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RESEARCH PAPER

Optimization of Solvent Extraction Parameters for Separation of Samarium and Lutetium from Acidic Media Using Response Surface Methodology (RSM)

Hamed Tavakkoli[1], Mohammad Reza Aboutalebi[2*], Seyed Hosein Seyedein[2] and Seyed Nezameddin Ashrafizadeh[3]

* *mrezab@iust.ac.ir*

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[1] PhD Student of School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran
[2] Professor, School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran
[3] Professor, School of Chemical Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran

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Abstract: *Separation of samarium and lutetium was investigated through solvent extraction from their mixed aqueous species using commercial extractants of D2EHPA and PC88A. The Response Surface Method (RSM) was utilized to design the solvent extraction experiments. Where, a Central Composite Design (CCD) was applied to set the optimum conditions for highest separation factors between Sm and Lu. Design of Experiments (DOE) was conducted by making use of four operating variables, namely initial pH of the aqueous solutions (A: 0.2–2.6), extractant concentration (B: 0.01-0.09 molar), mole fraction of D2EHPA in the extractant mixture (C: 0 - 0.8) and a type of acidic solution (D: sulfuric and nitric acid) at three levels. The results indicated that the initial pH was the most paramount variable in solvent extraction of samarium and lutetium, while in the case of lutetium, the molar fraction of D2EHPA in the mixed extractants was non-influential. The statistical model predictions were confirmed by experiments for both samarium and lutetium extraction with high validity parameter of 97 and 98%, respectively. The optimum conditions for samarium and lutetium separation were identified as: A=0.8, B= 0.05, C= 0.2 and D= sulfuric acid. According to the findings of the model, the desirability value at the optimum conditions was evaluated as about 0.93, in which 71% of lutetium was extracted while the amount of extracted samarium was only less than 1%.*

Keywords: *Samarium, Lutetium, D2EHPA, PC88A, Separation, Response Surface Methodology.*

1. INTRODUCTION

Rare earth elements (REEs), known as “industrial vitamins”, are strategic metals which are widely employed in energy storage, chemicals, metallurgical and advanced industries. The demand for high pure elements has drawn attention to the separation and purification of REEs (1). These elements are divided into two categories. The first belongs to the light-weight rare earth elements (LREEs) which is also known as cerium group (Ce-group), i.e. lanthanum to europium (atomic number Z= 57-63). The second category belongs to heavy-weight rare earth elements (HREEs) including gadolinium to lutetium (Z= 64-71) (2). Nowadays, solvent extraction is one of the major techniques on industrial scale for the extraction and separation of rare earth metals (2). This process is affected by some parameters like different types of extractant, initial pH of solution, type of diluent, kinds of liquor solution, synergic effect, organic to aqueous volume ratio, temperature, concentration of extractant or metal ions, and ionic straight [3-9]. Some of these parameters, such as the initial pH of solution, a type of extractant and synergic effects are more dominant than other parameters [2, 4, 6, 10]. Solvent extraction method using Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is often employed for extraction and recovery of these elements. Additionally, some studies have been performed using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA or P507) for the separation of REEs in which P507 has high selectivity and admissible extraction efficiency. Furthermore, REEs can be easily stripped at low acidities in EHEHEPA containing systems [2, 10-12]. The implementation of various combination of acidic organophosphorus extractants to increase the efficiency and selectivity of REEs has been investigated during the last two decades [5, 13, 14]. Obtaining an efficient extractant system that neccessiates higher pHs for stripping resulted in using mixtures of D2EHPA and EHEHPA [15, 16]. Higher selectivity and extraction efficiency of REEs have been achieved by mixture of these extractants [16].

In order to obtain an efficient separation between LREEs and HREEs in solvent extraction process, a comprehensive understanding of the extraction system has to be obtained. A combination of experiments, theoretical chemistry and mathematical thermodynamics data could be employed to simulate and optimize the whole extraction process. As a typical example, an empirical equation for the extraction of REEs using D2EHPA was developed by Zhang[2]:

$$[M_{(0)}] = \alpha_1 [M_{(\alpha)}]^{\alpha_2} . \exp\left(\alpha_2 [M_{(\alpha)}]\right) . H^{(\alpha_3 + \alpha_4 H + \alpha_5 H_2)} \tag{1}$$

Where, $[M_{(0)}]$ and $[M_{(\alpha)}]$ are the REEs concentrations in the organic and aqueous solutions, respectively; H is the H^+ concentration, and α_1 to α_5 are constant coefficients for each element[2].

In another study, Safarzadeh et al. [4] has investigated the separation of Nd from Pr using Design of Experiments (DOE). They employed Taguchi's L16 orthogonal array to obtain the highest separation factor ($\beta_{Nd/Pr}$). The effects of pH of the aqueous solutions (2–5), concentration of REE (10–40 ppm), extractant type (DEHPA, PC88A, TOPO, and Cyanex 572), extractant concentration (10–60 mM), and acid type (sulfuric and hydrochloric acids) on the separation were investigated. It has been proved that the best separation of Nd from Pr occurred with a factor of 2.72. The authors also proved that pH, type of extractant, and type of acid had the highest influence on the separation and D2EHPA and hydrochloric acid were premier in organic extractant and acidic media, respectively. Response Surface Method (RSM) is a statistical modeling approach that is applicable and practical in analyzing and modeling various parameters effects in a complicated system [17]. This method has been applied to optimize the extraction process of REEs [17, 18]. According to the literature, one of the major steps in the production of REEs is the separation of light and heavy elements [8, 19, 20]. There are a few reports on the separation of the light and heavy rare earth metals in different acid solutions while to the best of authors' knowledge no published work has been found on the separation of samarium and lutetium from nitric and sulfuric solutions by mixture of extractants. Therefore, in the current study, co-extraction of samarium and lutetium from acidic aqueous solutions was investigated with the aim of predicting the effect of the main process variables on the extraction efficiency of samarium and lutetium and separation behavior of these elements. A Central Composite Design (CCD) was applied to study the impacts of process variables, including the initial pH of the aqueous solutions, extractant concentration, mole fraction of D2EHPA in the mixture of extractants, and acid type (nitric and sulfuric acids) on the separation of Sm from Lu. The DOE is composed of four factors at five levels which were used to achieve the optimum conditions of separation. ANOVA method was used to develop a statistical model representing the effects of different parameters on extraction efficiency of Sm and Lu.

2. EXPERIMENTAL PROCEDURES

2.1. Reagents and Analysis

Lutetium oxide, samarium oxide, lutetium nitrate and samarium nitrate (99.9% purity) obtained from Middle East Ferro Alloy Co. were used to prepare synthetic aqueous solutions of samarium and lutetium. The extractants of D2EHPA was provided from Merck Co., and PC88A was purchased from Daihachi Company. The organic diluent, kerosene, was obtained from Alfa Aesar Company. Ammonium hydroxide, and nitric and sulfuric acids were obtained from Chem-Lab Company.

The concentration of samarium and lutetium in acidic aqueous solutions were equal to 200 mg/L. Nitric solutions were prepared by dissolving lutetium and samarium nitrates in nitric acid followed by dilution with distilled water. Sulfuric solutions were also prepared by dissolving appropriate amounts of lutetium or samarium oxides in concentrated sulfuric acid and further dilution by distilled water.

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2.2. Design of Experiments

Central Composite Design (CCD) was employed to achieve the optimized extraction conditions. In this methodology, three numeric factors along with one categorical factor with 28 runs, and 12 repetitions of the center points were chosen to specify the best initial pH of the aqueous solution, extractant concentration, mole fractions of D2EHPA and PC88A in the mixture, and the type of acid. Experiments were devised by Design Expert 10.0.7 software. The CCD includes the following sections:

1. L^n factorial points
2. 2n axial points
3. n_c center points

In each section n is the number of selected parameters and L is the number of levels for each parameter. The levels of the independent parameters of this study are specified in Table 1. The selected parameters were coded according to the following equation:

$$M_i = \frac{(m_i - m_{i,0})}{\Delta m} \qquad i = 1,2,...,n \tag{2}$$

Where M_i is the coded value of i-th factor, m_i, $m_{i,0}$ are the real values of parameters (factors) representing current and null amounts, respectively; Δm is the real value of the factor-variation difference. This system is expressed by the following experimental equation [18, 21]:

$$X = \sigma_0 + \sum_{i=1}^{k} \sigma_i Y_i + \sum_{i=1}^{k} \sigma_{ii} Y_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \sigma_{ij} Y_i Y_j + \varepsilon \tag{3}$$

Where X is the predicted response, Y_i and Y_j are the input parameters, σ_0 is the intercept term, σ_i is the linear effect, σ_{ii} is the squared effect, and σ_{ij} is the interaction term. The polynomial equations for the response were validated by Analysis of Variance (ANOVA) to specify the significance of each term in equations and also to achieve the best fitting equation. Response surfaces were drawn from the experimental results obtained from the effect of different parameters on Sm and Lu extraction in order to determine the individual and cumulative effects of these parameters, and the mutual interactions [18, 21].

2.3. Batch Experiments

Extraction was carried out using a glass beaker and a magnetic stirrer hot-plate. The pH of the solution was set to the predefined value by adding dilute ammonium hydroxide, or sulfuric or nitric acid solutions. The initial pH of the aqueous phase was checked by a digital Mettler Toledo- Seven Compact S220 pH meter. For each test, 20 mL of aqueous phase was mixed with 20 mL of the organic phase at room temperature, so that the two phases were completely mixed with each other. The mixture was agitated for 30 min using a magnetic stirrer at a speed of 350 rpm [22]. After the test, the mixture was poured into a separation funnel to allow the phases to separate. The concentrations of Lu and Sm ions in the aqueous solution before and after the extraction were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, AGILENT735). The distribution coefficient (D) and the percent of extraction (E) were calculated using the following equations:

$$D = \frac{[M]_t - [M]_a}{[M]_a} \tag{4}$$

$$\%E = \frac{D \times 100}{D + \frac{V_a}{V_O}} \tag{5}$$

Table 1. Levels and codes of variables in Central Composite Design.

Categoric Factors		**Numeric Factors**	**Levels**				
			Low axial	**Low factorial**	**Center**	**High factorial**	**High axial**
			(α=-2)	**(-1)**	**(0)**	**(+1)**	**(α=+2)**
D: acid type	Sulfuric Acid or Nitric Acid	A: initial pH of aqueous solutions	0.2	0.8	1.4	2	2.6
		B: extractant concentration (mM)	10	30	50	70	90
		C: molar fraction of D2EHPA	0	0.2	0.4	0.6	0.8

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Where $[M]_t$ and $[M]_a$ express the initial and final concentrations of Sm or Lu ions in the aqueous phase, and V_a and V_O are the volumes of the aqueous and organic phases, respectively.

Finally, to evaluate the effect of the used variables (including A: initial pH of the aqueous solutions, B: concentration of extractant, C: mole fraction of D2EHPA in the mixture of extractants, and D: acid type (nitric and sulfuric acids)) on the extraction of samarium and lutetium, sum of math squares model is recommended over the suggested models (Linear, 2FI and Cubic) by design expert 10.0.7.

3. RESULTS & DISCUSSION

3.1. Data Analysis and Contour Plots

The results of extraction of samarium and lutetium from nitric and sulfuric aqueous solutions at various operating conditions are illustrated in Table 2. As it is demonstrated, the extraction of samarium has been achieved approximately within the range of 0-99 % and that of lutetium from 18 to 99 %.

ANOVA method for samarium extraction is presented in Table 3. The F-value which is equal to 153.3 demonstrates the validity of the model. There is only 0.01 percent probability that such a large value of F could occur as a result of noise.

In the case that Prob value is higher than F and less than 0.05 the terms of the model which are significant could be distinguished. In this case A, B, C, D, AB, AC, A^2, A^2D, B^2D are differentiated as paramount terms. When Prob value is higher than F and greater than 0.1, terms of the model which are not significant could be defined. The "Lack of Fit for value of F" of 2.15 implies that the Lack of F it is not significant in relation to the pure error. There is only 10.61% probability that such a large "Lack of Fit F-value" could occur as a result of noise. Hence, the "Lack of Fit F-value" is considered insignificant and this shows the validity of the model.

The "Predicted R-Squared" of 0.9579 is compatible with the "Adjusted R-Squared" of 0.9723; i.e. the difference is less than 0.2. "Adequate Precision" defines the signal to noise ratio and values higher than 4 are acceptable for this parameter. The ratio of 44.057 obtained here conveys an appropriate signal. This model can be used to draw a spatial pattern. Final equation in terms of coded factors would be as following:

$$\text{Sm Extraction }(\%)=+28.1+23.62\times A+11.49\times B+8.81\times C-7.86\times D+8.13\times AB+4.88\times AC+5.37\times A^2+1.35\times A^2D+2.46\times B^2D \qquad (6)$$

By default, the highest and lowest value of each parameter is coded as "+1" and "-1", respectively. Moreover, this equation is functional to identify the relative effect of the parameters by comparing the coefficients. The predicted equations for Sm extraction from different solutions are given as below:

Aqueous solution (HNO_3):

$$\text{Sm Extraction }(\%)=+32.08-52.48\times pH-373.54\times C_{\text{Extractant}}-12.81\times X_{\text{D2EHPA}}+677.08\times pH\times C_{\text{Extractant}}+40.62\times pH\times X_{\text{D2EHPA}}+15.22\times pH^2-736.71\times C_{\text{Extractant}}2 \qquad (7)$$

Aqueous solution (H_2SO_4):

$$\text{Sm Extraction }(\%)=+19.75-52.48\times pH-373.54\times C_{\text{Extractant}}-12.81\times X_{\text{D2EHPA}}+677.08\times pH\times C_{\text{Extractant}}+40.62\times pH\times X_{\text{D2EHPA}}+14.59\times pH^2-736.71\times C_{\text{Extractant}}2 \qquad (8)$$

Obviously, the models given for sulfuric and nitric acid solutions are almost the same except that the width of origin is different. According to these models, extraction of samarium in nitric solution is always more substantial than that of sulfuric solution under similar operating conditions.

Fig. 1 shows the validity of the model with the real extraction values provided in Table 2. The validity coefficient in samarium extraction is 97.87 which shows a significant value for the obtained model.

In Figs. 2(a) and 2(b) the effect of concentration of extractants on the samarium extraction from different acidic solutions is illustrated. It is evident that the extraction of samarium is enhanced by increasing the concentration of extractants. As can be noticed from the Figures, upon increasing the pH of the solution, the rate of extraction has significantly increased.

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Table 2. Sm and Lu extraction at various operating conditions.

No.	**Space Type**	**(A) Initial pH**	**(B) Concentration of extractant (g/L)**	**(C) Mole fraction of D2EHPA**	**(D) Acidic solution**	**Sm Extraction (%)**	**Lu Extraction (%)**
1	Center	1.4	0.05	0.4	HNO_3	39	99.8
2	Factorial	0.8	0.07	0.6	HNO_3	22	96
3	Factorial	2	0.03	0.6	HNO_3	52	86
4	Center	1.4	0.05	0.4	H_2SO_4	19	99.7
5	Factorial	0.8	0.03	0.6	H_2SO_4	2	45
6	Axial	2.6	0.05	0.4	HNO_3	99.9	99.9
7	Factorial	0.8	0.07	0.6	H_2SO_4	16	92
8	Center	1.4	0.05	0.4	H_2SO_4	12	100
9	Factorial	0.8	0.03	0.2	HNO_3	5	36
10	Axial	1.4	0.05	0.8	H_2SO_4	37	99.9
11	Center	1.4	0.05	0.4	HNO_3	37	99.5
12	Factorial	2	0.03	0.2	H_2SO_4	14	89
13	Center	1.4	0.05	0.4	HNO_3	35	99
14	Factorial	0.8	0.07	0.2	HNO_3	14	93
15	Factorial	2	0.07	0.2	H_2SO_4	67	99.9
16	Axial	1.4	0.09	0.4	H_2SO_4	45	99.9
17	Axial	1.4	0.09	0.4	HNO_3	42	99.9
18	Center	1.4	0.05	0.4	H_2SO_4	21	99
19	Axial	0.2	0.05	0.4	H_2SO_4	0	18
20	Center	1.4	0.05	0.4	HNO_3	33	99.1
21	Factorial	2	0.03	0.6	H_2SO_4	47	91
22	Factorial	2	0.07	0.6	H_2SO_4	89	99.9
23	Center	1.4	0.05	0.4	H_2SO_4	22	98.7
24	Factorial	0.8	0.03	0.6	HNO_3	14	41
25	Factorial	2	0.03	0.2	HNO_3	36	92
26	Center	1.4	0.05	0.4	H_2SO_4	24	97.8
27	Center	1.4	0.05	0.4	HNO_3	36	99
28	Factorial	0.8	0.07	0.2	H_2SO_4	13	85.4
29	Axial	1.4	0.05	0	HNO_3	12	99.6
30	Axial	2.6	0.05	0.4	H_2SO_4	90	99.9
31	Axial	1.4	0.05	0	H_2SO_4	0	99.9
32	Axial	1.4	0.01	0.4	H_2SO_4	6	42
33	Axial	0.2	0.05	0.4	HNO_3	2	19
34	Factorial	0.8	0.03	0.2	H_2SO_4	3	43
35	Center	1.4	0.05	0.4	HNO_3	38	100
36	Axial	1.4	0.05	0.8	HNO_3	58	99.9
37	Factorial	2	0.07	0.6	HNO_3	95	99.9
38	Factorial	2	0.07	0.2	HNO_3	69	99.9
39	Axial	1.4	0.01	0.4	HNO_3	3.2	35
40	Center	1.4	0.05	0.4	H_2SO_4	23	99.1

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Table 3. Analysis of Variance for the model of samarium extraction.

Source	Sum of Squares	Dgree of Freedom	Mean Square	F Value	p-value Prob> F
Model	28849.89	9	3205.54	153.30	< 0.0001
A-pH	17851.05	1	17851.05	853.72	< 0.0001
B-$C_{\mathrm{Extractant}}$	4222.81	1	4222.81	201.95	< 0.0001
C-X_{D2EHPA}	2485.12	1	2485.12	118.85	< 0.0001
D-Liqure	1151.86	1	1151.86	55.09	< 0.0001
AB	1056.25	1	1056.25	50.51	< 0.0001
AC	380.25	1	380.25	18.19	0.0002
A^2	1566.49	1	1566.49	74.92	< 0.0001
A^2D	96.76	1	96.76	4.63	0.0396
B^2D	319.26	1	319.26	15.27	0.0005

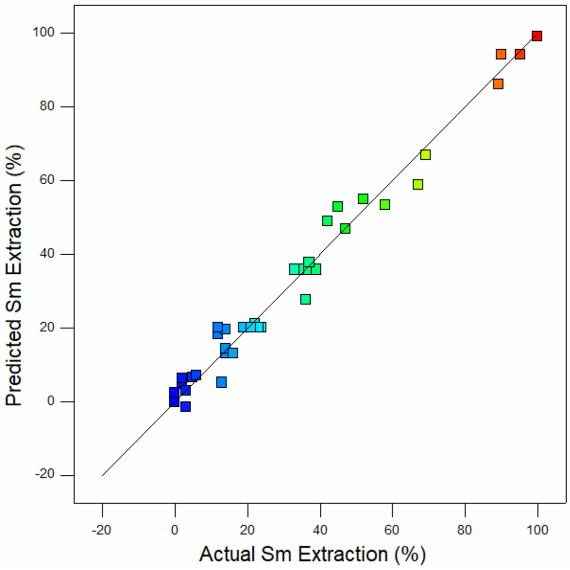

Fig. 1. Predicted versus actual extraction of samarium.

The effect of pH on the extraction of samarium from nitric and sulfuric acid solutions is shown in Figs. 2(c) and 2(d). The higher samarium extraction is obtained at higher molar fractions of D2EHPA in the mixed extractants. Due to the presence of an additional oxygen in the dimeric structure of the D2EHPA, this extractant has more dimerization and acidic constant compared to PC88A [16, 23]. Consequently, by increasing the amount of D2EHPA in the mixture of extractants, the extraction efficiency of samarium also increases. Furthermore, the synergic effect is higher in nitric solution rather than the sulfuric one. At pH=2, the samarium extraction has increased with increasing the molar fraction of D2EHPA from 37% to 64% and from 50% to 77% in sulfuric and nitric acid solutions, respectively. In addition, at pH=0.8 the samarium extraction increased with increasing the molar fraction of D2EHPA from 0% to 7% and from 12% to 20% in sulfuric and nitric acid solutions, respectively. Meanwhile, it is obvious that the samarium extraction is higher from nitric acid solution throughout the pH range. This difference can be related to the type of ionic complexes of the samarium element in nitric solutions in comparison with sulfuric solutions. It is because rare earth elements in different acidic environments show different stable ionic complexes. Since both types of used extractants were cationic, the electric charge of stable ion complexes can affect their extraction value.

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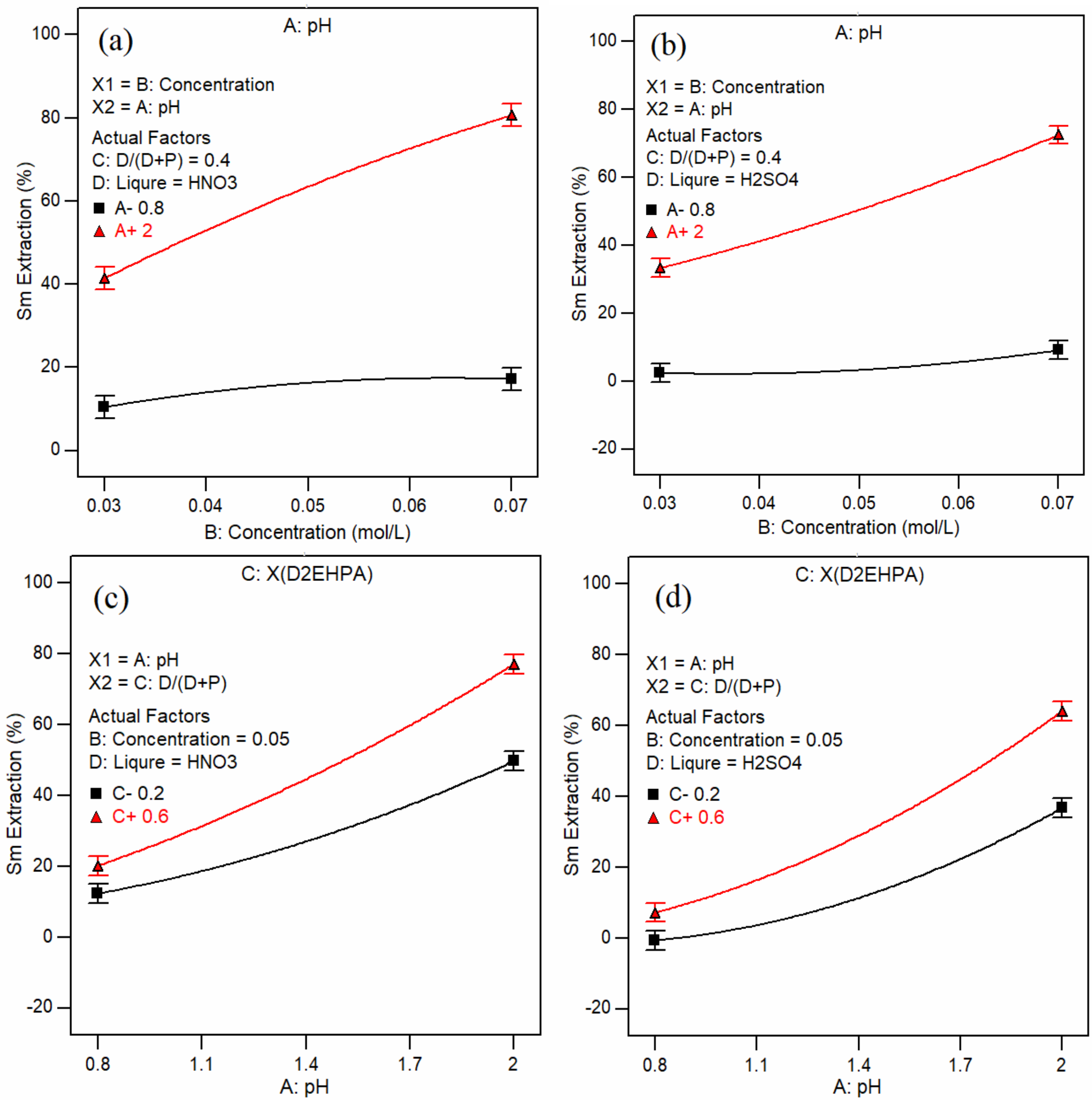

Fig. 2. The effects of extractant concentration and initial pH of solutions on Sm extraction (a), (c): nitric acid solution, (b), (d): sulfuric acid solution.

Analysis of variance for the lutetium extraction is presented in Table 4. The value of F which is 274.25 demonstrates the validity of the model. There is only 0.01 percent probability that such a large value of F could occur as a result of noise. If the Prob>F value is very small (less than 0.05 by default) then the source has tested significant, in this case A, B, AB, A^2, B^2 are significant terms of the model. F-values greater than 0.1 indicate the insignificant terms of the model. The "Predicted R-Squared" of 0.9675 is acceptable and compatible with the "Adjusted R-Squared" of 0.9800; because their difference is 0.0125 and less than 0.2. Here, the ratio of 49.313 for "Adequate Precision" indicates an adequate signal. Final equation in terms of coded parameters would be:

$$\text{Lu Extraction (\%)}=+99.3+17.24\times A+15.27\times B+0.14\times D-9.99\times AB-1.21\times BD-1.13\times A^2-7.63\times B^2 \quad (9)$$

Aqueous feed solution（HNO_3）:

$$\text{Lu Extraction (\%)}=-143.65+149.15\times pH+3896.77\times C_{Extractant}-832.29\times pH\times C_{Extractant}-28.14\times pH^2-19078.12\times C_{Extractant}2 \quad (10)$$

Aqueous feed solution (H_2SO_4):

$$\text{Lu Extraction (\%)}=-137.34+149.15\times pH+3776.14\times C_{Extractant}-832.29\times pH\times C_{Extractant}-28.14\times pH^2-19078.12\times C_{Extractant}2 \quad (11)$$

Fig. 3 shows the validity of the model with the actual extraction values given in Table 3. The validity coefficient in lutetium extraction is 98.36 which show the high efficiency of the model.

The effect of concentration of extractants on the lutetium extraction is shown in Figs. 4(a) and 4(b). It is obvious that the extraction of lutetium has increased by increasing the concentration of mixed extractants (according to the extraction reaction with cation exchange mechanism [3]). Also, upon the increase of the pH of the solution, although the extraction of lutetium is increased but dependency of the extraction to the concentration of extractants is decreased. In other words, the rate of extraction is reduced by increasing the pH and concentration of the extractants; because by increasing the initial pH of solutions, the possibility of decomposition of the dimers of the acidic extractants (D2EHPA and PC88A) and their participation in the extraction reaction increased [24].

The effect of pH on the extraction of lutetium in nitric and sulfuric solutions is shown in Figs. 4(c) and 4(d). As it is illustrated, no dependence on the composition of extractants is observed. This indicates that the synergistic effect of the two extractants on the extraction of lutetium is negligible.

The distribution ratios of Sm(III) is lower than Lu(III), that can be a direct result of higher hydrated Sm(III) radii than that of Lu(III) [2]. This makes the ionic charge density of Sm(III) to be less than that of Lu(III). In turn, it will bring some differences in the kinetically and thermodynamically behavior of these ions in aqueous and organic phases [2]. A smaller ionic radius can enhance the cationic binding and thus increase the extraction.

Table 4. Analysis of Variance for the model of lutetium extraction.

Source	Sum of Squares	Dgree of Freedom	Mean Square	F Value	p-value Prob> F
Model	25886.10	7	3698.01	274.25	< 0.0001
A-pH	9515.10	1	9515.10	705.66	< 0.0001
B- $C_{Extractant}$	7460.31	1	7460.31	553.27	< 0.0001
D-Liqure	0.78	1	0.78	0.058	0.8110
AB	1596.00	1	1596.00	118.36	< 0.0001
BD	46.56	1	46.56	3.45	0.0724
A^2	5409.85	1	5409.85	401.21	< 0.0001
B^2	3069.38	1	3069.38	227.63	< 0.0001
Residual	431.49	32	13.48		

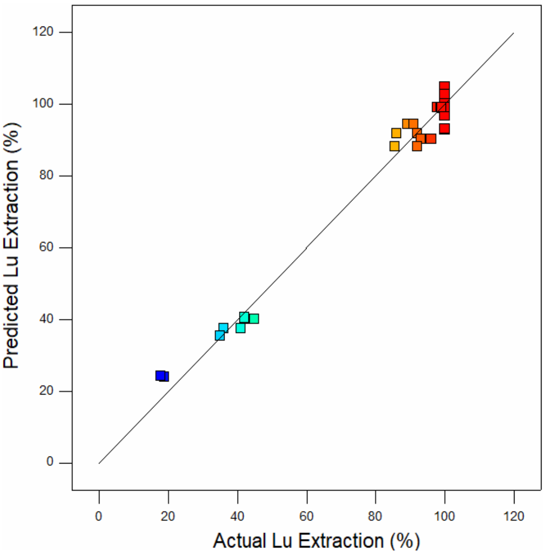

Fig. 3. Predicted versus actual extraction of lutetium.

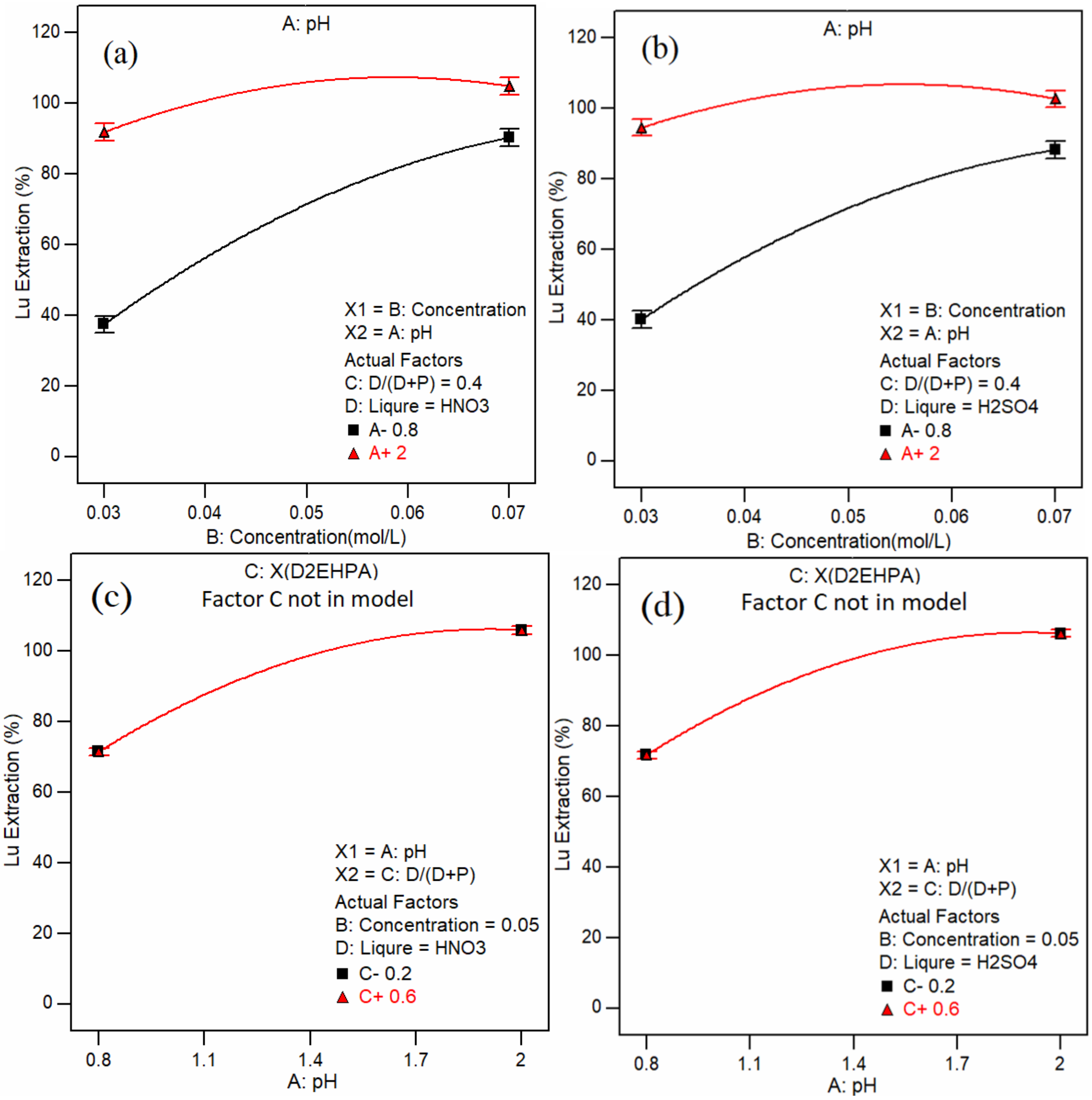

Fig. 4. The effect of extractants concentration on the Lu extraction from (a) nitric & (b) sulfuric solutions; and effect of initial pH on the Lu extraction from (c) nitric & (d) sulfuric solutions.

The 3D plots of extraction of samarium and lutetium are shown in Fig. 5 in which the effects of both extractant concentration and initial pH on the extraction of samarium and lutetium are presented. From the extraction of samarium point of view, according to Figs. 5(a) and 5(b), a better condition is provided with nitric solutions and thus the extraction of samarium is a little higher than sulfuric solutions. Under selected experimental conditions samarium and lutetium does not form any major nitrate species, whereas both of the elements form cationic and anionic complexes in sulfate solutions ($SmSO^{+}_4$, $LuSO^{+}_4$, $Sm(SO_4)^{-}_2$ and $Lu(SO_4)^{-}_2$) [4], therefore, increasing the extraction efficiency in the nitric solutions can be related to the type of stable ionic complexes. Comparing Figs. 5(c) and 5(d), it is perceptible that the extraction of lutetium is independent of aqueous solution medium because the electric charge density of lutetium is much greater than that of the samarium due to its lower ionic radius, the effect of the ion complex type on its extraction efficiency is negligible.

3.2. Optimization of Process Parameters

Table 5 shows the optimum conditions for separation of samarium and lutetium by solvent extraction using statistical model developed by Design Expert software. As it can be noticed, the optimum conditions for the separation of lutetium from samarium were predicted as initial

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pH of aqueous solutions: 0.840-0.850, concentration of extractants: 0.051- 0.052, mole fraction of D2EHPA: 0.2 and type of acidic solution: sulfuric acid.

The ramps view exhibited in Fig. 6 shows the desirability for initial pH, concentration of extractants, mole fraction of D2EHPA, and type of acidic solution as well as Sm and Lu extraction. The highlighted point in the Fig. 6 shows the exact values of each factor or response (horizontal shift of the point) and how this target is achieved (height of the ramp).

To verify the predicted results, a solvent extraction test was performed under the optimum conditions namely; initial pH of 0.85, extractants concentration of 0.05 and D2EHPA mole fraction of 0.2 in sulfuric acid solution. The measured samarium and lutetium extractions were compared with the predicted value (Table 6). As it is obvious, the deviations among the obtained and predicted values for the extraction of samarium and lutetium are negligible and these elements can almost completely be separated from each other by the identified solvent extraction process.

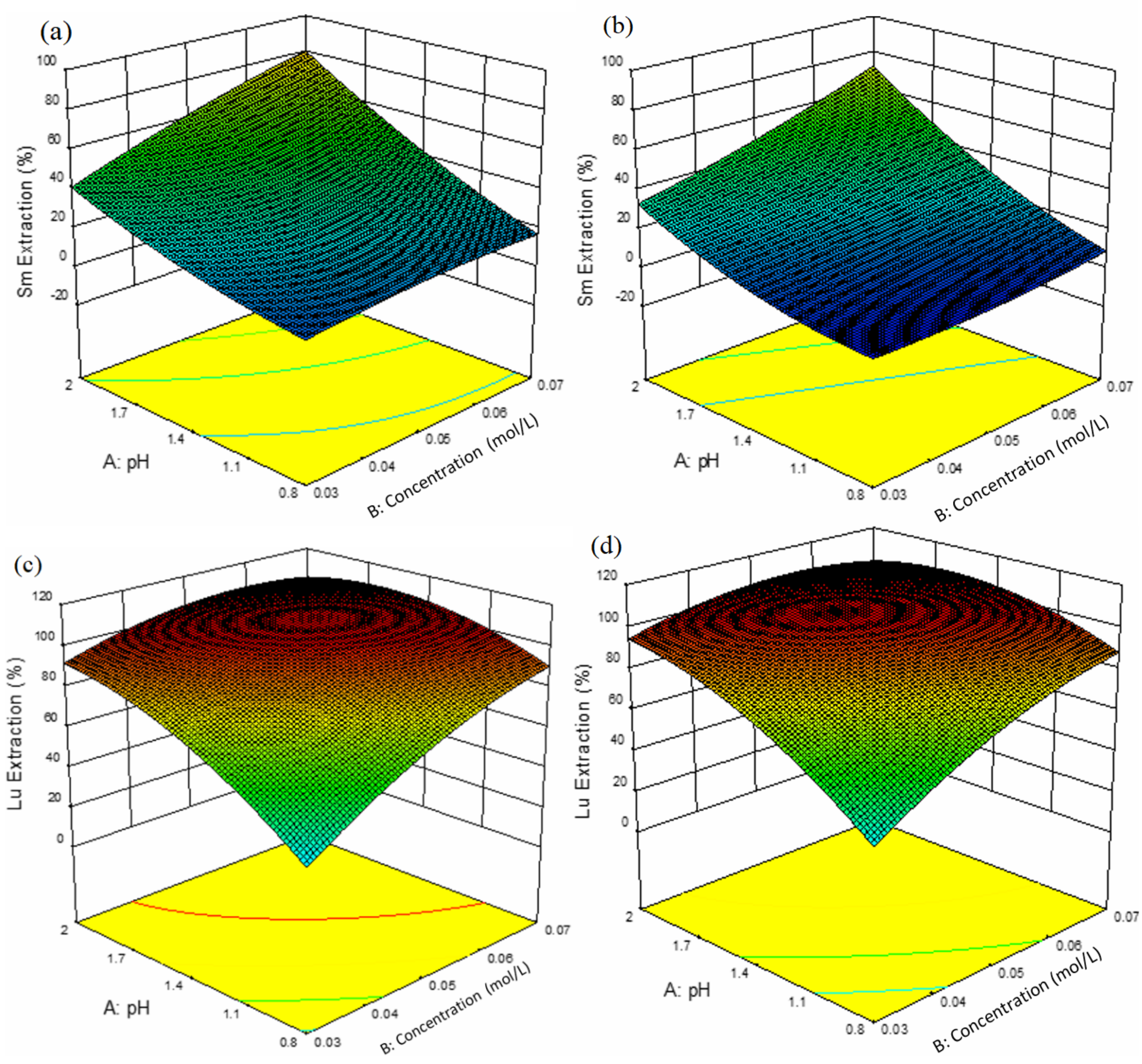

Fig. 5. The effect of extractants concentration and initial pH on the extraction of (a) samarium in nitric solution, (b) samarium in sulfuric solution, (c) lutetium in nitric solution, (d) lutetium in sulfuric solution.

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Table 5. Solutions for 2 combinations of categorical factor levels.

No.	pH	Concentration of extractants	X_{D2EHPA}	Type of acid solution	Sm Extraction (%)	Lu Extraction (%)	Desirability
1	0.840	0.052	0.200	H_2SO_4	0.009	75.955	0.929
2	0.836	0.052	0.200	H_2SO_4	0.004	75.930	0.929
3	0.845	0.051	0.200	H_2SO_4	0.021	76.019	0.929
4	0.841	0.051	0.200	H_2SO_4	-0.000	75.908	0.929
5	0.831	0.052	0.200	H_2SO_4	0.003	75.922	0.929
6	0.849	0.051	0.200	H_2SO_4	0.018	76.000	0.929
7	0.854	0.051	0.200	H_2SO_4	0.038	76.101	0.929
8	0.825	0.052	0.200	H_2SO_4	0.003	75.920	0.929
9	0.854	0.051	0.200	H_2SO_4	0.007	75.938	0.929
10	0.850	0.051	0.200	H_2SO_4	0.088	76.362	0.929

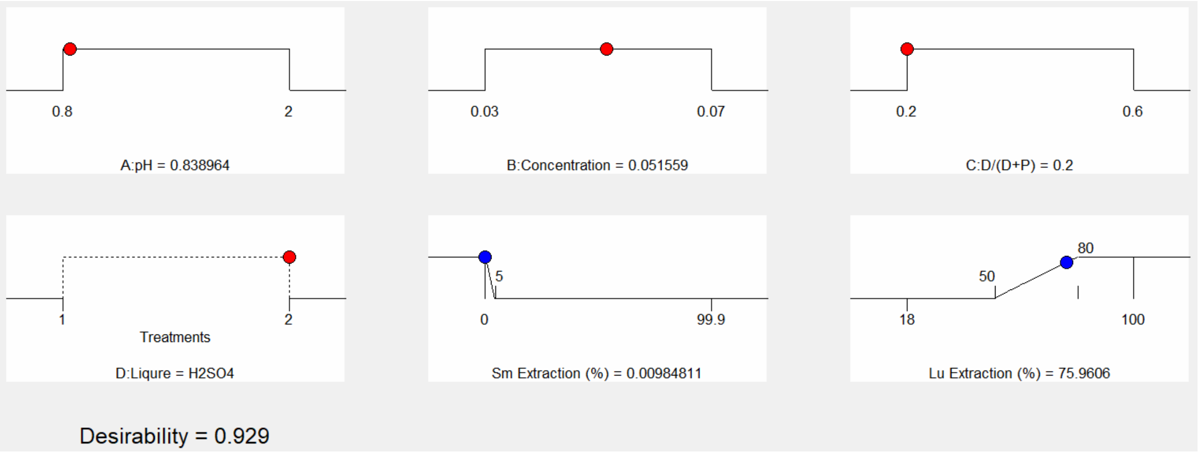

Fig. 6. Ramps of the numerical optimization.

Table 6. Optimum separation conditions for extraction of samarium and lutetium and comparison of the predicted and experimental results.

Factor				Sm Extraction (%)		Lu Extraction (%)	
pH	Concentration of extractants	X_{D2EHPA}	Type of acid solution	Predicted	Experiment	Predicted	Experiment
0.85	0.05	0.2	Sulfuric acid	0.01	0.9	76	71

4. CONCLUSION

The separation of samarium and lutetium from nitric and sulfuric aqueous solutions were successfully examined by DOE using Central Composite Design of Response Surface Method (RSM). The model predictions are confirmed with high validity number of about 97 and 98%, for both samarium and lutetium extraction respectively. The results show that when the maximum extraction of lutetium is obtained, the samarium extraction is too low. The extraction of samarium is preferentially occurs from nitric solution. In addition, in the extraction of

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lutetium there is no dependency on the type of aqueous medium. ANOVA indicated that the effect of initial pH of aqueous solution on the samarium and lutetium extraction was more effective than the other parameters. The best separation conditions for samarium and lutetium were identified as: pH_i=0.8, extractant concentration= 0.05 M, mole fraction of D2EHPA = 0.2 and type of acidic solution = sulfuric acid. According to the obtained model, the desirability value of such conditions is about 0.93; where 71% of lutetium is extracted while the amount of extracted samarium is less than 1%.

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