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Performance Study of Neodymium Extraction by Carbon Nanotubes Assisted Emulsion Liquid Membrane Using Response Surface Methodology

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***Abstract*—**The high purity rare earth elements (REEs) have been vastly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, superconductors, ceramics, alloys, catalysts, and etc. Neodymium is one of the most abundant rare earths. By development of a neodymium–iron–boron (Nd–Fe–B) permanent magnet, the importance of neodymium has dramatically increased. Solvent extraction processes have many operational limitations such as large inventory of extractants, loss of solvent due to the organic solubility in aqueous solutions, volatilization of diluents, etc. One of the promising methods of liquid membrane processes is emulsion liquid membrane (ELM) which offers an alternative method to the solvent extraction processes. In this work, a study on Nd extraction through multi-walled carbon nanotubes (MWCNTs) assisted ELM using response surface methodology (RSM) has been performed. The ELM composed of diisooctylphosphinic acid (CYANEX 272) as carrier, MWCNTs as nanoparticles, Span-85 (sorbitan triooleate) as surfactant, kerosene as organic diluent and nitric acid as internal phase. The effects of important operating variables namely, surfactant concentration, MWCNTs concentration, and treatment ratio were investigated. Results were optimized using a central composite design (CCD) and a regression model for extraction percentage was developed. The 3D response surfaces of Nd(III) extraction efficiency were achieved and significance of three important variables and their interactions on the Nd extraction efficiency were found out. Results indicated that introducing the MWCNTs to the ELM process led to increasing the Nd extraction due to higher stability of membrane and mass transfer enhancement. MWCNTs concentration of 407 ppm, Span-85 concentration of 2.1 (%v/v) and treatment ratio of 10 were achieved as the optimum conditions. At the optimum condition, the extraction of Nd(III) reached the maximum of 99.03%.

***Keywords*—**Emulsion liquid membrane, extraction of neodymium, multi-walled carbon nanotubes, response surface method.

I. Introduction

REEs consist of 15 lanthanides, plus yttrium and scandium. They are divided conventionally into two main groups: the light REEs (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd) and the heavy REEs (Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) [1]. In the last few decades, REEs have gained great attention and vastly used for additives to steel or alloys [2], magneto-optic storage discs, metallurgy, hydrogen storage materials, ceramic industry [3], permanent magnets, nuclear fuel control, electro or cathode rays, and household batteries [4], [5] owing to their unique properties.

As neodymium is the basis for the most common solid-state lasers used in material processing such as in medicine, it is one of the most abundant of rare earth metals [6]. Neodymium is also used as raw material for high-strength neodymium–iron–boron (Nd–Fe–B) permanent magnets [7] and it costs less than samarium–cobalt (Sm-Co) permanent magnets [8]. Very similar chemistry of REEs made them difficult to separate [9]. Various methods can be used to extract these metals from aqueous solutions. At a very low concentration of metal ions, traditional methods such as ion exchange, precipitation and solvent extraction have been found to be ineffective [10].

Liquid membranes are used an alternative separation technology, in order to extract REEs [11]–[13]. One of the promising methods of liquid membrane processes is ELM. ELM offers some advantages over solvent extraction such as simplicity, requirement of small quantities of extractant, simultaneous extraction and stripping in a single stage and low energy consumption [14], [15]. ELMs are usually made by creating a water-in-oil emulsion which is stabilized by a surfactant. This emulsion contains the extractant (carrier) in the oil phase and the stripping agent in the internal aqueous phase. The emulsion is then dispersed by a relatively low agitation into an aqueous feed phase containing the solutes to be separated [16].

The problem that prevents the application of ELM technology in industrial equipment is the lack of stability of the emulsion globules which resulted in the loss of extraction efficiencies. The resistance of the individual globules against coalescence is called as the stability of emulsions [17]. Although the emulsion resistance to creaming mainly increased due to an increase in viscosity by addition of surfactant to a particle-stabilized emulsion, it surprisingly led to increasing the coalescence. Simultaneous emulsification of particles and surfactant caused to synergistic stabilization at intermediate concentrations of surfactant. In this case, emulsions are completely stable to both creaming and coalescence which exist at low overall surfactant concentration [18].

The objective of the present work is to investigate the

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extraction of Nd(III) through ELM stabilized by simultaneous emulsification of MWCNTs and span 85. RSM was employed to achieve the optimal conditions for high extraction efficiency of Nd(III) ions. The effects of MWCNTs concentration, span-85 concentration and treatment ratio and interaction between them were studied. A regression model for extraction percentage of Nd(III) was developed.

II. Materials & Methods

A. Chemical Materials

All chemicals were of analytical grade and were used as received without further purification. Diisooctylphosphinic acid (CYANEX 272) was purchased from Fluka (Buchs, Switzerland) and used as mobile carrier. Neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3.6H_2O$, 99.9% purity) was purchased from Sigma-Aldrich Chemie GmbH (Schnelldorf, Germany). MWCNTs (diameter <8 nm, length= 30 μm, purity >98%) were obtained from the Research Institute of the Petroleum Industry (RIPI, Tehran, Iran). Span 80 as a surfactant and kerosene (reagent grade) as a diluent were procured from Sigma-Aldrich (Schnelldorf, Germany). Nitric acid (HNO_3 (65%)) and Sodium hydroxide (NaOH) were purchased from Merck, Co. (Darmstadt, Germany). The stock standard solution of 1000 $mg.L^{-1}$ of Nd(III) was prepared by dissolving $Nd(NO_3)_3.6H_2O$ in deionized water. Feed phase solutions were made by diluting the stock solution. The pH value of the feed phase was measured by a Metrohom 780 pH meter with a combined electrode.

B. Experimental Design

An orthogonal 2^3 factorial central composite experimental design with six star points (α=1.68) and six replicates at the center point, all in duplicates, resulting in a total of 20 experiments were used to optimize the chosen key variables for the extraction of Nd(III). The experiments with five different MWCNTs concentration of 0, 152, 375, 598, and 750 ppm, surfactant concentration of 0.5, 1.41, 2.8, 4.1, and 5% (v/v) and treatment ratio (TR) of 10, 15, 23, 30, and 35 were employed simultaneously covering the spectrum of variables for the percentage extraction of Nd(III) in the CCD. In order to describe the effects of MWCNTs concentration (X_1), surfactant concentration (X_2), and treatment ratio (X_3) on percentage of chromium extraction, batch experiments were conducted. The table coded values of the process parameters were determined by (1):

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (1)$$

where x_i is the coded value of the i^{th} variable, X_i 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 I. The coded values of variables for CCD and experimental data and predicted responses are shown in Table II. The regression analysis was performed to estimate the coefficients of the response function as a second order polynomial:

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

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. k is the number of factors studied in the experiment.

TABLE I
The Levels of Different Process Variables in Coded And Uncoded Form for the Extraction of Neodymium (III)

Independent variable	Range and Levels		
	-1	0	+1
MWCNTs Concentration (X_1, ppm)	152	375	598
Span 85 Concentration (X_2, %v/v)	1.41	2.8	4.1
Treatment Ratio (X_3)	15	23	30

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 the Nd(III) extraction through identifying the coefficients of each term given in (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). Response surfaces and 3D plots were drawn to visualize the individual and interactive effects of the variables for the extraction of Nd(III). The optimum conditions were first achieved in coded values and then converted to the uncoded.

C. Experimental Procedure

MWCNTs assisted ELM was prepared by dispersing required amounts of MWCNTs for each concentration of 152, 375, 598, and 750 ppm into the surfactant solution by Ultra-Turrax T18 Basic homogenizer (IKA-WERK, Germany) at 15000 rpm for 5 minutes. The surfactant solution consisted of different portions of Span 85 as the surfactant, a carrier reagent (1M CYANEX 272) and kerosene as an organic diluent Then, the dispersion was followed by sonication in an ultrasonic bath (DSA100-SK2, DESEN, China, 40 kHz, 100 W) for 30 minutes.

To make a primary W/O emulsion, the internal stripping phase (30 ml of 1 M HNO_3) was added drop wise to the prepared MWCNTs dispersion. The mixture was stirred continuously at 6000 rpm for 10 minutes to obtain a milky-white stable emulsion. The fresh MWCNTs assisted emulsion was prepared each time before experiments.

The experiments were carried out in a 2-liter glass reactor. The reactor was equipped with two PTFE crescent-shaped paddles, rotating motor, digital agitation speed controller, circulator, thermal jacket, thermometer, temperature controller and sampling valve. The prepared emulsion was smoothly

dispersed into mixing chamber with feed phase solution (pH=2) and stirred for about 10 min. The impeller speed was 180 rpm. At the end of the mixing, the stirred solution was allowed to separate by gravity. Samples of about 5 ml were taken from solution.

TABLE II
CCD MATRIX ALONG WITH PREDICTED AND EXPERIMENTAL VALUES OF PERCENTAGE EXTRACTION OF NEODYMIUM

Run	X_1	X_2	X_3	% Extraction of Nd(III)	
				Experimental	Predicted
1	1	-1	-1	84.37	83.55
2	0	-1.68	0	59.76	60.29
3	1	-1	1	65.75	65.22
4	0	0	0	82.27	81.17
5	0	0	-1.68	97.12	99.30
6	-1	-1	-1	72.12	70.99
7	1	0	0	81.23	81.17
8	-1	1	-1	74.38	73.20
9	1	0	1.68	67.31	67.55
10	1	0	0	81.97	81.17
11	1.68	0	0	62.81	64.27
12	-1.68	0	0	50.79	51.74
13	1	1	1	56.7	56.12
14	0	0	0	80.36	81.17
15	-1	-1	1	48.41	48.62
16	0	0	0	79.22	81.17
17	-1	1	1	54.66	53.78
18	0	0	0	82.41	81.17
19	-1	1	-1	73.41	71.50
20	0	1.68	0	52.61	54.50

To avoid any probable mass transfer and remove remained emulsion droplets, samples were filtered through a filter paper (Whatman, No.1, USA). Then, the samples were analyzed by ICP-AES (Thermo Jarrell Ash, Model Trace Scan, Canada) Nd(III) ions' concentration after extraction. All experiments were performed at 25±0.5°C.

III. RESULTS & DISCUSSION

The process variables of MWCNTs assisted ELM for the extraction of Nd(III) were examined using the RSM according to CCD. The application of RSM yielded the following regression quadratic model equation which is an empirical relationship between the extraction percentages of Nd(III) and the test variables in coded unit

$$Y = 81.17 + 3.73X_1 - 1.72X_2 - 9.44X_3 - 3.56X_1X_2 + 1.01X_1X_3 + 0.74X_2X_3 - 8.19X_1^2 - 8.41X_2^2 + 0.80X_3^2 \quad (3)$$

where Y is the percentage removal efficiency of Nd(III) by MWCNTs assisted ELM, X_1 is the MWCNTs concentration, X_2 is the surfactant concentration, and X_3 is the treatment ratio. The predicted values calculated from (3) were in very good agreement with the experimental values, as shown in Fig. 1. Hence, this quadratic model is well suited for this experimental set up. ANOVA was used to check the significance and fitness of model, as shown in Table III.

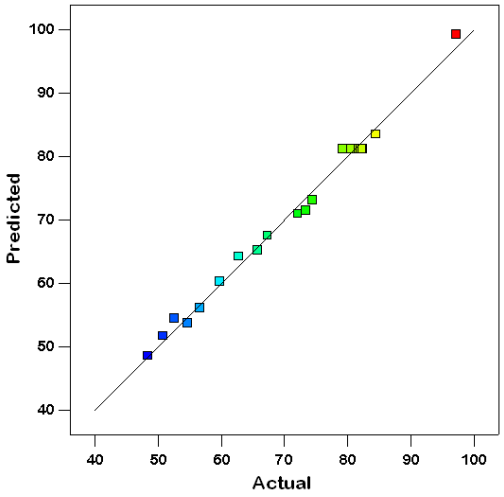

Fig. 1 Comparison of predicted extraction efficiency and actual values for the extraction of Nd(III) by MWCNTs assisted ELM

The Model F-value of 136.83 implies that the model is significant. There is only a 0.01% chance that a large "Model F-value" could occur due to noise. Values of "prob> F" less than 0.0500 indicate that model terms are significant, and the rest are considered as insignificant. In this case, X_1, X_2, X_3, X_1X_2, X_1^2, X_2^2, X_3^2 are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. The "Lack of Fit F- value" of 2.58 implies that it is not significant in comparison with the pure error. There is a 16.10% chance that a large "Lack of Fit F-value" could occur due to noise. It is always necessary to have the value of "Lack of Fit F-value" non-significant to make the model best fit.

Predicted R^2 represents the prediction of a response value estimated by the model. The difference between adjusted R^2 and predicted R^2 is always wanted to be in the range of 0–0.200 for the adequacy of the model. In this case, the difference between them is 0.0321, which implies that both the values are in good agreement. Adequate precision is an estimation of the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 42.857 implies an adequate signal. Hence, this model can be used to navigate the design space. Coefficient of variation indicates the error expressed as a percentage of the mean.

To understand the interaction of the variables and to determine the optimum level of each variable for maximum response, the response surface curves are plotted. The response surface plots for significant interaction between two variables against extraction of Nd(III) by MWCNTs assisted ELM are shown in Figs. 2–4.

TABLE III
ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Sum of Squares	df	Mean Square	F Value	p-value, Prob > F	
Model	3444.31	9	382.70	136.83	<0.0001	significant
X_1-MWCNTs	189.52	1	189.52	67.76	<0.0001	
X_2-Span 85	40.52	1	40.52	14.49	0.0034	
X_3-TR	1216.51	1	1216.51	434.95	<0.0001	
X_1X_2	101.67	1	101.67	36.35	0.0001	
X_1X_3	8.20	1	8.20	2.93	0.1176	
X_2X_3	4.35	1	4.35	1.56	0.2407	
X_1^2	966.77	1	966.77	345.66	<0.0001	
X_2^2	1018.79	1	1018.79	364.26	<0.0001	
X_3^2	9.11	1	9.11	3.26	0.1013	
Residual	27.97	10	2.80			
Lack of Fit	20.15	5	4.03	2.58	0.1610	not significant
Pure Error	7.82	5	1.56			
Cor Total	3472.28	19				

Std. Dev.: 1.67; R2: 0.9919; mean: 70.38; Adj R2: 0.9847; C.V. %: 2.38; Pred R2: 0.9526; Adeq precision: 42.857

The interaction between the MWCNTs concentration and the Span 85 concentration is shown in Fig. 2. Parabolic contours signify that the interaction between them is significant. The curve demonstrates that both the values increase the extraction efficiency upon increment from lower level, but after certain values, the extraction efficiency tend to decline until the higher level. The optimum values can be found out easily since the contours are parabolic.

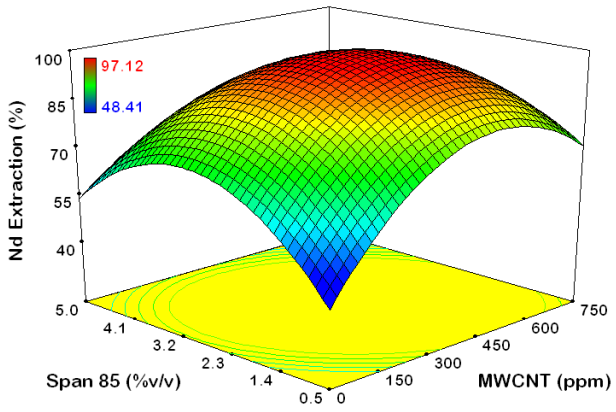

Fig. 2 The 3D plot showing the effects of MWCNTs, span 85 concentration and their mutual interaction on extraction of Nd(III) by MWCNTs assisted ELM

A possible explanation could be either the replacement of surfactant by particles at the oil-water interface or a greater affinity of the surfactant for the particle surface rather than the oil-water interface. By addition the MWCNTs into the system, solid particles do adsorb act as bridges between droplets facilitating coalescence. Further increase in MWCNTS concentration led to increase the viscosity of ELM, which caused to form larger globules. As a result, the extraction of Nd(III) reduced.

The treatment ratio defined as the volume ratio of the feed phase to emulsion, plays a major role in determining the efficiency of ELM process. To make an ELM process more cost effective over the solvent extraction, always the least volume of ELM is considered. Fig. 3 illustrates the interaction between the MWCNTs concentration and the treatment ratio on the extraction of Nd(III). The treatment ratio was varied from 10 (V_{Feed}:$V_{emulsion}$=10:1) to 35 (V_{feed}:$V_{emulsion}$=35:1). As shown in Fig. 3, increasing the treatment ratio had negative influence on Nd(III) extraction. Although fewer portions of the viscose emulsion caused to reduction in the size and thickness of the emulsion globules and membrane, the number of available globules of emulsion and interfacial area of mass transfer per unit volume of feed phase reduced. As a result, the extraction of Nd(III) was reduced.

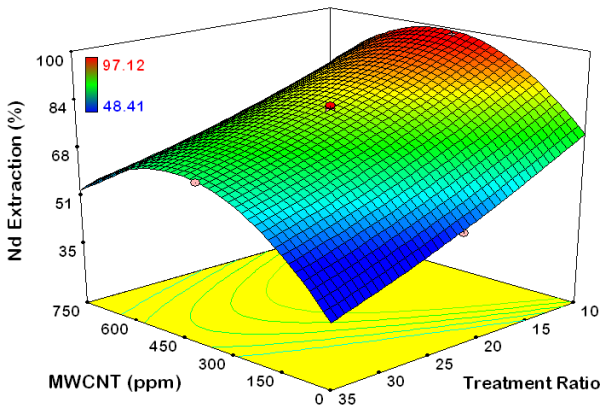

Fig. 3 The 3D plot showing the effects of MWCNTs, treatment ratio and their mutual interaction on extraction of Nd(III) by MWCNTs assisted ELM

Emulsion stability is strongly dependent on the surfactant concentration. Interaction between the Span 85 concentration and the treatment ratio is shown in Fig. 4.

It can be observed from the figure that the increasing the surfactant concentration led to increasing the stability of the membrane by means of extra surfactant molecules. Hence, the extraction of Nd(III) is also increased. Meanwhile, increasing the surfactant concentration up to limiting value led to

lowering the interfacial tension between phases. It promotes the formation of more fine-droplets, which produces the more stable emulsion.

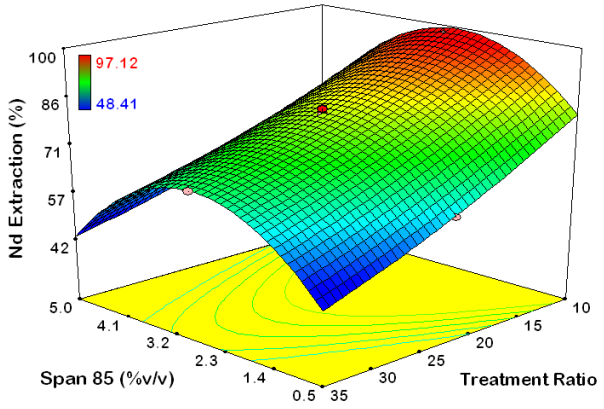

Fig. 4 The 3D plot showing the effects of span 85, treatment ratio and their mutual interaction on extraction of Nd(III) by MWCNTs assisted ELM

The statistical optimization of all three parameters was done and the optimum condition was obtained. By seeking from 30 starting points in the response surface changes, the maximum Nd(III) extraction was found to be at MWCNTs concentration of 407 ppm, surfactant (Span 85) concentration of 2.1 (%v/v), treatment ratio of 10. The other operational parameters were kept constant. Under the optimal condition the maximum predicted efficiency was 99.03%.

IV. Conclusion

In this paper, MWCNTs assisted ELM has been successfully applied to extract Nd(III) from aqueous solution. A CCD was employed to optimize the three process variables, i.e. MWCNTs and Span-85 concentrations and treatment ratio. A regression quadratic model for extraction of Nd(III) was achieved and its R^2 (99.19%), R^2 (adj) (98.47%), and standard deviation (1.67%) values were determined. The ANOVA has ensured the significance of model with the experimental data. The optimum conditions of MWCNTs and Span-85 concentrations and treatment ratio were found to be 407 ppm, 2.1 (%v/v) and 10, respectively. Under the optimum condition, the predicted value for extraction percentage of Nd(III) was obtained 99.03%.

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