

Extraction of La(III) by a nonionic microemulsion containing D2EHPA in hollow fiber contactor

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Abstract. This study aimed to prepare a W/O nonionic microemulsion system (MEs) consisting of OP-4 [polyoxyethylene(4) nonylphenol], OP-7 [polyoxyethylene(7) nonylphenol], 1-hexanol, D2EHPA, kerosene and HCl solution and applied to the extraction of La(III) from chloride aqueous solution within the polysulfone hollow fiber contactor (HFC), laboratory-scale experiments were carried out to investigate the recovery of La(III) using as-prepared microemulsion from the simulation wastewater containing La(III), Al(III) and Fe(III). The right weight ratio (Rs) of OP-4 to OP-7 was firstly confirmed through determination of the solubilization capacity of HCl solution ($W_{0,HCl}$) in microemulsion, the effect of several factors such as the HCl concentration, temperature and effective extraction time on the extraction efficiency of La(III) was discussed. Results showed that the acceptable Rs was 4:6 to prepare the W/O MEs. The extraction yield of La(III) increased with the increasing of HCl concentration, temperature and effective extraction time and reaches to 97.3% while using five-stage modules. The recovery yield of La(III) from simulation La-bearing wastewater was 90.6%.

Keywords: microemulsion; preparation; lanthanum; extraction; wastewater; hollow fiber contactor

1. Introduction

Rare earth elements comprise the fifteen elements of the lanthanide series as well as yttrium, among the rare earth elements, lanthanum (La) is one of the most common rare earths found in nature and of high commercial interest of all rare earths (Panda *et al.* 2016). Nowadays, La has been widely used in many industries such as organic synthesis (catalysts), semi-conductor and ceramic industries, the waste water emanating from these industries are often associated with high concentrations of La(III). Therefore, there is a scope to recover La(III) from La-bearing waste water (Devlina *et al.* 2014).

Over the past decades, different conventional methods had been proposed for the recovery of La(III), such as co-precipitation, adsorption, solvent extraction, ion-exchange, and solid-phase extraction. Ion-exchange and solvent extraction are the two most common methodologies for the recovery of La(III) from aqueous solutions. The ion exchange technique is based on the selective formation of La(III)-anionic complex which is separated by strong anion exchange resin. On the other hand, liquid-liquid extraction method is based on the selective extraction of La(III) in the organic phase using extractant (Biswas *et al.* 2014). Although the conventional solvent extraction process has been in use since many years, it suffers from several limitations, such as the restriction of thermodynamic

equilibrium, tedious multistep extraction, phase separation, stripping and scrubbing operations as well as the solvent loss, emulsion formation. In this regard, these drawbacks can be overcome by dispersion-free extraction using immobilized support liquid membrane (SLM) (Chen *et al.* 2017) or emulsion liquid membrane (ELM) in hollow fiber contactor (HFC) (Adya *et al.* 2013, Bieluszka *et al.* 2014, Pabnya *et al.* 2017, Ansari *et al.* 2016, Chen *et al.* 2018, Yadav *et al.* 2018). Although such HFC-based dispersion-free extraction processes may result in a slower rate of mass transfer compared to traditional operation if membrane resistance is more significant, it could compromise possible advantages such as the mass transfer rate offered by higher surface area/volume associated with microporous hollow-fiber modules. Apart from those, such membrane contactors present several advantages: (i) no direct mixing of the aqueous and organic phases, eliminating emulsion formation, phase entrainment and downstream phase separation, (ii) no limitation on the phase flow rate ratio, the capability of treating a large amount of dilute solutions is available, and (iii) there is greater flexibility in equipment configuration (Juang and Huang 2000, Guell *et al.* 2008, Shen *et al.* 2009, Alguacila *et al.* 2011, Agarwal *et al.* 2015, Sribudda *et al.* 2016).

ELM is a multiple water-in-oil-in-water (W/O/W) emulsion system stabilized by emulsifier, the innermost phase is usually an aqueous phase (stripping solution), the intermediate phase is a membrane phase containing the organic extractant in a suitable diluent along with a surfactant to stabilize the emulsion droplet and the outer phase is aqueous feed solution. ELM is an efficient technique for the extraction of heavy metal ions and has the

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advantages of high mass transfer and simultaneous extraction (at the outer interphase) and stripping (at the inner interphase) in the same system over solvent extraction (Anitha *et al.* 2015). Even so, ELM still suffers from the main shortcomings of the emulsion breakage and emulsion swelling in the process (Ahmad *et al.* 2013, 2016, Biswas *et al.* 2014, Berrama *et al.* 2015).

Microemulsions are dispersions of either ‘water in oil (W/O)’ or ‘oil in water O/W’ stabilized by pure or mixed amphiphiles. They are thermodynamically stable with optically isotropic and normally of low viscosity. Microemulsions have proved to be promising for the extraction of metals from aqueous solution, such mercury (Larson, *et al.* 1994), gallium and heavy metals (Dantas *et al.* 2002, 2003), cobalt (Zhu *et al.* 2006, Jie *et al.* 2018), nickel (Yang *et al.* 2008), gold (Lu *et al.* 2002, Tong *et al.* 2012), thorium(IV) (Gao *et al.* 2002), Re(VII) (Lou *et al.* 2015, 2016), precious metals (Zheng *et al.* 2016, Nguyen *et al.* 2017), and Fe, Co, Ni, Cu (Nataliya *et al.* 2018). However, the microemulsions used for extraction reported in literatures were mainly ionic microemulsion without extractants and stripping agent, thus the extraction efficiency is restricted by thermodynamic equilibrium and require tedious re-extraction as the solvent extraction.

In this study, a new W/O nonionic microemulsion system (MEs) with extractant and stripping agent was prepared. The microemulsion was composed of the six components: OP-4 [polyoxyethylene (4) nonylphenol], OP-7 [polyoxyethylene (7) nonylphenol], 1-hexanol, D₂EHPA (di-2-ethylhexyl phosphonic acid), kerosene and HCl solution. The OP-4 and the OP-7 are oil-soluble nonionic surfactants and used as the emulsifier. The 1-hexanol was used as co-surfactant. The D₂EHPA was used as the mobile carrier, which is the acidic phosphorus-containing extractant and has been widely used for the extraction and separation of individual rare earths including lanthanum. The kerosene was used as the dilute solvent and the HCl solution was acted as the stripping reagent in the receiving phase (i.e., internal phase) of W/O microemulsion. The as-prepared MEs was applied in the recovery of lanthanum from simulation La-bearing wastewater. The recovery of lanthanum was carried out in the polysulfone HFC. Until the present time, the use of W/O nonionic microemulsion containing D₂EHPA for La(III) extraction from aqueous solution has rarely reported.

2. Experiments

2.1 Chemicals and materials

OP-4 of technical grade (>97%) and OP-7 of technical grade (>97%) were provided by Jiangsu Hai'an Petrochemical Plant (Jiangsu, China) and used without any purification. D₂EHPA (>95%) was obtained from Shuanghai Chemical Reagent Corporation (Shanghai, China). All other chemicals were of analytical reagent grade and purchased from Shuanghai Chemical Reagent Corporation. Sulfonate kerosene was purchased from China National Petroleum Corp.

La-bearing feed solution was prepared by dissolving

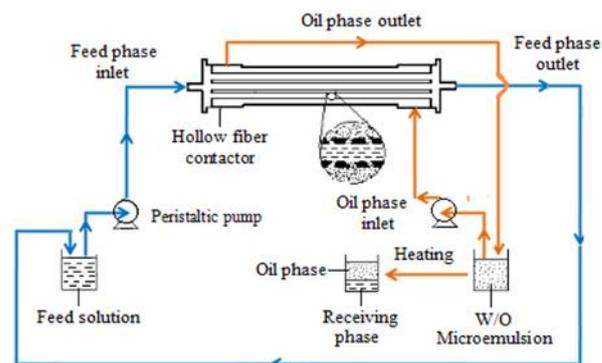


Fig. 1 Single-stage HFLM module for La(III) extraction in a counter-current flow model

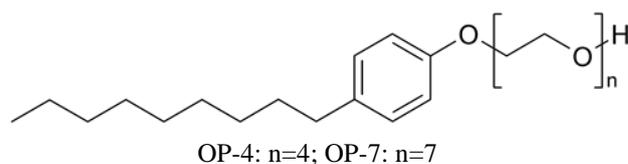


Fig. 2 Molecular structure of polyoxyethylene(n) nonylphenol

LaCl₃·7H₂O in 0.1 mol·L⁻¹ HCl solution. To maintain a constant H⁺ concentration gradient between the feed solution and the receiving phase, the initial feed solution was adjusted to around pH 5 using 1 mol·L⁻¹ NaOH solution and CH₃COONa as buffer agent was added in the feed solution at 10 g per liter. The polysulfone HFC was purchased from Tianjin Lanshizi membrane technology Corp. P. R. China. The main specifications of the hollow fiber contactor are as follows: Inner diameter of membrane (2r₁) 0.4 mm, Outer diameter of membrane (2r₂) 1.2 mm, Molecular Weight Cut Off (MWCO) 50 kDa, Porosity 0.43, Inner diameter of contactor (2r₃) 4 cm, Length of hollow fiber (L) 30 cm, Number of hollow fibers (N), 300.

2.2 Preparation of W/O microemulsion

In the present paper, all the experiments were conducted at room temperature (25°C) unless otherwise stated. Samples of W/O microemulsions were prepared by mixing the required amounts of OP-4, OP-7, 1-hexanol, D₂EHPA, kerosene and HCl solution and stirred well, the optically clear W/O microemulsions were obtained after resting in balance for 24 h.

2.3 Extraction procedure

Fig. 1 shows the single-stage module for La(III) extraction with W/O EMs within a hollow fiber contactor. Generally, feed solution flow through the lumen of the hollow fibers, while the W/O EMs flow outside the hollow fibers in a counter-current flow model. The flow rate was controlled by the speed of the pump. After the extraction, the W/O EMs was heated to 60°C until a clear lower phase appeared. The concentration of La(III) in the lower layer (i.e., the receiving phase) and raffinate were determined

using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Optima 5300DV PerkinElmer Inc., USA). The extraction yield and enrichment fold were calculated using the following equations.

$$E = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$F = \frac{C_i}{C_0} \quad (2)$$

where E represents extraction yield, F stands for enrichment fold; C_0 , C_i , and C_t are the initial feed concentration, receiving phase concentration and raffinate concentration of La(III), respectively.

3. Results

3.1 Effect of weight ratio of OP-4/OP-7 on the HCl solution solubilization capacity

The water solubilization capacity of in microemulsion is an important parameter of W/O microemulsion system, which is of fundamental importance for various applications. For the goal of extraction of La(III) from aqueous solution, a higher solubilization capacity of HCl solution can improve the extraction efficiency, so the major assessment criterion to evaluate the nonionic microemulsion system is the solubilization capacity of HCl solution ($W_{0,HCl}$). The nonionic surfactants of OP-4 and OP-7 applied in this work are polyoxy ethylene nonylphenol with a different proportion of ethoxythene groups, their hydrophilic-lipophilic balance (HLB) are 8.9 and 11.7, respectively. Their chemical structural formula of OP-4 and OP-7 are expressed as follows in Fig. 2.

There is a strong hydrogen bond between the oxyethylene group (C_2H_4O-) and the water molecule and H^+ ions, so the water or aqueous solution can spontaneously solubilization in surfactant micelle and form W/O microemulsion. The $W_{0,HCl}$ depended on the number of ethoxythene groups, the more ethoxythene groups, the greater the water solubilization capacity. The preliminary experiment showed that single surfactant of OP-4 or OP-7 did not necessarily produce the expected microemulsion, because the $W_{0,HCl}$ of OP-4 was too small, the OP-7 had a larger $W_{0,HCl}$ but easy to form the O/W microemulsion. Thereby, the using of mixture of OP-4 and OP-7 was considered. Meanwhile, was observed that the addition of a certain proportion of 1-hexanol and D₂EHPA could promote the formation of clear W/O microemulsion. Herein, to prepare a W/O microemulsion suitable for extraction, 40 wt% (OP-4+OP-7), 10 wt% D₂EHPA and 10 wt% 1-hexanol were mixed together with 40% kerosene. The optimization of the weight ratio of OP-4 to OP-7 (R_s) was conducted by determined the $W_{0,HCl}$, which was detected visually as the transition from a transparent to cloudy within 30 min upon addition of a small amount of excess HCl solution. The relationship of $W_{0,HCl}$ with R_s is shown in Fig. 3. We can see that the $W_{0,HCl}$ increased with the increase of

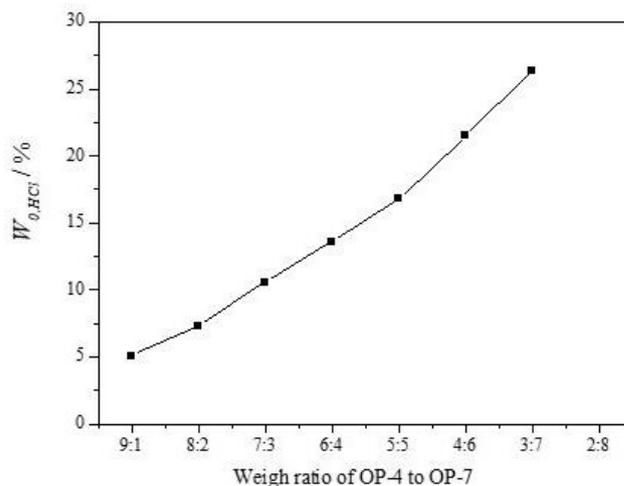


Fig. 3 Relationship between $W_{0,HCl}$ with weigh ratio of OP-4 to OP-7

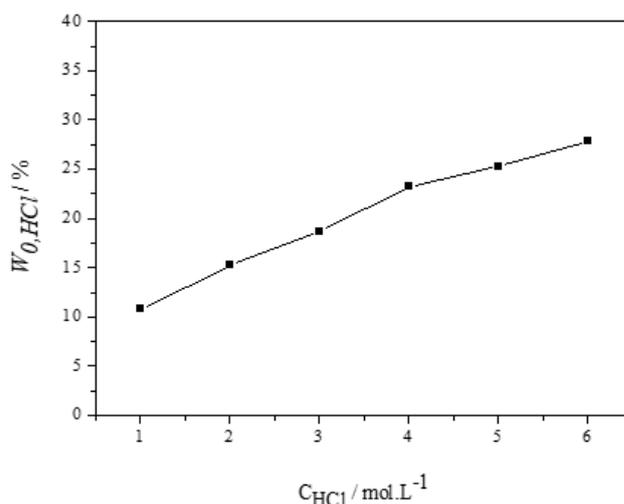


Fig. 4 Relationships between $W_{0,HCl}$ and HCl concentrations

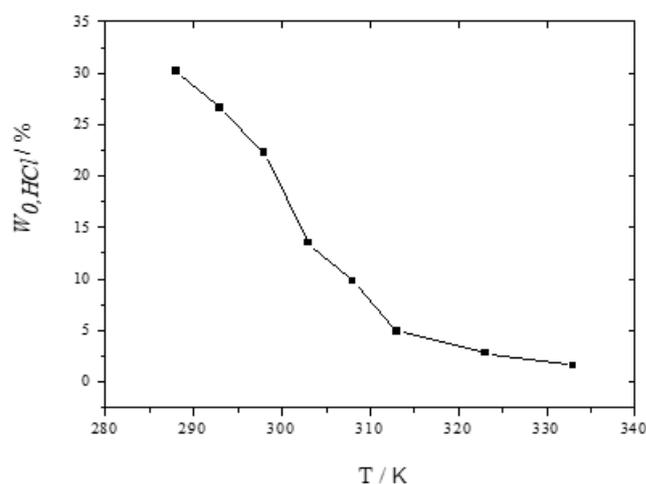


Fig. 5 Relationships between $W_{0,HCl}$ and temperature

the proportion of OP-7, this is a predictable rational result. However, it was found that while the $R_s \cong 4:6$, W/O microemulsion was easily transfer to O/W microemulsion,

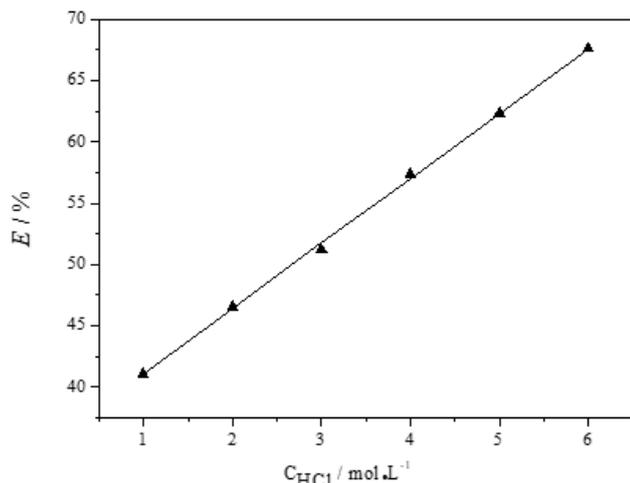


Fig. 6 Relationships between La(III) extraction yield and HCl concentration

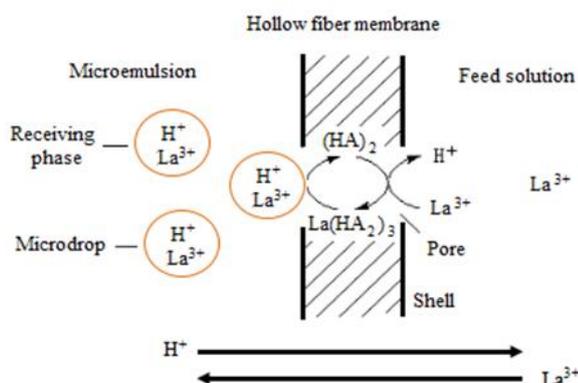


Fig. 7 Transport mechanism illustration of La^{3+} using W/O microemulsion

therefore, the right R_s was chosen as 4:6 to prepare the W/O microemulsion for extraction.

3.2 Effect of HCl concentration on the solubilization capacity of HCl solution

The HCl solution acted as the receiving phase in W/O microemulsion. As shown in Fig. 4, the $W_{0,HCl}$ increased with the increase of HCl concentration, indicating that HCl concentration has a great effect on the $W_{0,HCl}$. This may be attributed to the strong hydrogen bonding interaction between the oxyethylene group and the hydrated H^+ ions.

3.3 Effect of temperature on the solubilization capacity of HCl solution

Fig. 5 shows the relationship between the $W_{0,HCl}$ and the temperature. The result indicated a significant decrease in $W_{0,HCl}$ with the increase of temperature, and dropped almost to zero at 333 K. In other words, almost thorough phase separation occurred at 333 K for the prepared microemulsion, meaning that the receiving phase containing enriched target solutes can be collected while the microemulsion is heated at 3 after extraction.

3.4 Effect of HCl concentration on the La(III) extraction efficiency

Fig. 6 shows the La(III) extraction yield at different HCl concentrations in the receiving phase (operation conditions: the volumetric flow rates of microemulsion and feed solution were 4 and 12 $\text{mL}\cdot\text{min}^{-1}$ respectively, the La(III) concentration in feed solution (C_0) was $100 \text{ mg}\cdot\text{L}^{-1}$). The extraction yield of La(III) increased linearly with the increasing of HCl concentrations, indicating that HCl concentration has a great effect on the extraction of La(III). The result can be explained from both aspects. On one hand, higher HCl concentration may yield higher $W_{0,HCl}$, which is good for loading more La(III) in the receiving phase; on the other hand, high H^+ ion concentration promotes the La(III) transporting from feed to the receiving phase as described in the following: in a W/O microemulsion, an aqueous pool in the microemulsion is surrounded by an adsorbed surfactant layer at the oil/water interface, which is similar to W/O type coarse emulsion in structure, so it is considered that the extraction mechanism of microemulsion in HFC is the same as emulsion liquid in HFC extraction (Larson *et al.* 1994) that can be described as: (a) Transport of La(III) from feed aqueous to the tube side of the fiber membrane (outer oil/aqueous interface); (b) Formation of the $\text{La}(\text{HA}_2)_3$ complex at the feed aqueous-liquid membrane interface; (c) Diffusion of the complex $\text{La}(\text{HA}_2)_3$ through the membrane pores to the inner oil/aqueous interface; (d) Stripping of the La(III) from the $\text{La}(\text{HA}_2)_3$ complex by the internal phase stripping solution (HCl) and enrichment of the La(III) in the internal phase droplets. The extraction mechanism can be depicted in Fig. 7.

In general, the extraction of La(III) using D_2EHPA is expressed as Eq. (3) (Acharya *et al.* 2015, Panda *et al.* 2016)



where the subscript “org” refers to the oil phase, the item $(\text{HA})_2$ means D_2EHPA predominantly exists as dimers in kerosene due to its strong intermolecular hydrogen bonding. From Eq. (3), it is evident that the extraction of La(III) with D_2EHPA is promoted by increasing the aqueous phase pH, that is to say the H^+ concentration gradient is the driving force for La(III) transporting from feed to the receiving phase, so the greater the HCl concentration in the receiving phase, the higher the La(III) extraction rate and enrichment fold.

3.5 Effect of La(III) concentration in feed on the extraction efficiency

It is generally accepted that the ELM technique is well-suited for extraction in dilute solutions. Table 1 presents the La(III) concentrations in raffinate (C_r) and in receiving phase (C_i), the extraction yield and the enrichment-fold when the La(III) concentration in feed changed in the range of 25–400 $\text{mg}\cdot\text{L}^{-1}$. The extraction experiment was carried out under the conditions: the HCl concentration in the receiving phase was $4 \text{ mol}\cdot\text{L}^{-1}$, the volumetric flow rates of microemulsion and feed aqueous

Table 1 Data of La(III) extraction at different initial La(III) concentrations in feed

| C_0 [mg·L ⁻¹] | C_f [mg·L ⁻¹] | C_i [mg·L ⁻¹] | E / % | F |
|-----------------------------|-----------------------------|-----------------------------|---------|------|
| 25 | 4.2 | 712.2 | 83.2 | 28.5 |
| 50 | 10.4 | 1080.5 | 79.2 | 21.6 |
| 100 | 26.3 | 1560.2 | 73.7 | 15.6 |
| 200 | 63.8 | 2322.6 | 68.1 | 11.6 |
| 300 | 110.1 | 2756.6 | 63.3 | 9.2 |
| 400 | 166.0 | 3166.8 | 58.5 | 7.9 |

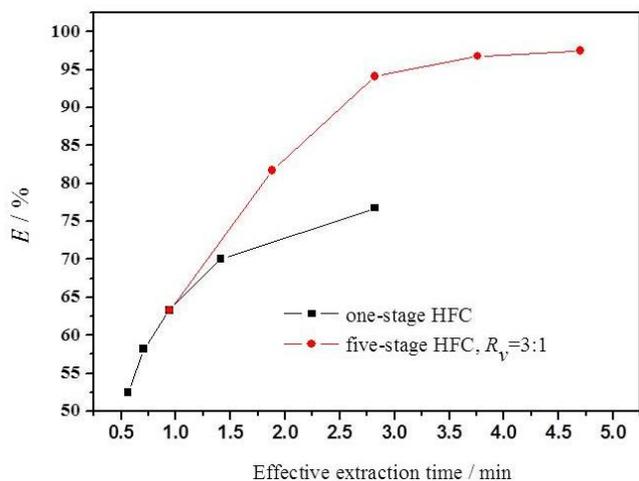


Fig. 8 Plot of La(III) extraction yield and effective extraction time

solution were 4 and 12 mL·min⁻¹ respectively. As illustrated in Table 1, the lower the La(III) concentration in feed, the higher the extraction rate and enrichment-fold.

3.6 Effect of flow ratio of feed solution to microemulsion on La(III) extraction efficiency

The variation of flow ratio of feed solution to microemulsion (R_v) will cause the change of extraction time between the feed and microemulsion and ultimately influence the effective extraction yield. To investigate the effect of flow rate on the La(III) extraction efficiency, the volumetric flow rate of microemulsion was fixed at 4 mL·min⁻¹, the flow ratio of feed solution to microemulsion (R_v) changed from 5:1 to 4:1, 3:1, 2:1, 1:1, the other parameters were: $C_{HCl} = 4$ mol·L⁻¹, $C_0 = 100$ mg·L⁻¹. As an example, $Q_w = 20$ mL·min⁻¹, $R_v = 5:1$, the effective extraction time (t) in one HFC can be obtained by Eq. (4),

$$t = \frac{L}{u_w} = \frac{L}{Q_w / (\pi r_i^2 N)} = \frac{30}{20 / (3.14 \times 0.02^2 \times 300)} = 0.564 \text{ min} \quad (4)$$

where u_w is the flow rate of feed solution (cm·min⁻¹), Q_w is the volumetric flow rate of feed solution (mL·min⁻¹), and N is the number of hollow fibers, $N=300$. Accordingly, the effective extraction time at different R_v can be obtained. The relationship of La(III) extraction yield and the effective extraction time is shown in Fig. 8 (black line), one can see from Fig. 8 (black line) that the La(III) extraction yield

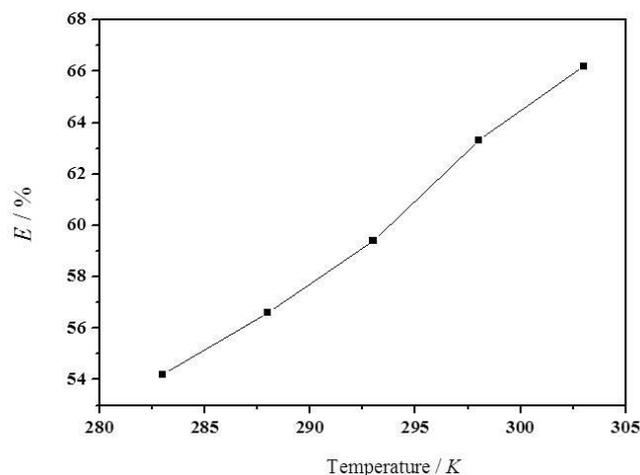


Fig. 9 Plot of La(III) extraction yield vs. temperature

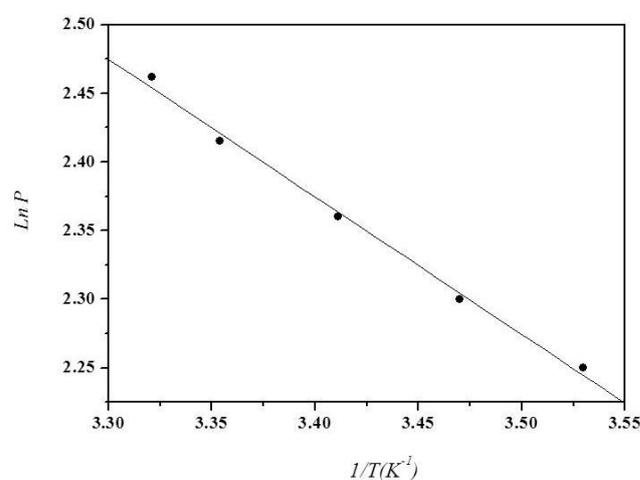


Fig. 10 Plot of lnP vs. 1/T

increased with the increase of the effective extraction time, the maximum yield was 76.8%. Further study was performed using five-stage modules, and the results shown in Fig. 8 (red line) indicating that the maximum yield reached 97.3%, at the same time, the La(III) concentration in the receiving phase was determined to be 3025 mg·L⁻¹, which was 30.25 folds compared with its initial feed concentration.

3.7 Effect of temperature on La(III) extraction efficiency

The influence of temperature on La(III) extraction is shown in Fig. 9. It indicates that the extraction yield increased with the increase of temperature in the range of 283 to 303 K. By means of the extraction yield of La(III) at different temperatures, the value of the permeation activation of the extraction process can be calculated, which may help to identify the controlling step of the extraction.

The apparent permeation coefficient P is calculated as follows (Ortiz *et al.* 2001):

$$P = \frac{E \times Q_w}{\pi d_i L N} \quad (5)$$

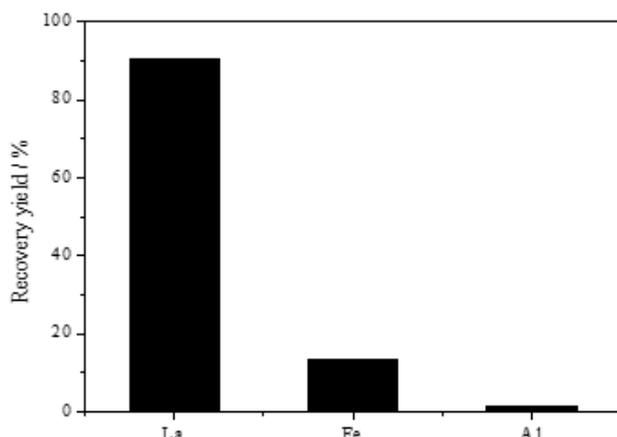


Fig. 11 The recovery yield of La(III), Fe(III) and Al(III) from simulation wastewater

where d_i and L are the inner diameter and the effective length of hollow fiber, respectively.

Considering the extraction as a permeating activated process, the relationship between the apparent permeation coefficient and temperature abides the Arrhenius equation shown below:

$$\ln P = -\frac{E_p}{RT} + \ln P_0 \quad (6)$$

where E_p indicates the permeation activation energy, P_0 is the pre-exponential factor, and R is the gas constant.

Fig. 10 represents the linear relationship between $\ln P$ and $1/T$ which agrees with Eq. (6). The fitting linear regression equation is: $\ln P = 5.7824 - 1.0023/T$. From the slope of the line, the permeation activation energy E_p was obtained to be $8.33 \text{ kJ}\cdot\text{mol}^{-1}$. This value is much lower than the reaction activation energy, which, on an average, is around 40 to $50 \text{ kJ}\cdot\text{mol}^{-1}$. This suggests that the diffusion of La^{3+} ions from the bulk solution to the interface of the membrane, and the permeation of La(III)—D₂EHPA complex through the porous fiber membrane, are not the rate-controlling steps of the extraction process, the complexation reaction between La(III) and D₂EHPA is the rate-controlling step.

3.8 Recovery of lanthanum from simulation La-bearing wastewater

The recovery of rare elements had attracted attention of many scholars in the last years. One example is the recovery of lanthanum from fluid catalytic cracking catalysts (FCCC) via hydrometallurgical processes. The major ingredient of FCCC is La(III), Al(III) and Fe(III) (Innocenzi *et al.* 2015). Similarly, the simulation wastewater containing La(III), Al(III) and Fe(III) (100 mg/L, 500 mg/L, 50 mg/L, respectively) was prepared by dissolving their corresponding chloride salts. The recovery experiment was conducted using five-stage modules under the following conditions: $Q_{org}=4 \text{ mL}\cdot\text{min}^{-1}$, $Q_w=2 \text{ mL}\cdot\text{min}^{-1}$. The result is illustrated in Fig. 11. It is observed that the recovery yield of La(III) reached 90.6%, while the recovery yield of Fe(III) and Al(III) that were the main impurity were 13.2% and

1.3%, respectively, showing a good recycling and separation for La(III) with the other two elements, and suggesting that this extraction method using as-prepared nonionic W/O microemulsion in HFC may be a feasible approach for the recovery of lanthanum from La-bearing wastewater.

4. Conclusions

The preparation of a W/O nonionic microemulsion system consisting of OP-4 and OP-7, 1-hexanol, D₂EHPA, kerosene and HCl solution and its application for the extraction of La(III) from chloride aqueous solution have been studied in this paper.

- A six-component water-in-oil nonionic microemulsion consisting D₂EHPA are prepared.
- The weight ratio of OP-4 to OP-7, the HCl solution concentration and the temperature has a great effect on the $W_{0,HCl}$. the Optimum weight ratio of OP-4 to OP-7 is 4:6.
- The extraction yield of La(III) increases with the increasing of HCl solution concentration, the temperature and the effective extraction time.
- The extraction percentage of 97.5% and enrichment folds of 30.25 of La(III) are obtained while using five-stage modules.
- The recovery yield of La(III) from simulation La-bearing wastewater reaches 90.6%.

Acknowledgments

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- R_v flow rate ratio of feed solution to microemulsion
- t effective extraction time (min)
- u_w flow rate of feed solution ($\text{m}\cdot\text{s}^{-1}$)
- $W_{0,HCl}$ solubilization capacity of HCl solution in microemulsion

CC

Notation

- C_0 initial concentration of metal ions in feed solution ($\text{mg}\cdot\text{L}^{-1}$)
- C_i concentration of metal ions in receiving phase ($\text{mg}\cdot\text{L}^{-1}$)
- C_r concentration of metal ions in raffinate ($\text{mg}\cdot\text{L}^{-1}$)
- d_i inner diameter of hollow fiber (m)
- E extraction yield
- E_p permeating activation energy ($\text{KJ}\cdot\text{mol}^{-1}$)
- F La(III) enrichment fold in receiving phase
- L hollow fiber length (m)
- N number of hollow fibers
- Q_{org} volumetric flow rate of organic phase ($\text{m}^3\cdot\text{s}^{-1}$)
- Q_w volumetric flow rate of feed solution ($\text{m}^3\cdot\text{s}^{-1}$)
- P permeating coefficient ($\text{m}\cdot\text{s}^{-1}$)
- P_0 pre-exponential factor
- R gas constant ($\text{KJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
- R_s weigh ratio of OP-4 to OP-7