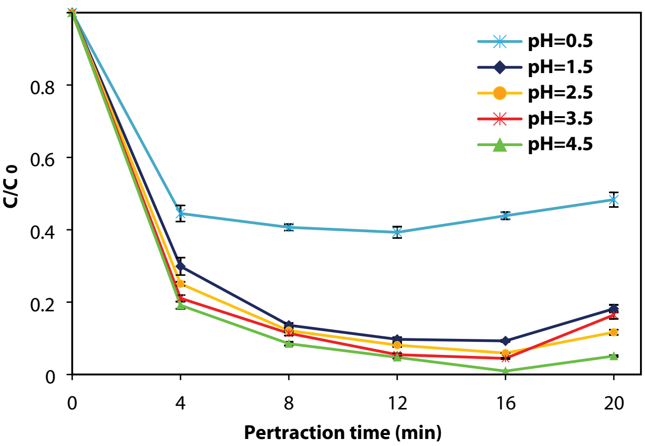


Fig. 1. Effect of external phase pH on the extraction of Nd by ELM (Feed concentration: 50 mg/L; stirring speed: 370 rpm; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase concentration: 1 M; diluent: sunflower oil).

eventually breakage which results in enhancement of Nd concentration in the feed phase as shown in Fig. 1. Similar observations have been made previously [25,69].

Fig. 2 represents the effect of external phase pH on the stability of the liquid membrane. According to it, the membrane is easy to break at low values of external phase pH. The main reason is that the properties of Span 80 were changed which results in destabilization of the emulsion [25]. Hence, increasing the external phase pH reduced the emulsion breakage leading to increase the mass transfer efficiency. On the other hand, when pH of the feed phase is increased up to 4.5, the extraction of Nd was found to decrease due to increase in swelling ratio which stems from the increase in osmotic pressure difference [61]. As mentioned before, swelling refers to the permeation of water from the external phase into the internal phase through the membrane phase. Swelling can trigger breakage phenomenon due to thinning of membrane layer. In fact, when the degree of swelling becomes high enough and the size of internal droplets is increased until a certain limit, rupturing of emulsion globules occurs. Emulsion breakage can be also due to shear forces or instability of the emulsion caused by hydrolysis of surfactant in acidic or basic media. High values of breakage and leakage are related with higher values of swelling. However, high values of swelling are not essentially associated with high values of breakage [64,70]. Similar observations are reported in the literature [28,61,64,71]. According to the above mentioned results, further studies were carried out at pH 3.5 for.

### 3.2. Effect of stirring speed

It is well known that stirring speed has a profound effect on the mass transfer rate of solute through an ELM. In order to achieve effective transfer of Nd in ELM process, the experiments were accomplished at different stirring speeds in the range of 270–420 rpm and the obtained results are shown in Fig. 3. It is observed that increasing the stirring speed from 270 to 370 rpm increases the rate and extent of extraction. The reason is that an increase in stirring speed leads to higher turbulence energy and accordingly formation of smaller emulsion globules, so the external interfacial area for mass transfer and extraction efficiency is increased. According to this figure, further increase in the stirring speed from 370 rpm to 420 rpm results in a decrease in the extent of extraction at the final intervals (between 12 to 20 min). The reason is that increasing the stirring speed also affects the stability of the emulsion. In addition, that stability of the membrane decreases with time [25]. At higher stirring speed, hydrodynamic shear and swelling work together lead to lower extraction at the final intervals. As shown in Fig. 4, agitation-induced shear leads to increase in emulsion breakage. Furthermore, the shear induced breakage of fragile emulsion droplets near the tip of the impeller. Hence, the emulsion could not resist the excessive shear provided by the impeller as well as the contactor wall [72]. This leads to rupture of the membrane wall and leakage of Nd in to the external phase which make the extraction efficiency to reduce. According to Fig. 4, the emulsion phase becomes highly unstable by increasing the stirring speed due to the agitation-induced swelling. At this stage, the emulsion globules dispersed and then coalesce repeatedly which caused the entrainment of feed phase into the stripping phase, that is, some water from the external phase were enclosed in the emulsion phase and dilutes the internal stripping phase [73,74]. As a result, the Nd extraction decreases. These findings are in agreement with the experimental results of other researchers [16]. Thus, as the highest extraction efficiency at the end of 20 min of mixing was obtained with stirring speed

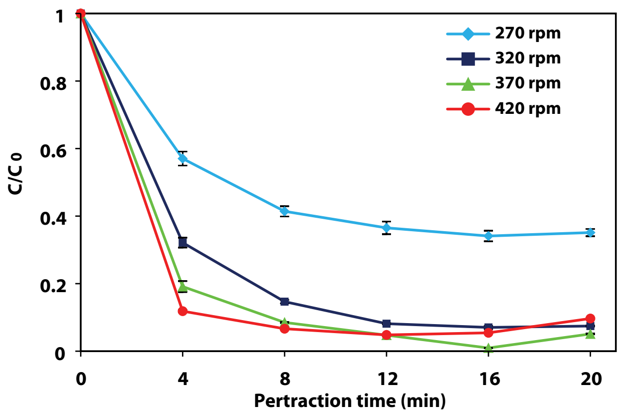


Fig. 3. Effect of stirring speed on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase concentration: 1 M; diluent: sunflower oil).

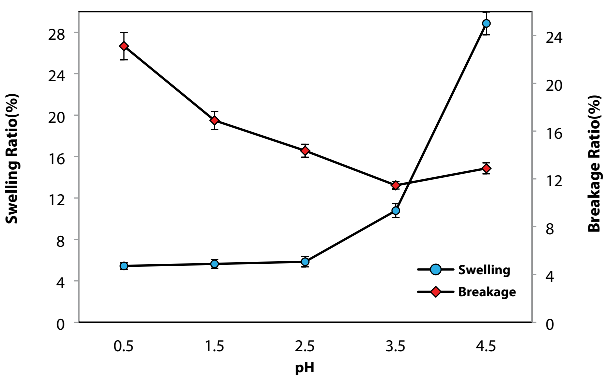


Fig. 2. Effect of external phase pH on the ELM stability.

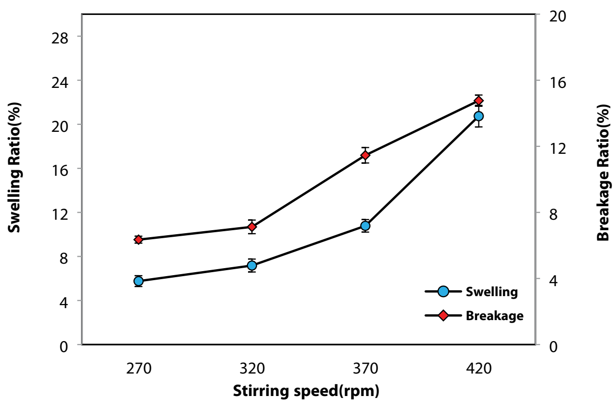


Fig. 4. Effect of stirring speed on the ELM stability.

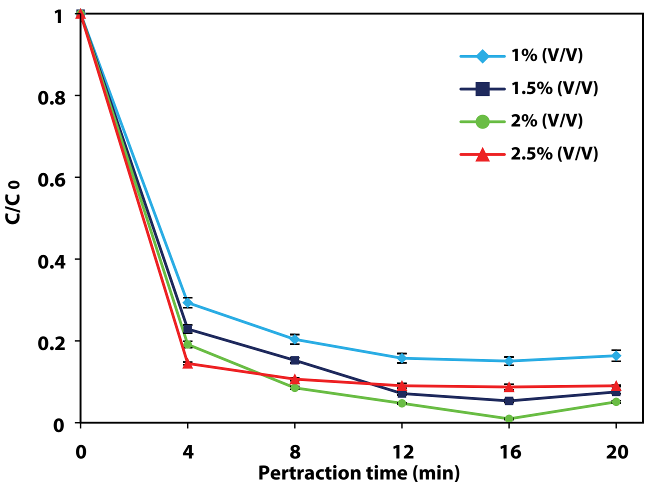


Fig. 5. Effect of carrier concentration on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase concentration: 1 M; diluent: sunflower oil).

of 370 rpm, this speed was accepted as the most appropriate stirring speed.

### 3.3. Effect of carrier concentration

Carriers being added to the membrane phase play a vital role in the overall extraction behavior in ELM processes. To study the effect of carrier concentration on the extraction of Nd from aqueous solution containing 50 mg/L of this metal, D2EHPA/M2EHPA concentration varied from 1%–2.5% (v/v) and the results are presented in Fig. 5. It can be seen that the extraction of Nd increases with increase of carrier concentration up to 2%. This increase is due to more Nd-carrier complex formation with the increasing carrier concentration.

At higher carrier concentration, that is, above 2%, the rate of extraction slowed down and Nd extraction decreased. The reduction in extraction is caused by the respective increase in membrane phase viscosity which leads to larger globules and represents a significant impediment to Nd transport. Furthermore, increasing the concentration of the carrier has a negative influence on the stability of the primary W/O emulsion because of its interfacial properties that favors the formation of a reversed emulsion [75]. As can be seen in Fig. 6, increase in carrier concentration leads to increase in swelling of the emulsion, thereby diluting the stripping phase. Hence, 2% (v/v) D2EHPA/M2EHPA was chosen as the carrier concentration in the succeeding tests.

### 3.4. Effect of surfactant concentration

Surfactant concentration is an important parameter as it has major impact on emulsion stability thereby affecting Nd extraction. The surfactant concentration ranged from 0.5% to 2.5% (v/v). Influence of surfactant concentration in the membrane phase of the emulsion on Nd extraction is shown in Fig. 7. As shown in this figure, an increase in Span 80 concentration leads to increasing the extraction efficiency

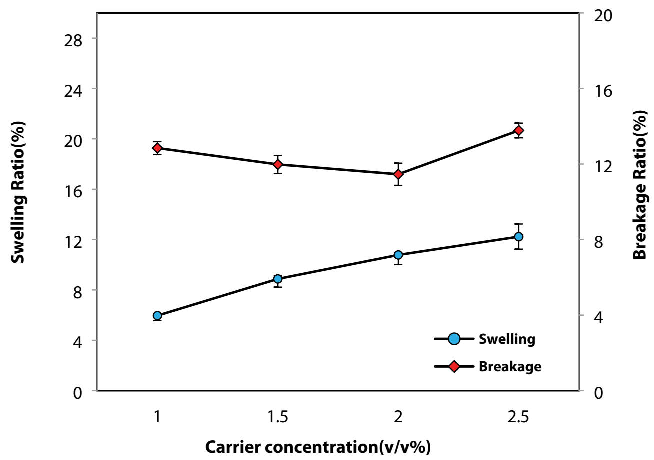


Fig. 6. Effect of carrier concentration on the ELM stability.

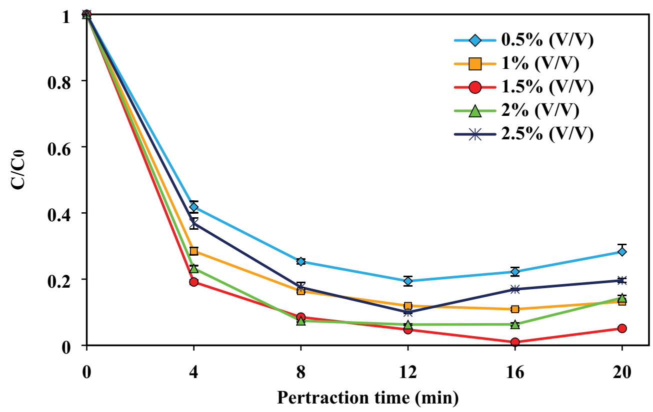


Fig. 7. Effect of surfactant concentration on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; carrier concentration: 2% (v/v); treatment ratio: 1/3; internal phase concentration: 1 M; diluent: sunflower oil).

of Nd. It shows that emulsion stability has been improved with increasing surfactant concentration up to 1.5%.

Fig. 8 shows effect of surfactant concentration on membrane stability. It suggests that low surfactant concentrations result in lower viscosities in the membrane phase and less stable membranes because the extent of surfactant has not been enough to stabilize the emulsion, so the ELM was easy to break [76]. However, using more amounts of Span 80 in the membrane phase caused a decrease in extraction efficiency. One possible reason is that applying unnecessarily high content of surfactant lowers diffusivity of complexes in the membrane solution which can be ascribed to the viscosity enhancement of the membrane phase.

As reported by Wan and Zhang [51], there is a “critical concentration” of surfactant to form a stable liquid membrane against the internal phase leakage in an ELM system. Beyond this critical concentration, a further increase in surfactant concentration increases the membrane stability slightly, while the emulsion osmotic swelling increases significantly with increasing of surfactant concentration because of its hydration properties (see Fig. 8).

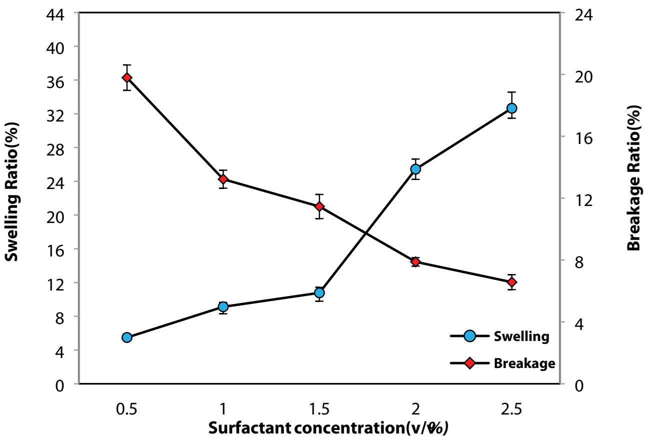


Fig. 8. Effect of surfactant concentration on the ELM stability.

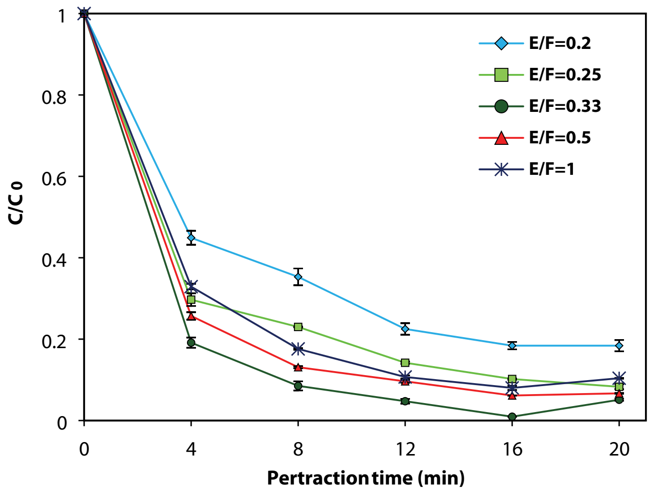


Fig. 9. Effect of treatment ratio on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); internal phase concentration: 1 M; diluent: sunflower oil).

Surfactant molecules attach to each other and aggregate in bulk of the solution to form macromolecules or micelles if the concentration exceeds a certain concentration called critical micelles concentration. From the experimental results, it can be inferred that 1.5% (v/v) Span 80 is the corresponding critical concentration and the increase in the amount of Span 80 beyond it resulted in formation of reverse micelles. The surfactant aggregates play the role of reservoir for water and promote the transportation of water molecules to the internal or external phase (swelling or breakage) which adversely affects the emulsion stability [77]. Consequently, use of excessive surfactants reduces overall extraction efficiency. From the experimental results, it can be inferred that 1.5 % (v/v) Span 80 is the optimum surfactant concentration.

### 3.5. Effect of treatment ratio

Treatment ratio is defined as the volume ratio of emulsion phase to the feed phase, exactly like solvent to feed ratio in conventional liquid-liquid extraction. It is a determining factor in effectiveness and economy of the ELM process.

Fig. 9 demonstrates the effect of the treatment ratio on Nd extraction. As mentioned before, the treatment ratio was changed by changing the volume of the feed phase and keeping the volume of the emulsion phase constant. For example, in the first run the volume of the feed phase was five times the emulsion phase, that is, $E/F = 1/5$ and finally the volume of feed phase and emulsion phase was kept equal at the final run ($E/F = 1$).

The stability results are illustrated in Fig. 10. When the treat ratio is 1/5, Nd extraction is the least. At the lowest treat ratio, emulsion swelling was observed. This may be due to the fact that the emulsion did not disperse very well and the contact area between the phases considerably decreased. Simultaneously, the surfactant would also provide the co-transport of water thereby diluting the internal phase [74]. Increasing the treat ratio from 1/5 to 1/3 tends to enhance the overall extent of extraction. The volume fraction of emulsion in the system increases by increasing the treat ratio. This results in a greater amount of emulsion globules per unit volume of the feed solution in the

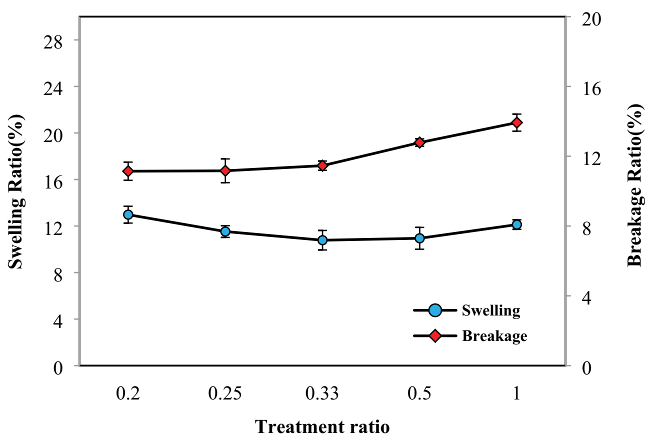


Fig. 10. Effect of treatment ratio on the ELM stability.

mixture vessel. Thus, higher interfacial area for mass transfer caused higher mass transfer from external phase to the emulsion globule. With increasing the volume fraction of emulsion, the volume fraction of the carrier available for Nd pertraction in the system increases which in turn leads to a higher degree of extraction [27]. However, a further increase in treatment ratio up to 1 showed a decline in the extraction efficiency as shown in Fig. 9. This can be explained by the formation of larger globules at higher treat ratios which leads to a decrease in external mass transfer areas. Furthermore, effective diffusion path length within the larger globules increases which results in a decline in mass transfer. This reduction in the degree of extraction can be also attributed to the coalescence of emulsion globules which leads to emulsion breakage and release of the encapsulated Nd back to the feed phase (see Fig. 10). In that case, mass transfer area reduces and higher residence time of the emulsion for extraction is required, so extending the time of extraction brings about an increase in emulsion breakage [78,79]. Consequently, the treatment ratio of 1/3 was chosen as the optimum value for further study.

### *3.6. Effect of internal phase concentration*

The capacity of the emulsion to extract solute is affected by the internal phase acid concentration. To investigate the influence of acid concentration in the internal phase on the Nd transport, the experiments were performed with various concentrations of nitric acid in over a wide range of 0.25–2 M. The internal phase concentration has been inevitably doubled in each step and the results are presented in Fig. 11.

This figure clearly shows that both Nd extraction extent and rate increased over the whole duration of experiments when the acid concentration was varied from 0.25 to 1 M. As mentioned before, the concentration difference of $[H^+]$ between the feed and the internal aqueous phases acts as a driving force for Nd transport in presence of D2EHPA/M2EHPA carrier in the ELM system. Thus, higher nitric acid concentration in the internal aqueous phase results in Nd extraction improvement. However, Nd extraction decreased with more increase in nitric acid concentration up to 2 M. This can be explained by the fact that an excessive amount of nitric acid in the internal phase leads to swelling of the emulsion as shown in Fig. 12. In addition, the reaction of acid with Span 80 leads to deterioration of emulsion stability owing to a partial loss of its surfactant properties which causes emulsion breakage [28].

The concentration of the internal phase has a profound effect on Nd enrichment and stripping. Thus, the effect of nitric acid concentration on Nd enrichment and stripping efficiency was also studied and the results are displayed in Fig. 13. It can be seen that the enrichment and in turn stripping efficiency increased with an increase in the internal phase concentration up to 1 M. However, further increase in nitric acid concentration was found to reduce the extent of enrichment and stripping because of swelling problem and dilution of the concentrated Nd ion in the internal phase. According to the results, maximum enrichment of 10.24 and stripping efficiency (~89%) has been obtained at 1 M concentration of nitric acid as the internal phase. Hence, it was found that $HNO_3$ of 1 M concentration gives the best Nd extraction and stripping efficiency, so it was used for succeeding experiments.

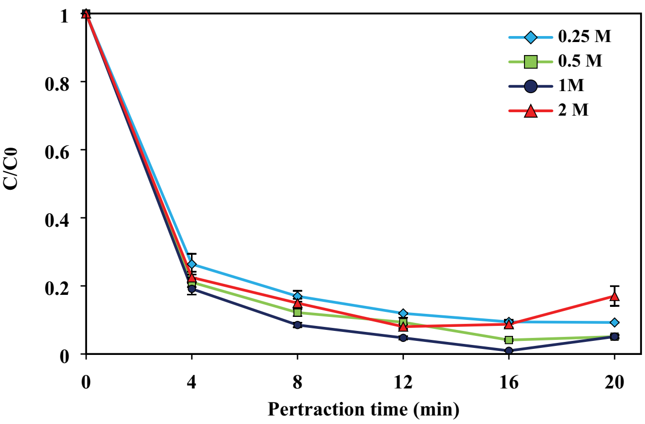


Fig. 11. Effect of internal phase concentration on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase: $HNO_3$; diluent: sunflower oil).

### *3.7. Effect of diluent type*

Since petroleum-based diluents are frequently used in the ELM method according to the literature [1,26,29,30,32,37], the differences in the performance between the applied vegetable oil and conventional petroleum-based diluents are highlighted in this work. Hence, the performance of organic solvents such as toluene, butyl acetate, chloroform, and kerosene was also examined. Experiments were carried out in the same operational conditions that previously optimized.

Fig. 14 shows the efficiency of the diluents for Nd extraction by ELM. It is observed that sunflower oil gave the greatest performance with an extraction efficiency of more than 99% among the other diluents tested.

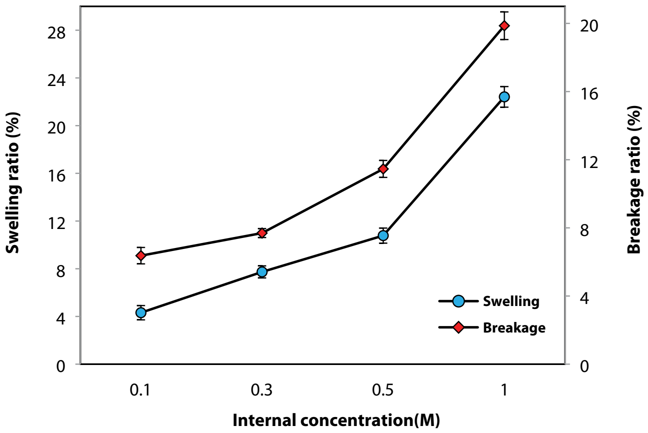


Fig. 12. Effect of internal phase concentration on the ELM stability.

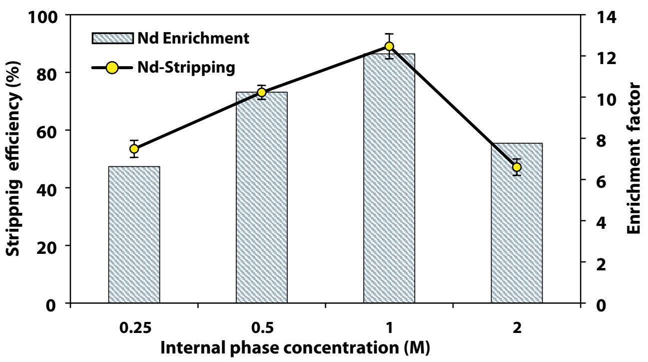


Fig. 13. Effect of internal phase concentration on the enrichment and stripping efficiency of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase: $HNO_3$; diluent: sunflower oil).

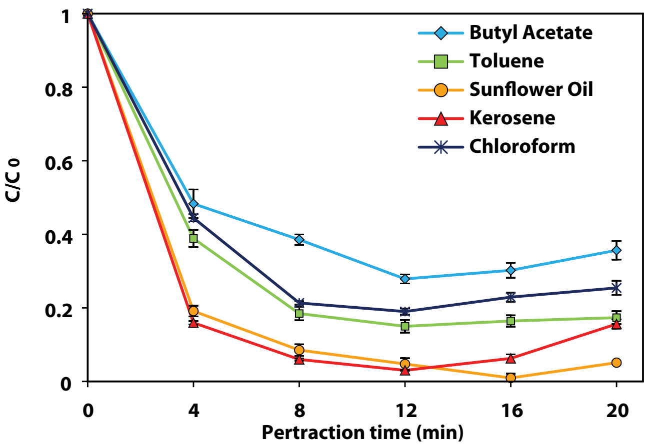


Fig. 14. Effect of type of diluent on the extraction of Nd by ELM (Feed concentration: 50 mg/L; external phase pH: 3.5; stirring speed: 370 rpm; carrier concentration: 2% (v/v); Span 80 concentration: 1.5% (v/v); treatment ratio: 1/3; internal phase concentration: 1 M).

Organic diluents affect the performance of ELM process. Change in organic diluent in the emulsion preparation step results in changes in emulsion stability and extraction efficiency. Table 2 gives the viscosity of the diluents used for making the emulsion.

In the ELM method, the total mass transfer resistances of reaction is expressed as following [80–82]:

$$\frac{1}{K_0} = \frac{1}{k_M} + \frac{1}{k_f}, k_f = \frac{k_{f'}}{C_H^3} \tag{6}$$

$k_M$ is the external phase mass transfer coefficient, $k_f$ the interfacial reaction rate constant, and $K_0$ is the overall mass transfer coefficient. $k_f'$ and $C_H$ are the apparent interfacial reaction rate constant and concentration of hydrogen ions concentration in external solution, respectively. Interfacial reaction rate constant for a constant pH of the external phase was obtained from the following Eq. (7) which was derived by Kasaini et al. [82]:

$$\ln\left[1-E\right] = \ln\left(\frac{C_e}{C_{e0}}\right) = -A \cdot t \cdot k_f \tag{7}$$

where $A$ is the interfacial area which was calculated by using the correlation of Ohtake et al. [83] for W/O emulsion globule size in ELM systems.

The mass transfer coefficient ($k_M$) of the external phase in agitated vessels was calculated from a correlation proposed by Skelland and Lee [84]:

$$\frac{k_M}{\sqrt{ND}} = 2.932\times10^{-7}\left(\frac{V_i+V_m}{V_i+V_m+V_e}\right)\left(\frac{d_I}{T}\right)^{0.548}\mathrm{Re}^{1.371} \tag{8}$$

where $N$ is the mixing speed (rpm), $D$ is the diffusion coefficient (m² s⁻¹), $V_i$ is the volume of internal phase, $V_m$ is the volume of organic phase, $V_e$ is the volume of external phase, $d_I$ is the impeller diameter, $T$ is the mixing vessel diameter and Re is the Reynolds number based on continuous phase.

The interfacial reaction rate constant ($k_f$), external phase mass transfer coefficient ($k_M$), and overall mass transfer coefficient ($K_0$) in the ELM systems using different diluents are also presented in Table 2.

It is observed that the overall mass transfer coefficient showed the following tendency: kerosene > sunflower oil > toluene > chloroform > butyl acetate which is in agreement with the results of extraction in Fig. 14.

It is known that higher viscosity results in a lower diffusion coefficient. On the other hand, greater viscosity produces more stable membrane. An increase in emulsion viscosity improves the resistance to globule breakage. Also, viscosity of diluent considerably affects the degree of swelling phenomenon of emulsion during the ELM process. It has been reported that the diffusion of reversed micelles and also entrainment swelling decreases with increasing emulsion viscosity [85,86].

According to the obtained results, kerosene and sunflower oil which have higher viscosity compared with the other diluents yield higher Nd extraction efficiency. It should be noted that there is a marginal difference between the performance of kerosene-based and sunflower oil-based ELM after 16 min of contact time. Although the overall mass transfer coefficient by using sunflower oil in ELM is lower than kerosene, its higher viscosity resulted in more stable liquid membrane which allowed better extraction performance in comparison to kerosene and the other diluents.

This result is in line with the previously reported papers which confirmed that the lower viscosity of the diluent negatively influences the emulsion stability and consequently causes lower solute transport and poor performance of ELM [87]. Hence, sunflower oil was chosen as the best diluent from an economical and environmental viewpoint. From the obtained results, sunflower oil revealed a high potential for Nd pertraction and opens a future possibility of comparing

Table 2
Comparison of some properties of the used diluents along with the interfacial reaction rate constant and mass transfer coefficients

| Diluent | Viscosity (Cp) | $k_M$ | $k_f$ | $K_0$ |
|---|---|---|---|---|
| Sunflower oil | 39.1 | $7.5 \times 10^{-5}$ | $1.76 \times 10^{-6}$ | $1.72 \times 10^{-6}$ |
| Kerosene | 1.64 | $7.5 \times 10^{-5}$ | $1.99 \times 10^{-6}$ | $1.94 \times 10^{-6}$ |
| Toluene | 0.55 | $7.5 \times 10^{-5}$ | $1.13 \times 10^{-6}$ | $1.11 \times 10^{-6}$ |
| Chloroform | 0.53 | $7.5 \times 10^{-5}$ | $9.76 \times 10^{-7}$ | $9.63 \times 10^{-7}$ |
| Butyl acetate | 0.685 | $7.5 \times 10^{-5}$ | $7.14 \times 10^{-7}$ | $7.07 \times 10^{-7}$ |

the efficiency of sunflower oil with the other vegetable oil types.

## 4. Conclusions

Neodymium is a critical REE that is important in modern technologies, so efficient processes are needed for its extraction and purification. An experimental study on pertraction of Nd from aqueous solutions was carried out through an ELM containing a mixture of M2EHPA and D2EHPA as carrier in sunflower oil as an environmentally benign diluent. The effect of pH value of the external phase, stirring speed, carrier's concentration, surfactant concentration, treatment ratio, and internal phase concentration on Nd extraction were also investigated. As a result, the optimum condition of Nd pertraction was obtained as the external phase pH was 3.5, stirring speed was 370 rpm, carrier concentration was 2% (v/v), surfactant concentration was 1.5% (v/v), treatment ratio was 1/3, and internal phase concentration was 1 M. Under the optimum conditions, nearby complete extraction of Nd was achieved within less than 20 min and the enrichment and stripping efficiency of 10.24% and 89% has been obtained, respectively. Finally, results were compared with some organic diluents and mass transfer coefficients were calculated in each case. It has been found that using sunflower oil in ELM not only is interesting from both economic and environmental perspectives but also leads to an increase in the Nd extraction efficiency in comparison to the other organic diluents tested.

## Acknowledgements

The authors would like to thank Academic Center for Education, Culture & Research (ACECR), School of chemical engineering, University of Tehran.

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