

Stripping dispersion hollow fiber liquid membrane containing carrier PC-88A and HNO₃ for the extraction of Sm³⁺

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Received 24 June 2011

Available online 8 November 2011

Abstract

Stripping dispersion hollow fiber liquid membrane system (SDHFLM) containing feed phase adding acetate buffer solution and dispersion solution with HNO₃ solution as the stripping solution and membrane solution of 2-ethyl hexyl phosphoric acid-mono-2-ethylhexyl ester (PC-88A) dissolved in kerosene, has been studied for the extraction of Sm³⁺. Many factors including pH value, volume ratio of membrane solution to stripping solution (O/W) and carrier concentration on Sm³⁺ extraction were investigated. Experimental results indicate that the optimum extraction conditions of Sm³⁺ were obtained as that PC-88A concentration was 0.120 mol/L, and O/W was 1.00 in the dispersion phase, and pH value was 4.80 in the feed phase. When initial Sm³⁺ concentration was 1.20 × 10⁻⁴ mol/L, the extraction percentage of Sm³⁺ was up to 92.8% in 160 min.

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Keywords: Stripping dispersion hollow fiber liquid membrane; 2-Ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester; Samarium; Dispersion phase; Extraction flux; Extraction rate

Rare earth metal has been widely used. It can be used alone, also in mixed form of Re. The performance of the metal alloy can be improved by joining amount of rare earth metals or compound in it. Therefore, rare earth elements are called the vitamin of metallurgical industry [1]. With rare earth elements in production and life, the application of rare earth elements and widely for extraction and enrichment became very necessary, at home and abroad in recent years, there are many agencies in the research of this aspect [2].

Liquid 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 [3].

Currently, there is little report on the use of stripping dispersion hollow fiber liquid membrane system (SDHFLM) for extraction of Sm³⁺. It is mainly to explore and study the extraction feasibility of SDHFLM for Sm³⁺, achieve the extraction of rare earth metal through the membrane module design, vector optimization, extraction percentage control and other aspects, study extraction process of rare earth metals, and establish new methods and new system of SDHFLM for extraction of rare earth metal, which is expected to achieve a breakthrough in industrial applications.

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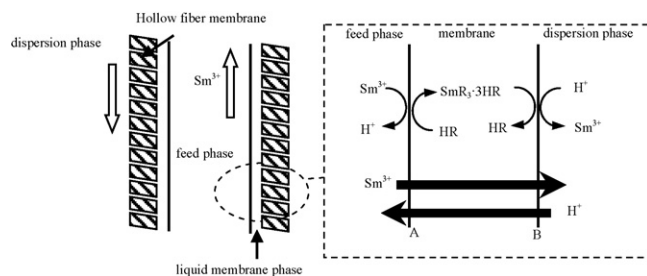


Fig. 1. Schematic principle and description of Sm³⁺ extraction in SDHFLM.

1. Theoretical analysis

Fig. 1 is the principle of SDHFLM process, in which concentration change and extraction processes are depicted. The co-extraction involves various equilibrium reactions, which are described as follows [4,5]: (a) Sm³⁺ diffuses from the feed phase to the interface A. (b) On the feed side interface of the SDHFLM. (c) The metal-complex (SmR₃·3HR) diffuses through the membrane A–B. (d) At the stripping side interface of the SDHFLM, the SmR₃·3HR dissolved in membrane solution and the metal ion Sm³⁺ are stripped by stripping agent. (e) Carrier PC-88A returns from B to A. In this mechanism the transport of Sm³⁺ across SDHFLM will be described by considering only diffusion coefficient of Sm³⁺, because the complex reaction between the Sm³⁺ and PC-88A at the interfaces is much faster compared to the diffusion in the feed phase and membrane phase [4]. To formulate the model, the following assumptions were made: (1) The Sm³⁺ diffuses in the organic medium only as the SmR₃·3HR complex. (2) There is no net flow due to convection within the liquid membrane. (3) The metal ions react only with PC-88A at the membrane interfaces. (4) The PC-88A monomer and dimer are in equilibrium at all times throughout the organic phase. (5) The solubility of PC-88A in the aqueous acid solution has been found to be negligible, therefore, its concentration in the SDHFLM is assumed to remain constant.

2. Experimental

Sm(CH₃COO)₃·4H₂O, Arsenazo III (C₂₂H₁₈As₂O₁₄N₄S₂), HNO₃, NaH₂PO₄, Na₂HPO₄, CH₃COONa, and CH₃COOH, etc. used in the present work were of analytical grade. Di(2-ethylhexyl)phosphoric acid (PC-88A) is a commercial extractant (purity > 95%) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 185–225 °C.

All the experiments were the self-designed systems. The hollow fiber membrane were laboratory scale versions with two 0–1 L/min pumps and flowmeters, which makes it possible to evaluate the performance without having to prepare large amounts of feed, stripping and organic phases, and also to avoid the influence of non-ideal flow in the shell side of the component. Membrane component had a PVDF module of commercial product with a nominal porosity of 65%, a tortuosity of 2.08, effective component length of 20 cm, inner diameter of 8 mm of module with fiber number of 20. Inner diameter of fiber, outer diameter, thickness and effective membrane area of fiber are 0.9 mm, 1.2 mm, 0.3 mm and 188 cm², respectively. Samples containing Sm³⁺ 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 lengths: 653 nm).

3. Results and discussion

Based on mechanism of mass transfer process, the concentration difference between feed phase and dispersion phase is the driving power of mass transfer process [6]. So in the feed phase the lower the H⁺ concentration is, the stronger the driving power of mass transfer process will be. Stronger power will promote the extraction flux of Sm³⁺. Equally, the greater the pH value in the feed phase is, the higher the extraction flux of Sm³⁺ is. The effect of pH in the feed phase on extraction of Sm³⁺ was studied in the pH range of 2.50–5.40. Initial concentration of Sm³⁺ in the feed phase was 1.20 × 10⁻⁴ mol/L. HNO₃ concentration solution was 4.00 mol/L, volume ratio of membrane solution to

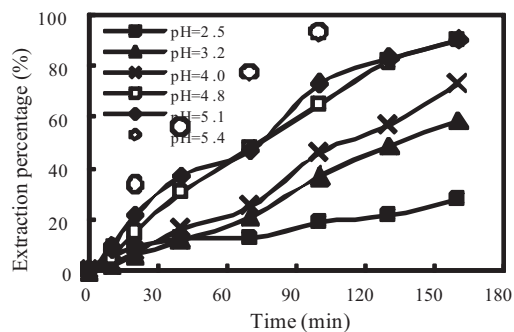
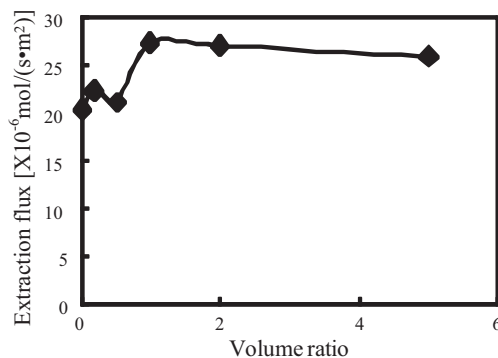


Fig. 2. Effect of pH of the feed phase.

Fig. 3. Effect of volume ratio of membrane solution to HNO₃ solution.

stripping solution (O/W) was 1.00, PC-88A concentration was 0.100 mol/L in the dispersion phase. The results were shown in Fig. 2. So we chose pH of 4.80 as the optimum pH condition in the feed phase for the following experiments.

From Figs. 3 and 4, we chose 1.00 and 0.120 mol/L as the optimum volume ratio of membrane solution to stripping solution (O/W) and concentration of carrier in the dispersion phase. Under the conditions, the extraction percentage of Sm³⁺ was 92.8% during 160 min.

From Fig. 5, we can know the membrane solution can be reused many times after the re-extraction with the strong acid after every condition experiment. According to the concentration of Sm³⁺ in both feed phase and stripping phase, the concentration of Sm³⁺ in membrane phase can be obtained, then the effect of stripping in dispersion phase and retention phenomenon of membrane phase can be obtained. The results were shown in Fig. 6.

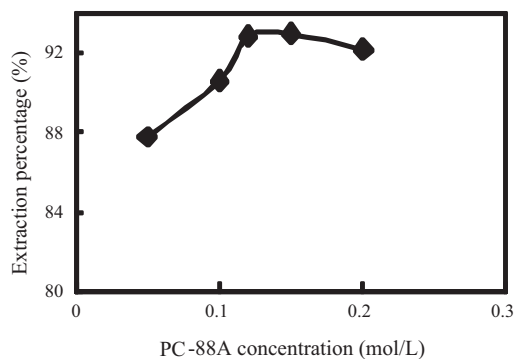


Fig. 4. Effect of carrier concentration.

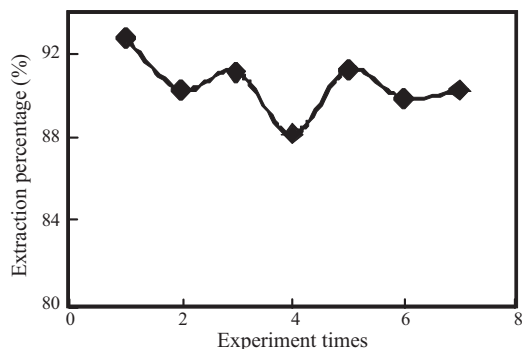


Fig. 5. Reuse effect of membrane solution.

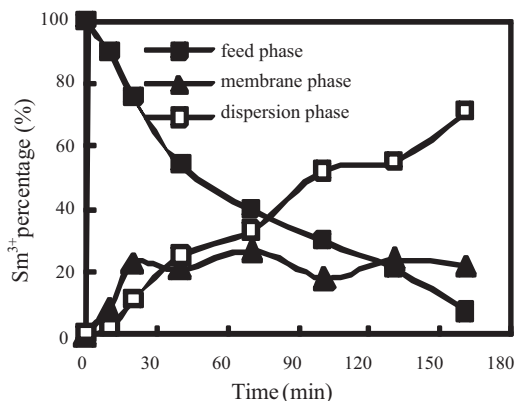


Fig. 6. Retention in membrane phase and effect of stripping.

4. Conclusion

Optimum extraction condition of Sm^{3+} in the SDHFLM system is that the volume ratio of membrane solution to stripping solution (O/W) was 1.00, the concentration of PC-88A was 0.120 mol/L in the dispersion phase, pH value was 4.80 in the feed phase. When initial concentration of Sm^{3+} was 1.20×10^{-4} mol/L, the extraction effect of Sm^{3+} was very obvious in the optimum condition and the extraction percentage of Sm^{3+} was up to 92.8% during the extraction time of 160 min.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China for Young Scientists (Nos. 51109197 and 51009126), the Action Plan for the Development of Western China of the Chinese Academy of Sciences (No. KZCX2-XB2-13), the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KSCX2-YW-N-003), and Research Fund for Excellent Doctoral Thesis of Xi'an University of Technology (Nos. 602-210805 and 602-210804).

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