Study on a novel flat renewal supported liquid membrane with D2EHPA and hydrogen nitrate for neodymium extraction

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Abstract: The Nd(III) extraction in flat renewal supported liquid membrane (FRSLM), with polyvinylidene fluoride membrane and renewal solution including HNO\(_3\) solution as the stripping solution and di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in kerosene as the membrane solution, was investigated. The effects of pH in the feed phase, volume ratio of membrane solution to stripping solution, concentration of HNO\(_3\) solution and concentration of carrier in the renewal phase on extraction of Nd(III) were also studied, respectively. As a result, the optimum extraction conditions of Nd(III) were obtained when concentration of HNO\(_3\) solution was 4.00 mol/L, concentration of D2EHPA was 0.100 mol/L, and volume ratio of membrane solution to stripping solution was 1.00 in the renewal phase, and pH was 4.60 in the feed phase. When initial concentration of Nd(III) was 2.00×10\(^{-4}\) mol/L, the extraction percentage of Nd(III) was up to 92.9% in 75 min.

Keywords: membrane extraction; flat renewal supported liquid membrane; di(2-ethylhexyl) phosphoric acid; neodymium; extraction flux; rare earths

Rare earth metals being used alone or in the form of mischmetals are widely used. The performance of alloys can be greatly improved by adding appropriate amount of rare earth metals or their compounds. Therefore, rare earth elements are also known as the vitamin of metallurgical industry\(^{[1]}\). For example, after being added with a number of rare earth elements in steel, the plasticity, heat resistance, toughness, oxidation resistance, abrasive resistance and corrosion resistance of the steel can be increased. The rare earths can be used to make pyrophoric alloys, permanent magnetic materials, dyeing materials, superconducting materials, luminescent materials, trace element fertilizer and so on. Therefore, rare earth metals have not only been widely used in metallurgy, petrochemical industry, glass ceramics, fluorescent materials, electronic materials, medicine and agriculture, but also gradually penetrated into many areas of modern science and technology. As the application is more and more extensive in the production and life, it is very necessary to separate and enrich the rare earth elements. Many people at home and abroad have made researches in this area recently\(^{[2-6]}\).

Liquid membrane extraction of rare earth metals is characterized by a short process, high speed, great enrichment ratio, little reagent-consuming and low cost, which has broad industrial application prospect. In China, the research in this area began in the early 1980’s. Organic solvents to extract liquid membrane system of rare earth metal ions were dissolved with kerosene or common sulfonated kerosene, supporter used LA, P204, P507 and so on, internal phase used hydrochloric acid, nitric acid, sodium hydrate and so on. Leaching liquid of rare earths can be grouped, purified and extracted under the necessity\(^{[7]}\).

Konda used double stearic acid and phosphate base as a carrier to study supported liquid membrane (SLM) system to purify rare earth Sm and to establish a migration model\(^{[8]}\). Lee used polypropylene porous membrane as supported membrane and PC-88A as a carrier to establish supported liquid membrane system to purify rare earth element europium(III) and to establish the supported liquid membrane system and a mathematical model of migration process of Co(II)\(^{[9]}\). Yahaya and coworkers used composite supported liquid membrane to deal with La in rare earth wastewater\(^{[10]}\). In recent years, Yi and others studied on flat sandwich SLM system, tested experimentally permeability coefficient to extract La\(^{3+}\), compared the differences of supported membrane with different materials and thickness in extraction, and investigated extraction percentage and stability of liquid membrane system\(^{[11]}\).

SLM is a simple one of the operations without the expensive surfactants. However, the contradiction between the decline of membrane stability caused by the membrane solution (organic solvent, extraction agents and modifiers) dissolved in aqueous phase and high transmission flux has still been not well solved\(^{[12]}\). As for SLM problems, some experts
at home and abroad have turned to explore new liquid membrane configuration in recent years. They wanted to maintain characteristics of membrane extraction, at the same time to overcome the shortcomings of instability of supported liquid membrane. Therefore, supported liquid membrane with renewal phase and combination technique had been proposed\[13–16\]. It combined solid membrane or various chemical processes with liquid membrane, which can effectively overcome the leakage problem of the carrier from membrane phase in supported liquid membrane and supply carrier to the membrane support. In this work, renewal phase and supported liquid membrane were combined, and flat renewal supported liquid membrane (FRSLM) were proposed\[17\].

There was no report on FRSLM for Nd(III) extraction. This is a new liquid membrane process with several advantages: increased stability of the membrane, reduced costs, increased simplicity of operation, extremely efficient stripping of the target species from the organic phase to obtain high flux and a high concentration of the recovered target species in the stripping solution. It is mainly to investigate and study the extraction feasibility of flat renewal supported liquid membrane and dispersion of Nd(III), achieve the extraction of rare earth metal through the membrane vector optimization, module design, extraction percentage control and other aspects, study extraction process of rare earth metals, and establish new methods and new system of flat renewal supported liquid membrane extraction of rare earth metals, which is expected to achieve a breakthrough in research area and industrial applications.

1 Experimental

1.1 Reagent

All the reagents such as Nd(CH₃COO)₃·4H₂O, arsenazo III (C₂₂H₁₈As₂O₁₄N₄S₂), HNO₃, NaH₂PO₄, Na₂HPO₄, CH₃COONa, CH₃COOH, etc. used in the present work were of analytical grade. Di(2-ethylhexyl) phosphoric acid (D2EHPA) is a commercial extractant and used without any further purification. Kerosene was washed with concentrated sulfuric acid.

1.2 Experimental procedure and detection

The Nd(III) measurements for the FRSLM were performed as follows: the experiments were accomplished at 20 ± 2 °C with a simple diffusion flat cell. The diffusion flat cell consisted of two-compartment perspex flat half-cells. Two half-cells were separated by the membrane (Fig. 1). The membrane was impregnated with D2EHPA dissolved in kerosene and clamped between the two half-cells. The effective volume of each flat half-cell is 100 ml. A microporous PVDF membrane was used as a solid support. It had a 75 μm thick film with a nominal porosity of 75% and a tortuosity of 1.67. The effective area is 20 cm². The feed phase in feed pool (150 ml) consisted of Nd(III) and buffer solution, and was poured into the perspex half-cell from feed pool with pump. The flow rates of two pumps were all 10.8 ml/min. The mixed renewal phase in renewal pool (80 ml) consisted of the different volume ratios of the membrane solution containing the carrier D2EHPA and HNO₃ stripping solution was placed into another half-cell from renewal pool with pump. Samples of the feed phase were taken at timed intervals from feed pool. The pumps of two phases were stopped until phase extraction occurred. Then the Nd(III) sample from the renewal phase was collected. Samples containing Nd(III) in the feed phase only were analyzed for ion concentration with a UV-1200 spectrophotometer using Arsenazo III as the chromogenic agent (under the detection wave length 653 nm).

1.3 Experimental principle and theoretical analysis

Fig. 2 is the principle of FRSLM process, in which concentration change and extraction processes are depicted. The co-extraction involves various equilibrium reactions, which are described as follows:

(a) Nd(III) diffuses from the feed phase to the interface M.

(b) On the feed side interface of the SLM, the extraction of Nd(III) from feed solution with carrier D2EHPA (can be as (HR)₂) in kerosene can be expressed as\[18,19\]:

\[
Nd^{3+} + 3(HR)\_{m} \xrightarrow{K_{f}} NdR\_{3}(HR)\_{m} + 3H^{+}
\]

where m and f stand for membrane phase and feed solution, respectively; (HR)₂ indicates that the D2EHPA in kerosene mainly exists as a dimer; K_f and K_f⁻ stand for forward and backward reaction percentage constant at the interface between the feed phase and membrane phase.

(c) The metal-complex (NdR₃(HR)₃) diffuses through the membrane M-N.

(d) At the stripping side interface N, the NdR₃(HR)₃ dissolved in membrane solution and the Nd(III) are stripped by stripping agent. In the interphase of the drops of the stripping phase and the organic phase, the interchange between Nd(III) loaded in the organic phase and the H⁺ of the stripping phase
occurs, then the Nd(III) diffuse to the bulk of the stripping phase and the extractant regenerates. The stripping reaction can be written as follows:

\[
\text{NdR}_{3}(HR)_{3m} + 3H^{+} \overset{K_{-2}}{\underset{K_{2}}{\leftrightarrow}} \text{Nd}^{3+} + 3(\text{HR})_{2m}
\]  

where \( s \) represents the renewal phase; \( K_{2} \) and \( K_{-2} \) stand for forward and backward reaction rate constant at the interface \( N \).

(e) Carrier D2EHPA returns from \( N \) to interface \( M \).

According to Ref. [3], equation of permeability coefficient can be defined as:

\[
P_{c} = \frac{1}{d_{f} + \frac{d_{m} \varepsilon K_{e} [\text{HR}]}{D_{l} + D_{m} \tau [\text{H}^{+}]^{2}}}
\]

where \( D_{l} \) stands for the diffusion coefficient of Nd(III) in the membrane, \( d_{l} \) stands for the thickness of diffusion layer between the feed phase and the membrane phase, \( D_{m} \) stands for the coefficient of Nd(III) in the membrane, and \( d_{m} \) stands for thickness of the membrane, respectively. The \( \tau \) and \( \varepsilon \) stand for tortuosity and porosity of membrane, respectively.

The flux was measured as\(^{[20]}\)

\[
J = \frac{\Delta c \times V_{m}}{A \times \Delta t}
\]

where \( J \), \( \Delta c \), \( V_{m} \), \( A \) and \( \Delta t \) stand for membrane flux [mol/(s·m²)], concentration change of Nd(III) (mol/L), solution volume in feed or strip (L), effective membrane area (m²) and time interval (s), respectively.

2 Results and discussion

2.1 Effect of volume ratio of membrane solution to stripping solution

With the decreasing of the volume ratio, the membrane solution decreases and stripping solution increases, that is to say, stripping rate increases and complexing rate decreases. Likewise, with the increasing of the volume ratio, the membrane solution increases and stripping solution decreases, that is to say, stripping rate decreases and complexing rate increases. The extremely high stripping rate with extremely low rate of complexing or extremely high rate of complexing with extremely low stripping rate are not beneficial to extraction behaviour of Nd(III). So choosing proper volume ratio is necessary.

The effect of volume ratio of membrane solution to stripping solution in the renewal phase on extraction of Nd(III) was studied. The assumed experimental conditions chosen were in the certain pH in the feed phase, which was adjusted to 3.80. Initial concentration of Nd(III) was 2.00 × 10⁻⁴ mol/L in the feed phase, the concentration of HNO₃ solution was 3.00 mol/L and the concentration of D2EHPA was 0.160 mol/L in the renewal phase. The effect of volume ratio of membrane solution to stripping solution in the renewal phase on extraction of Nd(III) is shown in Fig. 3. The volume ratio was increased from 0 to 2.50. It can be seen that the most effective volume ratio was 1.00, which gave a extraction flux of Nd(III) much higher than others.

This indicates that the extraction flux of Nd(III) increases with the increasing of the volume ratio in the renewal phase. When volume ratio in the renewal phase increases, the droplets of the renewal solution disperse obviously in the mem-
brane phase and the chances of contacting between D2EHPA and Nd(III) increase. In this way, the mixing of the membrane phase and renewal phase provides an extra stripping surface and renewal percentage of liquid membrane, which leads to extremely stripping percentage for the target species from organic phase and life of liquid membrane. With increasing of the volume ratio, the flux reduced, because H+ decreased in renewal phase. We chose 1.00 as the optimum volume ratio of membrane solution to stripping solution in the renewal phase during the following experiments.

2.2 Effect of concentration of HNO3 solution in renewal phase

The stripping reaction in the renewal phase plays a vital role in the extraction of metal ion from the feed phase to the stripping phase. So the effect of the concentration of HNO3 solution in the renewal phase on extraction flux of Nd(III) was studied in this section. All the other parameters, such as pH, initial concentration of Nd(III) in the feed phase, volume ratio and concentration of D2EHPA were adjusted to 3.80, 2.00×10^{-4} mol/L, 1.00 and 0.160 mol/L, respectively. The effect of concentration of HNO3 solution in the renewal phase on extraction flux of Nd(III) is shown in Fig. 4. It is indicated that, with the increasing of acid concentration in the renewal phase, the extraction flux of Nd(III) increased. It can be seen that the effective concentration of HNO3 solution for extraction was 3.00 mol/L. Under the condition of concentration of HNO3 3.00 mol/L, the extraction flux of Nd(III) was 27.4×10^{-6} mol/(s·m²).

The increasing of concentration of HNO3 solution from 1.00 to 2.00 mol/L had no significant effect on extraction flux of Nd(III), because the number of Nd(III) complex and the concentration of membrane solution which transfers through the membrane per unit area of the membrane per unit time are definite. However, under the condition of 6.00 mol/L HNO3 solution, the extraction flux was a little lower than 5.00 and 4.00 mol/L, by reason of higher acidity or oxidizability of HNO3 resulting in receding of complexation ability of D2EHPA. Considering controlling acidity as well as increasing extraction flux, we chose 3.00 mol/L as the optimum concentration of HNO3 solution in the renewal phase during the following experiments.

2.3 Effect of pH in feed phase

Based on mechanism of mass extraction process, the concentration difference between feed phase and renewal phase is the driving power of mass extraction process. So in the feed phase the lower the H⁺ concentration is, the stronger the driving power of mass extraction process will be. Stronger power will promote the extraction percentage of Nd(III). Equally, the greater the pH value in the feed phase is, the higher the extraction percentage of Nd(III) is. The effect of pH in the feed phase on extraction of Nd(III) was studied in the pH range of 3.00 to 5.00. Initial concentration of Nd(III) in the renewal phase was 3.00 mol/L, volume ratio of membrane solution to stripping solution was 1.00, and concentration of D2EHPA was 0.160 mol/L in the renewal phase. The results are shown in Fig. 5. The extraction percentage of Nd(III) increased when the pH in the feed phase increased from 3.00 to 5.00, and a maximum extraction percentage observed at pH 4.60 was 93.8% during 75 min. Above the pH of 4.60 in the feed phase, the extraction percentage of Nd(III) was 97.3% during 60 min because the feed phase emulsifies. It is large because the extraction process is mainly governed by the driving power of mass extraction caused by the distribution equilibrium, when the renewal effect of the liquid membrane and the diffusion mobility of Nd(III) ions were determined under specific experimental conditions[19]. As far as our researching conditions are concerned, considering saving chemical agents as well as increasing extraction rate, we chose pH of 4.60 as the optimum
pH condition in the feed phase during the following experiments.

2.4 Effect of concentration of D2EHPA

D2EHPA concentration in the membrane phase and renewal phase also plays a significant role in extraction of Nd(III). Effect of concentration of D2EHPA on extraction percentage of Nd(III) was studied in the D2EHPA concentration range from 0.036 to 0.230 mol/L. The pH value was adjusted to 4.60, initial concentration of Nd(III) was 2.00×10⁻⁴ mol/L in the feed phase, volume ratio of membrane solution to stripping solution was adjusted to 1.00 and concentration of HNO₃ solution was also adjusted to 3.00 mol/L in the renewal phase. The results are shown in Fig. 6. With the increasing of carrier concentration, the extraction percentage of Nd(III) increased, however, when concentration of D2EHPA increased to 0.230 mol/L from 0.160 mol/L, the increasing of extraction percentage was not obvious. Within this concentration of D2EHPA range from 0.036 to 0.230 mol/L in the renewal phase, the availability of D2EHPA at the feed-membrane-renewal interfaces increases with the increasing of concentration of carrier. The positive reaction trend of chemical equilibrium equation is stronger than negative reaction trend. Similarly, when concentration of D2EHPA becomes low, the negative reaction trend is stronger. With the increase of concentration of D2EHPA to a significant extent, the extraction percentage of Nd(III) will no longer increase with time. When the concentrations of D2EHPA were 0.100, 0.160 and 0.230 mol/L, the extraction percentages were 92.9%, 93.8% and 95.1%, respectively. The concentration of D2EHPA was suitable with Nd(III) concentration in membrane phase. When the concentration of D2EHPA in the membrane phase increased in comparison to Nd(III) concentration in the feed phase, there were not enough Nd(III) ions to react with D2EHPA, so the increasing of extraction percentage of Nd(III) will become slow. This indicated that the number of D2EHPA used to Nd(III) transportation through the membrane per unit area of the membrane per unit time are definite, when the initial concentration of Nd(III), the effect area of membrane and time are definite. 0.100 mol/L was chosen as the optimum concentration of carrier. Under the conditions, the extraction percentage of Nd(III) was 92.9% in 75 min.

2.5 Retention in membrane phase

The pH value was adjusted to 4.60, initial concentration of Nd(III) was 2.00×10⁻⁷ mol/L in the feed phase, volume ratio of membrane solution to stripping solution was adjusted to 1.00 and concentration of HNO₃ solution was also adjusted to 4.00 mol/L in the renewal phase. D2EHPA concentration was adjusted to 0.100 mol/L. According to the concentration of Nd(III) in both feed phase and stripping phase, the number of Nd(III) ions in membrane phase can be calculated, then the retention phenomenon of membrane phase can be obtained. As a result, the concentrations of Nd(III) were 1.42×10⁻⁵ and 1.47×10⁻⁴ mol/L in the feed phase and renewal phase, respectively. That is to say some Nd(III) ions are detained in the membrane phase in support and renewal solution.

2.6 Effect of different stripping agents on extraction of Nd(III)

The stripping agent at the membrane-renewal side plays a vital role in extraction of metal ions from feed phase to stripping phase. So the effects of different stripping agents in the renewal phase on extraction of Nd(III) were studied. The effects of different stripping agents in the renewal phase on the extraction percentage of Nd(III) is shown in Fig. 7. Using hydrochloric acid (HCl), sulfate acid (H₂SO₄) and nitric acid (HNO₃) as the stripping agent respectively under the same acidity condition, it was found that the difference of extraction percentage of Nd(III) with three acids is not obvious.

3 Conclusions

Optimum extraction conditions of Nd(III) in the FRSLM system were the concentration of HNO₃ solution 4.00 mol/L, volume ratio of membrane solution to stripping solution 1.00, the concentration of D2EHPA 0.100 mol/L in the renewal phase and pH 4.60 in the feed phase. When initial concentration of Nd(III) was 2.00×10⁻⁴ mol/L, the extraction effect of Nd(III) was very obvious in the optimum condition and the extraction percentage of Nd(III) was up to 92.9% in 75 min. Some Nd(III) ions could be detained in the membrane phase in support and renewal solution.
References:


