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Optimization of Samarium Extraction via Nanofluid-Based Emulsion Liquid Membrane Using Cyanex 272 as Mobile Carrier

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Abstract**—**Samarium as a rare-earth element is playing a growing important role in high technology. Traditional methods for extraction of rare earth metals such as ion exchange and solvent extraction have disadvantages of high investment and high energy consumption. Emulsion liquid membrane (ELM) as an improved solvent extraction technique is an effective transport method for separation of various compounds from aqueous solutions. In this work, the extraction of samarium from aqueous solutions by ELM was investigated using response surface methodology (RSM). The organic membrane phase of the ELM was a nanofluid consisted of multiwalled carbon nanotubes (MWCNT), Span80 as surfactant, Cyanex 272 as mobile carrier, and kerosene as base fluid. 1 M nitric acid solution was used as internal aqueous phase. The effects of the important process parameters on samarium extraction were investigated, and the values of these parameters were optimized using the Central Composition Design (CCD) of RSM. These parameters were the concentration of MWCNT in nanofluid, the carrier concentration, and the volume ratio of organic membrane phase to internal phase (Roi). The three-dimensional (3D) response surfaces of samarium extraction efficiency were obtained to visualize the individual and interactive effects of the process variables. A regression model for % extraction was developed, and its adequacy was evaluated. The result shows that % extraction improves by using MWCNT nanofluid in organic membrane phase and extraction efficiency of 98.92% can be achieved under the optimum conditions. In addition, demulsification was successfully performed and the recycled membrane phase was proved to be effective in the optimum condition.

Keywords**—**Cyanex 272, emulsion liquid membrane, multiwalled carbon nanotubes, nanofluid, response surface methodology, Samarium.

I. Introduction

RARE earth elements (REE) are a group of metals including yttrium, lanthanides, and scandium. REE have been widely used in many fields such as catalysts, metallurgy, ceramics, and permanent magnets due to their unique physical and chemical properties [1]. Samarium (Sm), which is one of the 15 lanthanides, plays an important role in the production of samarium-cobalt permanent magnet, special catalyst, microwave and infrared ray equipment, laser, and nuclear energy industry [2].

In recent years, the separation and purification of rare earth metals and their compounds have received considerable attention because of an increasing demand of them. Various methods such as chemical precipitation, ion exchange, and solvent extraction are used to recover these metals from aqueous solutions [3], [4]. Traditional liquid–liquid extraction (LLE) is considered time consuming and involves large quantities of expensive organic solvents [5]. Membrane-based technology is a simple and cost effective alternative to solvent extraction technique which has acquired a prominent role in separation and purification processes in various areas [6]. Liquid membranes combine extraction and stripping processes in a single unit, and they have benefits of non-equilibrium mass transfer, high selectivity, high fluxes, and low energy consumption. The main configurations of the liquid membranes are bulk liquid membranes (BLM), supported liquid membranes (SLM), and ELM [7]. ELM processes have great applicability for extraction and separation of very low to high concentrations of metal ions by using lower volume ratio of organic phase to aqueous feed solution compared with LLE and allow very high mass transfer rate due to its large surface area available within the emulsion globules and internal droplets [8], [9].

It has been found that nanoparticles have the potential for stabilizing emulsions. Nanoparticles in such emulsions can adsorb at the drops surface and act as a barrier preventing drops form coalescing [10], [11]. Carbon nanotubes (CNT) have shown promise in liquid-liquid interfaces in numerous applications such as drug delivery capsules, diesel engine, and enhanced oil recovery [12], [13]. In addition, Lee et al. showed that heat transfer and adsorption rate in ammonia–water system increases by using Al_2O_3 and CNT based nanofluids [14]. Mass transfer rate enhancement in LLE by using different nanoparticles (CNT, ZnO, and TiO_2) is also reported by Ghanadi et al. [15].

The aim of this paper is using nanofluid-based ELM for Sm extraction. For this purpose, MWCNT was used for preparing the nanofluids. The experimental data points were used to obtain experimental model from CCD, known as a standard RSM design. RSM was applied to study the linear, square, and interactive effects of the important operating variables such as concentration of MWCNT in nanofluid, carrier concentration, and the volume ratio of organic membrane phase to internal

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phase (Roi) on Sm extraction through nanofluid-based ELM process. Then, optimization of the process parameters was carried out.

II. Materials & Methods

A. Chemicals

All analytical reagent grade chemicals were used in this study and all aqueous solutions were prepared with deionized water. The mobile carrier Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) was obtained from Sigma Aldrich (Germany). The non-ionic surfactant used was sorbitan monooleate which is product of Sigma-Aldrich (Germany) and commercially known as Span 80. Kerosene (reagent grade) was also purchased from Sigma-Aldrich. Samarium (III) nitrate hexahydrate ($Sm(NO_3)_3.6H_2O$, 99.9% purity) was procured from Middle East Ferro Alloy Company (Iran) and nitric acid (HNO_3 (65%)) was purchased from Merck. The MWCNTs were obtained from the Research Institute of the Petroleum Industry (RIPI, Tehran, Iran). The mean diameter of the MWCNTs was <8 nm, the length was 30 μm and purity >98%. All these materials were used directly as received from the manufacturer.

B. Experimental Procedure

First, the organic solution was prepared by mixing 2% (v/v) of Span 80 and appropriate amount of Cyanex 272 in kerosene as diluent. In order to preparing nanofluid-based liquid membrane, required amounts of MWCNT were added to the organic solution and dispersed by a homogenizer (Ultra-Turrax IKA T18 ,Germany) at 15000 rpm for 5 min followed by sonication in an ultrasonic bath (DSA 100-SK2, DESEN, 120 W,40 kHz, China) for 30 min. Then, the stripping aqueous solution (internal phase) of 1 M nitric acid was added dropwise to the nanofluid-based liquid membrane under stirring at 6000 rpm during 10 min, to produce a milky-white W/O emulsion. The volume ratio of stripping solution to membrane was 0.5.

The prepared emulsion was dispersed in the feed phase solution (aqueous external phase, pH=2) containing 50 mg/l Sm where the ratio of feed solution to membrane was 10, and all were stirred by an overhead stirrer at 240 rpm for an extraction time of 10 min. The extracted samples were taken and external phase was separated from the emulsion by laboratory centrifuge and using a filter paper (Whatman, No.1, USA). Then, Sm concentration in the aqueous external phase was determined and the percentage of extraction was calculated as:

$$\%Extraction = \frac{C_0 - C}{C_0} \tag{1}$$

C_0 and C are the initial and final concentrations of Sm in the feed phase, respectively. All experiments were carried out at 25±0.5 °C. The emulsion phase was gathered for demulsification. In this study, demulsification was achieved by heating and centrifugation for 3 min at 5000 rpm.

C. Experimental Design

In this study, CCD and RSM were applied to determine the optimum levels of the chosen key parameters affecting the present ELM process. The statistical design and data analysis were accomplished by Design-Expert 8 software (trial version, Stat-Ease, Minneapolis, MN, USA). The design included three factors; namely, MWCNT concentration, carrier concentration, and the volume ratio of organic membrane phase to internal phase (Roi). The factors were studied at five levels (-α, -1, 0, 1, and α) as presented in Table I.

TABLE I
EXPERIMENTAL RANGE OF OPERATING PARAMETERS AND THEIR CORRESPONDING LEVELS (ALL FACTORS ARE IN UNCODED UNITS)

Parameters	Levels				
	-α	-1	0	1	α*
A-MWCNT concentration (wt.%)	0.00	0.03	0.08	0.12	0.15
B-Carrier Concentration (M)	0.50	0.70	1.00	1.30	1.50
C-Volume ratio of membrane phase to internal phase (Roi)	0.30	0.48	0.75	1.02	1.20

* α= 1.68

In this method, the number of experiments required to optimize the selected key variables was 20. The runs were performed randomly to minimize the effects of unexplained variability in the experiential response.

The regression analysis was accomplished to estimate the response function as a quadratic model shown by (2):

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

where Y is the dependent variable or predicted response, x_i and x_j are the studied factors (A, B, and C) chosen as the independent variables, β_o, β_i, β_{ii}, and β_{ij} represent the intercept, linear, quadratic, and interaction regression coefficients, respectively. k is the number of factors studied in the experiment. The model validation was assessed by means of the analysis of variance (ANOVA) within the framework of Design Expert software and terms of the model were selected or rejected based on the probability value with 95% confidence level.

III. Results & Discussion

A. Statistical Analysis

The possible effects and interactions of the three chosen process variables of nanofluid-based ELM for Sm extraction were examined using the RSM. A total of eight factorial points, six star points, and six replicates at the center points were employed. Table II shows the design matrix used along with the experimental and the predicted responses.

The effects of the individual and interactive process parameters on Sm extraction have been evaluated using ANOVA and least squares techniques. The importance of these factors on the responses was determined on the Fisher's variance ratio (F) and probability (P) values in the Fisher's statistical test. A quadratic regression model was first used to fit the experimental data, considering all variable terms (linear, square, and interaction), and ANOVA results are presented in Table III.

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

Run	A	B	C	%Extraction Experimental	%Extraction Predicted
1	0.08	1	0.75	95.3	96.44
2	0.08	1	0.75	97	96.44
3	0.12	0.7	1.02	72.7	71.34
4	0.08	1	0.75	95.38	96.44
5	0.12	0.7	0.48	62.47	63.74
6	0.15	1	0.75	72.6	71.52
7	0.03	1.3	0.48	76.29	77.03
8	0.03	0.7	0.48	65.48	63.34
9	0	1	0.75	77.39	78.22
10	0.08	1	0.75	96.09	96.44
11	0.03	1.3	1.02	86.5	84.61
12	0.08	1	1.2	93.35	93.38
13	0.12	1.3	0.48	64.28	63.04
14	0.08	1	0.3	81.01	80.73
15	0.08	1.5	0.75	63.6	63.29
16	0.12	1.3	1.02	74.81	76.17
17	0.03	0.7	1.02	65.13	65.39
18	0.08	0.5	0.75	47.79	47.85
19	0.08	1	0.75	96.58	96.44
20	0.08	1	0.75	98.23	96.44

Table III shows that A, B, C, AB, BC, AC, A^2, B^2, and C^2 are statistically significant for Sm extraction as the p-value for them is less than 0.05. This implies that the first-order main effects of all factors (the linear model terms), the interactive effects of MWCNT and carrier concentration, MWCNT concentration and Roi, carrier concentration and Roi, along with the square effects of MWCNT concentration, carrier concentration, and Roi are statistically significant parameters. The larger the magnitude of the F-values, the more significant is the corresponding factor. Therefore, the squared effects of MWCNT and carrier concentration are highly significant when compared with the individual and interactive effect.

According to Table III, we finally achieved the corresponding coefficient of each variable term in (1) by multiple regression analysis of the experimental data, and proposed a quadratic model using coded variables as represented by (3):

$$Y = +96.44-1.99X_1-4.59X_2+3.76X_3-3.53X_1X_2 +1.36X_1X_3+1.36X_2X_3-7.63X_1^2-14.45X_2^2-3.32X_3^2 \quad (3)$$

where Y is the percentage extraction of Sm, X_1 is MWCNT concentration, X_2 is the carrier concentration, and X_3 is Roi.

From the ANOVA of the regression model, the calculated F-value (208.30) and very low probability value (P <0.0001) shows that this model is highly significant. The "Lack of Fit F-value" of 2.73 implies that the Lack of Fit is not significant relative to the pure error. There is a 14.7% chance that a "Lack of Fit F-value" larger than this value could occur due to noise. Non-significant lack of fit is desired and it shows that the model is adequate for predicting the %E of Sm within the range of variables studied. The predicted R^2 of 0.9636 is in reasonable agreement with the adjusted R^2 of 0.9899. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable; hence, the ratio of 45.6 indicates an adequate signal. Fig. 1 is the normal probability plot of studentized residuals (the quotient resulting from the division of a residual by an estimate of its standard deviation) for Sm extraction illustrating that all points are distributed along a straight line, which confirms adequacy of the model significance and fitness of model.

TABLE III
ANALYSIS OF VARIANCE (ANOVA) FOR THE SIGNIFICANCE OF THE PARAMETERS IN THE MODEL

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	4256.675	9	472.9639	208.2984	< 0.0001
A	54.15675	1	54.15675	23.85121	0.0006
B	287.7624	1	287.7624	126.7336	< 0.0001
C	193.2523	1	193.2523	85.11038	< 0.0001
AB	99.82845	1	99.82845	43.96552	< 0.0001
AC	14.85125	1	14.85125	6.54065	0.0285
BC	14.74245	1	14.74245	6.492733	0.0290
A^2	837.9264	1	837.9264	369.0318	< 0.0001
B^2	3008.607	1	3008.607	1325.023	< 0.0001
C^2	158.575	1	158.575	69.83814	< 0.0001
Residual	22.70608	10	2.270608		
Lack of Fit	16.62368	5	3.324736	2.733079	0.1470
Pure Error	6.0824	5	1.21648		
Cor Total	4279.381	19			

(Std. Dev. =1.51, R^2=0.9947, Mean=79.10, Adj R^2=0.9899, C.V. %=1.91, Pred R^2=0.9636, Adeq Precision=45.600)

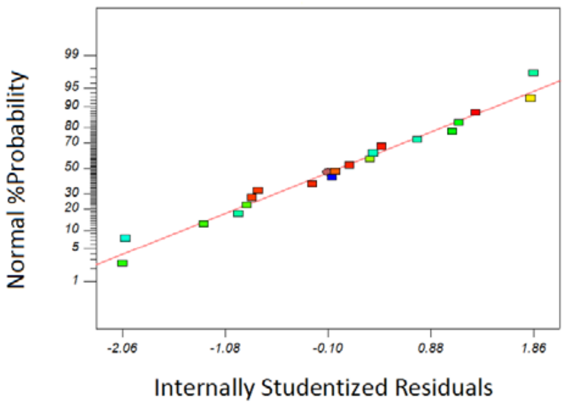

Fig. 1 Normal probability plot of studentized residuals for Sm extraction

B. Interactive Effects of the Variables

The three-dimensional (3D) plots of response surface curves are used to show the interactions between factors. The response surface curves for the extraction of Sm from aqueous solutions by nanofluid-based ELM are shown in Figs. 2-4. Each response surface curve represents the change in levels of two variables with the other two variables maintained at zero levels.

The interaction between MWCNT and carrier concentration is shown in Fig. 2. It can be seen that the extraction efficiency increases by increasing MWCNT concentration up to the value at about 0.07 wt.% and shows a decrease thereafter. This can be explained by the fact that growing MWCNT percentage in membrane leads to more stabilized emulsion. However, when MWCNT concentration reaches a certain value, further increase leads to the growth of membrane phase-internal phase interfacial viscosity and mass transfer resistance.

We observed that the increase in carrier concentration leads to increase in Sm extraction because of the formation of more Sm-Cyanex 272 complexes at the external interface between the feed and the membrane phase, resulting in increasing diffusion of Sm through the membrane.

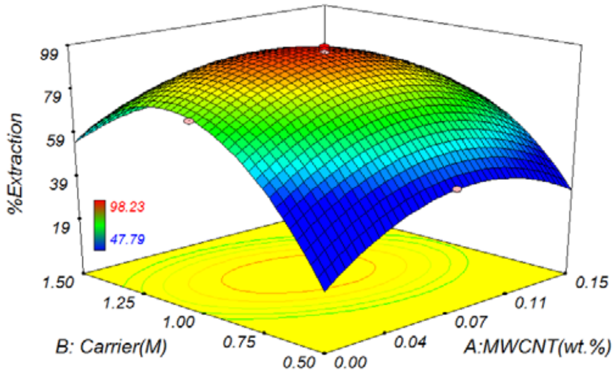

Fig. 2 Surface response plot for the interaction between MWCNT and carrier concentration in the nanofluid-based ELM

The plots in Figs. 2 and 4 imply that when carrier concentration increases to above certain limit, the extraction percentage shows a downward trend which may be attributed to an increase in the viscosity of the membrane phase reducing diffusion rate of Sm through the membrane phase. This finding is in agreement with the results of the other researchers [16].

From Figs. 3 and 4, it was found that extraction efficiency slightly increases with Roi which changes from 0.3 to 0.75, but then, the extraction percentage cannot be improved. This can be due to the fact that when Roi is low, the volume of membrane phase is insufficient for surrounding all the internal phase. Furthermore, the interfacial area between the membrane and internal phase is lower because of larger internal droplets, which results in lower extraction efficiency.

The possible reason for the interaction of Roi with MWCNT and carrier concentration can be provided as the direct proportionality of Roi to them. In fact, an increment in the volume ratio of organic membrane phase to internal phase increases the amounts of Cyanex 272 and MWCNT in the system, which directly affect the extraction efficiency, as mentioned before. Additionally, it is evident from the plots that the effect of Roi is more significant at higher concentrations of Cyanex 272 and MWCNT.

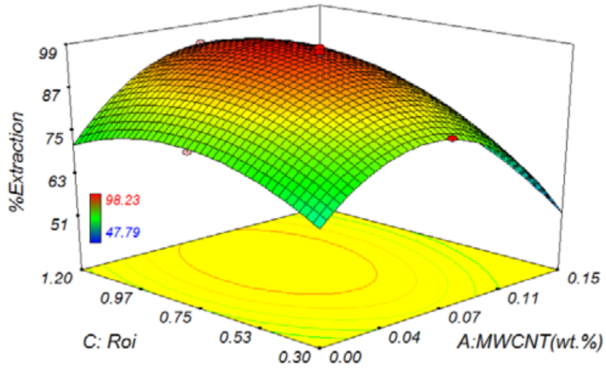

Fig. 3 Surface response plot for the interaction between Roi and MWCNT concentration in the nanofluid-based ELM

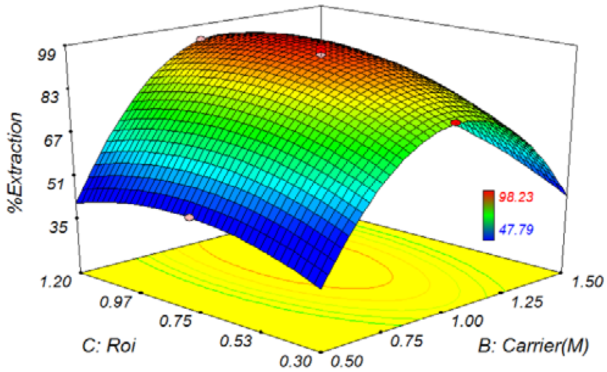

Fig. 4 Surface response plot for the interaction between Roi and carrier concentration in the nanofluid-based ELM

C. Optimization of the Variables

We conducted the statistical optimization of operating parameters by DOE, and the optimal experimental condition corresponding in this case to a maximum of the %extraction is presented in Table IV. Under the optimal condition, the maximum predicted extraction efficiency was 98.12% with high predicted desirability of 0.998.

The possibility of reuse of the organic membrane solution is an important factor for developing an economically feasible ELM process. In order to investigate the recycle performance, we collected the demulsified membrane phase of the optimum experiment of this design and reused it to examine the extraction efficiency.

Under the optimum operating conditions in this work, the value of the percentage extraction by fresh membrane was 98.92% showing the model is suitable and sufficient to predict the % extraction in the range of variables studied. Under the same experimental condition, the value of extraction percentage by the reused membrane was 96.35%. Hence, the organic membrane solutions recycled from the spent emulsions were reusable in the ELM process without any significant decline in extraction performance.

TABLE IV
RSM OPTIMIZED DATA FOR SM EXTRACTION USING NANOFLUID-BASED ELM

Parameters	Optimum value
A-MWCNT concentration (wt.%)	0.07
B-Carrier concentration (M)	1.06
C-Volume ratio of membrane phase to internal phase (Roi)	0.91

IV. CONCLUSION

The present study showed that nanofluid-based ELM can be successfully applied for Sm extraction from aqueous solution. The linear, square, and interactive effects of process parameters, namely MWCNT concentration, the volume ratio of organic membrane phase to internal phase (Roi), and carrier concentration were investigated by RSM according to CCD. Results show that the use of nanofluids as liquid membrane phase leads to higher extraction efficiency due to their stability and mass transfer enhancement.

A quadratic model for % extraction was developed, and the optimum conditions of MWCNT concentration, Roi, and carrier concentration were found to be 0.07 wt.%, 0.91, and 1.06 M, respectively. Under the optimum conditions, the experimental value of % extraction (98.92%) was in satisfactory agreement with that predicted from the model (98.12%).

For economical consideration, the nanofluid-based ELM was reused after demulsification without any noticeable deterioration in extraction performance.

The findings of the study open a future possibility of extending the nanofluid-based ELM for extraction of the other compounds in different applications.

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