Studies on yttrium permeation through hollow fibre supported liquid membrane from nitrate medium using di-nonyl phenyl phosphoric acid as the carrier phase

R. Vijayalakshmi [a,*], S. Chaudhury [b], M. Anitha [a], D.K. Singh [a], S.K. Aggarwal [b], H. Singh [a]

[a] Rare Earths Development Section, Materials Group, Bhabha Atomic Research Centre, Mumbai 400085, India
[b] Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

ABSTRACT

The transport behaviour of yttrium from nitrate medium was investigated using dinonyl phenyl phosphoric acid (DNPPA) as a carrier in liquid membrane phase, employing microporous hydrophobic hollow fibre supported liquid membrane (HFSLM) module. The influence of feed composition, carrier concentration, feed acidity, strip acid concentration and flow rate of feed on permeability and flux of Y(III) is discussed. The stripping solution was sulphuric acid solution. Increasing the carrier concentration increased the % transport of yttrium, while an increase in the feed metal concentration decreased the percentage transport. A lower acidity in the feed solution and 3 M H_2SO_4 concentration in the stripping phase are favourable for the transport process due to the increase of mass transfer driving forces. The % transport of yttrium increased with an increase in flow rates up to 100 mL/min. Under optimized conditions of 0.2 M DNPPA, 1 g/L Y(III), 0.05 M feed acidity, 3 M strip acid (H_2SO_4) and 100 mL/min flow rate, the % transport of yttrium was more than 95% in 5 h of operation.

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1. Introduction

High purity rare earths are in great demand for various applications in electronics, automobiles, petrochemical and magnetic materials industry. Yttrium in particular finds applications in superconductors, lasers, phosphors, industrial cutting and welding, distance sensing, photochemistry and digital communication. Apart from these applications, it is used as super alloys with nickel and cobalt in solid oxide fuel cells as well as in yttria stabilized zirconia used as ceramic oxygen sensor. These applications need high purity yttrium oxide as the starting material. The separation of rare earths is very difficult due to similar chemical properties. Solvent extraction (SX) and ion exchange (IX) techniques are mostly employed for their separation and purification (Marple, 1964; Xie et al., 2014). Purification of yttrium employing di-2-ethylhexyl phosphoric acid (D2EHPA), ethylhexyl ethylhexyl phosphonic acid (EHEHPA) etc. has been reported (Singh et al., 2012; Thakur and Mishra, 2000). Though these processes have been applied on industrial scale, they suffer from certain drawbacks like requirement of large number of stages in the SX circuit coupled with careful monitoring of process parameters. In addition, the IX process is tedious and time-consuming and has inherent disadvantage of low through-put. To overcome these limitations, many techniques are being explored. One of the promising techniques which has gained importance is the

use of micro-porous hollow fibre supported liquid membrane (HFSLM) modules for effective metal ion separation from aqueous solutions. This technique offers low capital and operating cost, low energy, less solvent inventory, large membrane interfacial area and high concentration factors. The basic principle of HFSLM is the immobilization of organic extractant into the pores of the hydrophobic membranes due to the wetting characteristics of the membrane. The supported liquid membrane (SLM) separates the aqueous feed solution and stripping solution where the liquid membrane acts as a solvent for the transported solute which is governed by its solubility in the membrane. The permeation of the species proceeds due to the chemical potential gradient or the driving force of the process existing on the two opposite sides of the SLM. The metal ions form a complex with the extractant at the interface. This complex diffuses through the membrane phase to the interface between membrane and the stripping phase, where exchange of rare earth (RE) ions with the counter ions (H^+) takes place. Several works exploring this technique have been published (Wannachod et al., 2011; Gaikwad and Rajput, 2010; Ramakul et al., 2009; Ansari et al., 2008; Bhattacharya et al., 2008; Rathore et al., 2001; Yang et al., 1998). Di-nonyl phenyl phosphoric acid (DNPPA), which is a strong cation exchanger has the potential to be used for the separation of metals from acidic solutions due to relatively higher pKa values, compared to D2EHPA and EHEHPA. Recently, work on uranium permeation from nitric acid solution using SLM technique has been reported (Biswas et al, 2012). Studies on Nd permeation from nitric acid solution were carried in hollow fibre membrane module, using DNPPA as a carrier phase has

* Corresponding author.
  E-mail address: rvijaya@barc.gov.in (R. Vijayalakshmi).

been reported (Ambare et al., 2013). Studies on yttrium transportation with CA 12 and Cyanex 272 have been reported (Y. Wang et al., 2011). The optimization of conditions for the separation of thorium and rare earth elements such as lanthanum, cerium and yttrium by Cyanex 272 and Cyanex 302 has been reported (Eskandari Nasab et al., 2011). They have adopted the Taguchi method for the experimental parameters. Recently, Anitha et al., 2014 have reported the extraction behaviour of lanthanum, dysprosium and yttrium with DNPPA dissolved in petrofin. They have also evaluated the separation factors of all the rare earth elements with DNPPA. DNPPA being a stronger extractant as compared to Cyanex 272, D2EHPA, EHEHPA, etc., is expected to extract rare earths at higher aqueous acidity. Accordingly, DNPPA has been selected as a carrier in the present investigation. As the reports on the permeation studies of rare earths are scanty in literature, it was felt worthwhile to investigate the transportation behaviour of rare earths using HFSLM. The present investigation is to study the transportation behaviour of yttrium from nitric acid using HFSLM with DNNPA. The effect of different experimental parameters including carrier concentration, feed metal concentration, feed acidity, strip acidity and flow rate, on yttrium transport was investigated and is reported in the present paper.

2. Experimental

Feed solution was prepared by dissolving yttrium oxide of 99.9% purity, obtained from Indian Rare Earths Ltd. (IREL), Alwaye, India, in nitric acid. Free acid content in the rare earth nitrate solution was determined by precipitating the rare earth with sodium oxalate followed by titration with NaOH using phenolphthalein indicator. The concentration of yttrium was determined by ICP-AES (JY Ultima2). DNPPA (>95% diester) obtained from Heavy Water Board (HWB), India, was used as supplied and was diluted with petrofin (an aliphatic hydrocarbon fraction of refined kerosene with C12–C14 carbon chain of >95% purity) to obtain the required concentration which was determined by titrating with standard NaOH solution using bromocresol purple as indicator. All other chemicals were of AR grade. The HFSLM module used in the work was of 15 cm length with pore size of 0.03 μm. The detailed specifications are given in Table 1.

3. Procedure

DNPPA of the desired concentration was loaded onto the hydrophobic microporous membrane of the HFM module. A schematic representation of HFM module has been shown in Fig. 1. The excess organic was washed out completely with sufficient distilled water prior to the introduction of feed solution. Y(III) ions in nitrate medium served as the feed solution. In all the experiments, the feed solution was passed through the lumen side and the strip solution (receiving phase) was passed through the shell side of the HFSLM module in a counter current mode. Flow rates were maintained using peristaltic pumps equipped with precise flow controllers. The run was made for 5 h in a re-
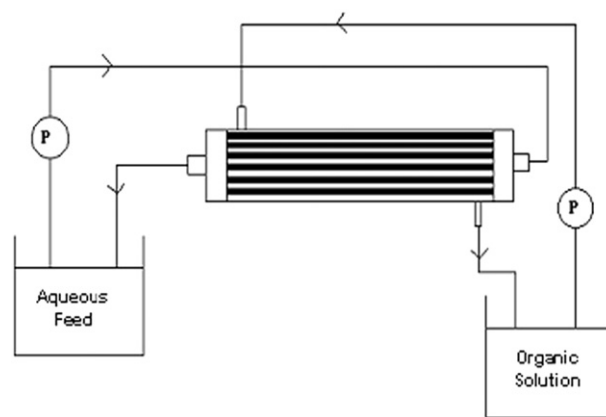
Table 1
Specifications of hollow fibre membrane contactor (Liqui-Cel® X50: 2.5X8 Membrane Contactor).

Parameter	Specification
Fibre type	Polypropylene
Number of fibres	9950
Fibre i.d. (μm)	240
Fibre o.d. (μm)	300
Fibre wall thickness (μm)	30
Effective pore size (μm)	0.03
Porosity (%)	40
Tortuosity	2.5
Effective fibre length (cm)	15
Effective surface area (m²)	1.4

Fig. 1. Schematic diagram of a hollow fibre supported liquid membrane module.

circulating mode of operation. The volume of feed and receiving phase was 500 mL each. Samples from the feed side were collected at fixed intervals of time and were analysed for yttrium concentration by ICP-AES.

4. Results and discussions

4.1. Extraction mechanism

Y(III) ions react with $(HR)_2$ where $(HR)_2$ is the dimer form of DNPPA, to form complex species as shown in equation:

$$Y^{3+} + 3(HR)_2 \leftrightarrow Y(HR_2)_3 + 3H^+. \tag{1}$$

The Y complex species diffuses to the opposite side of the liquid membrane by concentration gradient and reacts with strip acid to transfer Y(III) ions into the stripping phase as given in equation:

$$Y(HR_2)_3 + 3H^+ \leftrightarrow Y^{3+} + 3(HR)_2. \tag{2}$$

The performance of the liquid membrane is described in terms of permeability coefficient 'P' of a transported species. The permeation of a metal species through HFSLM in a recycling mode is expressed in terms of the equation given below (Danesi and Cianetti, 1984):

$$-\ln C_t/C_o = \frac{A \times P}{V_f} \times \frac{\varnothing}{(\varnothing + 1)} \times t \tag{3}$$

where, C_t (mol/L) is the metal ion concentration at an elapsed time t and C_o is the metal ion concentration at time 0, and V_f is the volume of the feed solution.

'A' represents the total effective surface area of the HFM (cm²) which is calculated as follows:

$$A = 2\pi RLN\varepsilon \tag{4}$$

where, L is the length of the hollow fibre (cm), N is the number of fibres in the module, ε is the porosity (%), and R is the internal radius of the hollow fibre (cm).

Parameter 'Ø' is defined as follows:

$$\varnothing = Q_f/(PRLN) \tag{5}$$

where, Q_f is the volumetric flow rate of feed (mL/min).

From the slope of the linear plot of ln C_t/C_o versus time t, the permeability and the flux J can be calculated from the equation:

$$J = P \times M \tag{6}$$