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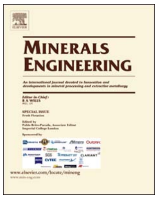

Selective separation and enrichment of neodymium and gadolinium by emulsion liquid membrane using a novel extractant CYANEX® 572

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ABSTRACT

In present study, the novel commercial extractant, CYANEX® 572, was applied for selective separation and enrichment of neodymium and gadolinium through an emulsion liquid membrane. Response surface methodology (RSM) based on central composite design (CCD) is carried out to explore the relationships between process variables namely, carrier concentration, initial pH of feed phase, surfactant concentration and mixing speed, and their interactions. The contours and 3D response surfaces of selective extraction of Gd(III) were achieved and significance of four important variables and their interactions on extraction efficiency of Gd(III) and Nd(III) and separation factor were found out. Also, three regression models for them were developed. A multiple optimization was performed to evaluate the best possible goals for the responses, simultaneously. Results indicated that the maximum separation factor of Gd(III) over Nd(III) was achieved using 0.75 M CYANEX® 572 as minimum concentration of carrier, initial feed pH of 1.56, surfactant concentration of 4% (v/v) and mixing speed of 135 rpm. Under the optimum condition, the extraction percentage of Gd(III) was maximum (67.45%), while the extraction percentages of Nd(III) was minimum (28.98) and the separation factor was found to be 3.78. Under the optimized condition, further experiments were conducted to investigate the effect of hydrochloric acid as internal stripping phase on the stripping efficiencies and enrichment factors were examined. At the internal concentration of 0.5 M, the stripping efficiency and enrichment factor reached the maximum of 89.04% and 12.01 for Gd(III), and 19.45% and 1.13 for Nd(III).

1. Introduction

The Rare Earth Elements (REEs) consist of the elements scandium (Sc), yttrium (Y) and the 15 so called lanthanides (Wannachod et al., 2015; Xie et al., 2014). The high purity REEs have received considerable attention in recent years due to limited supply, market availability and significant price fluctuations, and various industrial applications (Hasan et al., 2009; Hu et al., 2017; Torkaman et al., 2013).

Gadolinium (Gd) is one of the important REEs, which finds applications for both its high magnetic moment and its phosphors or scintillated property (Torkaman et al., 2016). Gadolinium has also found a variety of usages in nuclear and non-nuclear industries (Hasan et al., 2009; Torkaman et al., 2015; Vijayalakshmi et al., 2014). Xu et al. (2014), Bari et al. (2007), Hirai and Orikoshi (2004), Iljas et al. (2008). With ever-increasing demand and applications of Gd(III) or its compounds in high-purity and large amount, separation and enrichment of Gd(III) have received considerable attention (Pei and Wang, 2011; Zheng et al., 2017).

Neodymium (Nd) as one of the most abundant of REEs is the basis for the most common solid-state lasers used in material processing (Wu et al., 2007). Nd is also employed in the manufacturing of permanent magnets (Lee et al., 2005; Xie et al., 2014; Binnemans et al., 2013; Rout and Binnemans, 2014). By Rapid development of neodymium–iron–boron (NdFeB) permanent magnet in electronic devices (Wannachod et al., 2014), the importance of recycling of neodymium has dramatically increased (Binnemans et al., 2013a).

The separation and purification of individual REEs are not easily achievable due to similarities in their chemical and physical properties, especially the neighboring REEs (Anitha et al., 2013). According to rapidly increasing demand on a global scale, the development of new extractants and more efficient extraction techniques is essential for stable supply of REEs and their recycling (Tunsu et al., 2016; Wannachod et al., 2014). At a very low concentration of metal ions, traditional methods such as solvent extraction have been found to be ineffective (Suren et al., 2012). Liquid-membrane technology is employed as an alternative separation technique

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for REEs extraction (Anitha et al., 2015; Kocherginsky et al., 2007; Zhang et al., 2016). Emulsion liquid membrane (ELM) is one of the promising methods of liquid membrane processes which offers some main advantageous such as simplicity, requirement of small quantities of extractant, high mass transfer due to high interfacial area, high diffusion rate, simultaneous extraction and stripping in a single stage, low energy consumption and capability of treating of various compounds in industrial setting in a short time (Ghoshal and Saha, 2015; Kakoi et al., 1998; Kumbasar, 2009).

Cyanex 572 (C572) is a novel and highly stable phosphorus based chelating extractant that is specially formulated for the separation and purification of individual REEs (Cytec, 2014). This extractant is a mixture of phosphinic and phosphonic acids (Wang et al., 2015). By using C572, the stripping of REEs requires a lower acid concentration due to slightly higher pH of extraction. This is the main advantageous of C572, leading to significant acid saving over time (Cytec, 2014; Tunsu et al., 2016).

From the literature, some papers deal with the extraction of REEs by liquid membrane method (Anitha et al., 2015; Belova and Zakhodyaeva, 2014; Hasan et al., 2009; He et al., 2015; Hirai et al., 2002; Kakoi et al., 1997; Pei et al., 2014, 2011a, 2011b; Zhang et al., 2016). But, only a handful of publications exist on the extraction and separation of REEs using C572 in solvent extraction method (Cho et al., 2016; McCallum et al., 2014; Quinn et al., 2015; Tunsu et al., 2016; Wang et al., 2015). To the best of our knowledge, the extraction of REEs by ELM using C572 has not been reported before.

The main purpose of this study is to use of new commercially available extractant, C572, for the selective separation and enrichment of Nd(III) and Gd(III) by ELM process, which was not thoroughly investigated before. The process parameters such as carrier concentration, initial pH of the feed phase, surfactant concentration and mixing speed were studied. Response surface methodology (RSM) and central composite design was applied in this paper to investigate effect of the process parameters on Gd(III) and Nd(III) extraction and separation factor. Finally, multi response optimization was performed to determine the optimum conditions. Furthermore, the effect of internal phase concentration on the stripping efficiency and enrichment factor of Gd(III) and Nd(III) was studied under the optimum condition.

2. Materials and methods

2.1. Chemical Materials

All chemicals were of analytical grade and were used as received without further purification and saponification. C572 was kindly supplied by Cytec Industries Inc., Netherlands, and used as mobile carrier. Gadolinium (III) nitrate hexahydrate ($Gd(NO_3)_3·6H_2O$, 99.9% purity) and Neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3·6H_2O$, 99.9% purity) were purchased from Sigma-Aldrich Chemie GmbH (Schnelldorf, Germany). Sorbitan monooleate (Span-80) as a surfactant and kerosene (reagent grade) as a diluent were procured from Sigma-Aldrich (Schnelldorf, Germany). Hydrochloric acid (HCl (32%)) and Sodium hydroxide (NaOH) were purchased from Merck, Co. (Darmstadt, Germany). The stock standard solutions of 1000 mg l^{-1} of Gd(III) and Nd(III) were prepared by dissolving $Gd(NO_3)_3·6H_2O$ and $Nd(NO_3)_3·6H_2O$ in deionized water. Feed phase solutions containing 50 mg l^{-1} of both Gd(III) and Nd(III) were made by mixing and diluting the stock solutions. The pH value of the feed phase was measured by a Metrohom 780 pH meter with a combined electrode.

2.2. Experimental design

Design of experiments was performed with three responses namely Gd(III) and Nd(III) extraction and separation factor. An orthogonal 2^4 factorial central composite experimental design with eight star points ($\alpha = 2$) and six replicates at the center point, all in duplicates, resulting in a total of 30 experiments were used to optimize the chosen key variables for selective extraction of Gd(III) and Nd(III). The experiments with different carrier concentration, initial feed phase pH, surfactant concentration and mixing speed were employed simultaneously covering the spectrum of variables for selective extraction of Gd(III) from mixed solution in the CCD. In order to describe the effects of carrier concentration (X_1), initial feed phase pH (X_2), surfactant concentration (X_3) and mixing speed (X_4) on percentage of Gd(III) extraction, batch experiments were conducted. The table coded values of the process parameters were determined by Eq. (1) (Amini et al., 2008; Rajasimman and Karthic, 2010; Rajasimman and Sangeetha, 2009).

Table 1
Experimental ranges and levels of the process variables in coded and uncoded forms.

Independent variable	Range and levels				
	−α	−1	0	+1	+α
Carrier Concentration (X_1, M)	0.75	1	1.25	1.5	1.75
Initial Feed phase pH (X_2)	1.2	1.4	1.6	1.8	2
Surfactant Concentration (X_3, %v/v)	1	2	3	4	5
Mixing Speed (X_4, rpm)	120	135	150	165	180

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{1}$$

where x_i is the coded value of the *i*th variable, Xi the uncoded value of the *i*th test variable and X_0 is the uncoded value of the *i*th test variable at center point.

The range and different levels of individual variables in coded and uncoded form were given in Table 1. The coded values of variables for Central Composite Design (CCD) and experimental data and predicted responses are shown in Table 2. The regression analysis was performed to estimate the coefficients of the response function as a second order polynomial (Goyal et al., 2011; Jiao et al., 2013; Montgomery, 2012):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_j X_j^2 + \sum_{i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{2}$$

where Y is the predicted response, β_i, β_j, β_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cross products of X_1, X_2, X_3,… on response. ε represents the noise or error observed in the response Y. k is the number of factors studied in the experiment (Chang et al., 2011; Seifollahi and Rahbar-Kelishami, 2017).

The statistical design and data analysis of the results were carried out by Design-Expert 10.0.4 software (Stat-Ease Inc., Minneapolis, MN, USA). The equations were validated by Analysis of Variance (ANOVA) which evaluates the model and interactions of the three factors on each response through identifying the coefficients of each term given in Eq. (2).

To estimate the goodness of fit in each case, the significance of each term was verified by the F-test in the program. Model terms were chosen or eliminated based on the probability value with 95% confidence level (CL). The three dimensional (3D) response surface plots were drawn to visualize the individual and interactive effects of the process factors on the response variables within their predefined ranges. After that, optimum condition has been determined by multi response optimization. The optimum conditions were first achieved in coded values and then converted to the uncoded.

2.3. Apparatus and experimental procedure

A primary W/O emulsion was prepared by emulsification of organic phase and aqueous acidic solution using Ultra-Turrax T18 Basic homogenizer (IKA-WERK, Germany). 30 ml of 0.5 M HCl solution (internal stripping phase) was added drop wise to an equal volume of the organic phase. The membrane phase consisted of different portions of Span-80 as the surfactant, carrier reagent C572 and kerosene as an