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Optimization of Parameters for Separation of the Medium Rare Earth Element Group from Other Rare Earth Elements by Precipitation Method Using Box-Behken Design

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Rare earth elements (REEs) are important materials in various technologies and have high economic value. Indonesia has the opportunity to become a country that has the potential to produce rare earth metal because it has tin mining areas where the by-product is monazite sand that contains 50% REEs. Based on this, a precise and efficient method is needed for separating REEs from the mixture. This study is a continuation of previous studies that selected parameters that affect the separation of REEs in the medium group from other groups by the precipitation method. This research optimizes the parameters of the selected precipitation method using the response surface method (Box-Behnken Design). The method used in this study was the optimization of the selective deposition method of REE hydroxide samples based on the different REEs pH for heavy, medium, and light groups using Box-Behnken Design. The parameters used were the reactant concentration, temperature, stirring speed, and pH. The result of parameter optimization that gave relevance to the maximum response rate of the REEs medium group was the oxalic acid concentration (1.0 N), precipitation temperature with oxalic acid (25 °C), pH of heavy REEs precipitation (3.10), pH of the REEs medium group precipitation (7.30), and precipitation temperature (90 °C). The separation efficiency of the REEs from monazite-origin samples treated to obtain the REEs hydroxide was 72.55%.

Keywords: Rare earth elements, Rare earth hydroxide, Design of experiment, Box-Behnken, Precipitation method

INTRODUCTION

Rare earth elements (REEs), a group of elements with similar physicochemical properties, consisting of 15 elements of lanthanide, scandium (Sc), and yttrium (Y) [1]. REEs are grouped depending on their atomic number in 'light', 'medium', and 'heavy' [2]. REEs even though they are called rare earth metals, their abundance is not rare or small but quite abundant. All elements belonging to the REEs group have almost the same properties and characteristics, so the separation of each element is difficult [1].

Over the last decade, REEs play an important role and have been widely used in various types of modern industrial products, such as magnetic alloys, photoluminescence materials, optical glasses, electronics, and computer apparatus. They are also widely used as catalysts for petroleum refining or as reagents for the diagnosis of magnetic resonance imaging (MRI) in medicine and some fertilizers in agriculture [2]. The price of rare earth metal oxide in its pure form is much higher than that of monazite minerals. In Indonesia, the REEs are obtained from mineral by-products of gold and tin mining activities in the Bangka and Singkep islands [3]. A mineral in question is monazite mineral, which is a phosphate mineral, containing a mixture of Ce, La, Pr, and Nd as well as radioactive elements such as thorium (Th) and uranium (U) [4,5]. These minerals

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have not been further processed to obtain pure rare-earth metals or in the form of their oxides, due to our limited knowledge of separation and processing technology, so they still need to be improved and developed.

Based on molecular weight, REEs can be classified into three main groups, namely: heavy, medium, and light groups. The separation and refining of the REEs have great potential in the long term. Technology continues to develop rapidly so that the need for REEs availability will continue to increase. The process of separating REEs to obtain pure metal is not easy, because of its similar properties among The REEs. To date, the separation process with the precipitation method is still chosen and carried out because it is easy, fast, and inexpensive [6]. The precipitation method for separating the REEs group was performed based on the pH value of the hydroxide REEs precipitation because each REEs has a different pH value although the difference is not too far between one REEs and another. The pH value of each REE was determined based on the composition of REEs in the hydroxide REEs sample and the amount of Ksp REEs, respectively [7,8].

This research was more focused on the separation of the REEs medium group which includes elements europium, gadolinium, samarium, terbium, and dysprosium. The final objective of this series of research, both to be carried out and another further research, was to obtain pure rare-earth elements, both individually and as a group. The separation of REEs group with the precipitation method in this study would be developed to obtain a design for the REEs separation procedure which could later be used for large-scale and commercial separation of REEs. The development of the design for this precipitation procedure used a design of experiments, which is a design that can predict the results of an experiment based on chemical statistics. The experimental design plans the entire possible experiment from the initial stage to the final stage and determines what parameters are needed to judge whether input variables respond themselves, when combined, or not at all [9].

The experimental design of the separation method of the REEs group with precipitation was the Box-Behnken Design (BBD), which is a second-order design that functions to optimize the factors that influence the response by response surface methodology (RSM) [10,11]. This design optimized all the parameters that affect the precipitation process from the initial stage to the final stage, both low level and high level. The optimization results could be used as the basis for the optimization of larger-scale processes. The novelty of this research is to separate REEs into several groups based on the difference in atomic weight with an optimized deposition method using experimental design.

EXPERIMENTAL

The method used was an extension of the procedure for separating lanthanum from monazite samples that have been carried out by Soe *et al.,*[12] and by Nwe Nwe Soe and Lwin Thuzar Shwe [13].

Chemical and Reagent

The materials used in this research included samarium nitrate ($Sm(NO_3)_3$), europium nitrate ($Eu(NO_3)_3$), gadolinium nitrate ($Gd(NO_3)_3$), terbium nitrate ($Tb(NO_3)_3$), and dysprosium nitrate ($Dy(NO3)_3$), all ingredients 99.9% (pa)-Sigma Aldrich, Merck's ammonia solution (pa), Merck's nitric acid (HNO_3) (pa), oxalic acid ($H_2C_2O_4.2H_2O$) Merck (pa) and REEs hydroxide ($REEs(OH)_3$) samples (processed by -PTBGN BATAN).

Apparatus

The tools used in this research were digital analytical balance AL204 (Mettler Toledo), Agilent Technologies 700 Series ICP-OES tool, Jenway 3505 pH meter, Thermomagnetic stirrer, Furnace Thermocline F47950, and chemometric software used for data processing, namely Design Expert DX.9.0.

Experimental Procedure

Preparation of the initial sample solution and pH of the REES hydroxide. A 0.0500 g of REEs hydroxide sample was dissolved with concentrated nitric acid, and then diluted until 50 ml. The REEs and non-REE contents in the sample were measured using the ICP-OES tool. Each REEs group had its pH value calculated based on the product of the REEs concentration and the hydroxide concentration, where this product might exceed the Ksp value of the hydroxide REEs. The Ksp value of REEs hydroxide could be seen in Table 1.

Table 1. Rare Earth Element Ksp Values [14]

Metal	Ksp REE(OH)$_3$	pH	REE group
Dy	1.40×10^{-22}	7.16	Medium
Eu	9.38×10^{-27}	5,86	Medium
Gd	1.80×10^{-23}	6,44	Medium
Sm	8.30×10^{-23}	6.94	Medium
Tb	2.0×10^{-22}	7.19	Medium
Ce	1.6×10^{-20}	7.30	Light
La	2.0×10^{-19}	7.81	Light
Nd	1.9×10^{-20}	7.71	Light
Pr	6.8×10^{-22}	7.20	Light

Table 2. Parameters for Design of Experiment

Factor*	Unit	Level*		
		-1	0	1
Oxalic acid concentration (X_1)	N	1	2	3
ecipitation temperature with oxalic acid (X_2)	°C	25	57.5	90
Precipitation pH of REE heavy group (X_3)	-	3.0	3.5	4.0
Precipitation pH of REE medium group (X_4)	-	5.9	6,6	7.3
Precipitation temperature of REE medium group (X_5)	°C	25	57.5	90

Note: *Parameter level determination based on previous research.

Table 3. REE Hydroxide Material Content

Content in REE(OH)$_3$	%
REEs total	64.84
REEs heavy group	0.93
REEs medium group	6.01
REEs light group	57.90
Non REE	35.16

Design of Experiment and Optimization

Based on the results of the previous experiment [15], that experiments using Plackett Burman design to select the condition of the REEs group separation variable with the precipitation method. The selection is set on the variable that has a significant effect on the maximum recovery percentage of the medium REEs group. The variables were selected because they have a significant effect on the response, namely: concentration of oxalic acid, pH of precipitation of heavy group REEs, the pH of the precipitation of the medium REEs group, and the temperature of precipitation of medium REEs group.

In this research, a study on the optimization of the REEs separation process was conducted using Response Surface Methodology (RSM) software against the results of the selected factors. The RSM tool chosen was the Box-Behnken Design (BBD) method to optimize the 5 selected factors, as shown in Table 2. Equation (1) shows the generalized response surface model.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad (1)$$

Where Y is the yield of variable (impact strength), b_0 is the constant, ε is the residual term, bi is the linear coefficients, bii is the quadratic coefficient, bij is the interaction coefficient and Xi is the dimensionless independent variable with coded [11]. The accuracy of this proposed method is evaluated by the efficiency of the recovery medium REEs group, as described in Eq. (2)

$$\text{Recov}\textit{ery efficiency of}$$
$$\textit{the medium REES group}\ (\%) = \frac{\textit{\%The medium REES group results from design separation}}{\textit{\%The medium REE group from sample}} \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

REEs Content in REEs Hydroxide Using ICP-OES

Based on the analysis of the composition of REEs and non-REEs in the sample REEs hydroxide using ICP-OES, it was obtained as described in Table 3.

Response Analysis and Interpretation by Box Behnken Design (BBD)

In this research, the separation of the medium REEs

Table 4. Classic Assumption Test of Multiple Linear Regression Data

Asumsition test	Parameter	Value	Diagnostic
Normality test	Kolmogorov-Smirnov	Asymp. Sig. (2-tailed): 0.200	normally distributed
Multicollinearity test	VIF (variance inflitation factor)	1 (<10)	no symptoms of multicollinearity
	Tolerance	1 (>0.01)	no symptoms of multicollinearity
	Pearson corralation	0.000 (< 0.8)	no symptoms of multicollinearity
	Eigenvalue	0.002 (<0.01)	no symptoms of multicollinearity
Autocorrelation test	Durbin Watson	4-Du < d < 4-Dl	can't be concluded
Heteroscedasticity test	t-statistics	Constant: 0.895	not heterodistatic
		X1: 0.206	not heterodistatic
		X2: 0.103	not heterodistatic
		X3: 0.895	not heterodistatic
		X4: 1.000	not heterodistatic
		X5: 0.961	not heterodistatic

group from the other group was investigated to treat precipitation under different operating conditions such as oxalic concentration (1-3 N) and temperature precipitation (25-90 °C) to precipitate all REEs group, pH (3.0-4.0) to precipitate the heavy REEs group, temperature (25-90 °C) and pH (5.9-7.3) to precipitate the medium REEs group. Five factors with three levels of response surface design by BBD tool were employed to optimize and investigate the effect of process variables on the responses, such as recovery (%) of the medium REEs group.

The residual value (ε_i) in linear regression must be tested to meet the requirements, namely: normality, homoscedasticity, autocorrelation, and multicollinearity tests. The results of the residual data assumption test are shown in the Table 4. This assumption test is carried out to achieve a parameter estimate that is the best linear unbiased estimator. Based on the table above, the experimental design, data indicate that the data is normally distributed, there is no correlation between variables that can interfere with the relationship between x and y variables, in the regression model, there is no variance inequality from one observation residual to another observation, and there is no confounding error correlation in the linear regression model [16].

The design matrix of the variables in the uncoded and coded units by the BBD is shown in Tables 5a-b, along with the predicted and experimental values of the recovery of the responses (%) of the REEs medium group (Y). The predicted values of the responses were obtained from quadratic model fitting techniques for the percentage of recovery of the medium REEs group using the Design Expert 9.0 software. The characterization of the experimental design model construction produced is shown in Table 6.

Based on the model construction generated by the BBD design in Table 6, the output results inform about the value of the contribution that causes the simultaneous influence of the independent variable on the dependent variable based on the coefficient of determination of (0.769). This means that all independent variables simultaneously affect the response of 76.90%, while the other 23.10% are influenced by other variables outside the model that is not analyzed. The output results also obtained a correlation coefficient (R) of 0.877, which indicates a strong relationship between the independent variable and the dependent variable of 87.70%, while as much as 12.30% is influenced by variables outside

Table 5a. Arrangement Experimental Design with Uncoded Factor of Rare Earth Element Separation Using Precipitation Method by Box Behnken Design

Run	Oxalic acid concentration (X_1)	Precipitation temperature with oxalic acid (X_2)	Precipitation pH of REE heavy group (X_3)	Precipitation pH of REE medium group (X_4)	Precipitation temperature of REE medium group (X_5)	Response % REEs (medium-group)	
						Exp.	Pred.
1	2.0	57.5	4.0	7.3	57.5	3.83	3.33
2	2.0	90.0	4.0	6.6	57.5	1.80	2.18
3	2.0	57.5	4.0	5.9	57.5	0.97	1.19
4	2.0	57.5	4.0	6.6	90.0	2.80	2.44
5	2.0	57.5	3.5	6.6	57.5	1.82	1.66
6	1.0	57.5	3.5	6.6	90.0	1.89	2.14
7	2.0	90.0	3.5	7.3	57.5	4.09	3.87
8	3.0	57.5	3.0	6.6	57.5	1.63	1.77
9	1.0	57.5	4.0	6.6	57.5	1.78	1.99
10	2.0	57.5	3.0	6.6	90.0	2.96	2.70
11	3.0	57.5	3.5	7.3	57.5	4.18	3.91
12	3.0	57.5	3.5	5.9	57.5	1.02	0.89
13	2.0	25.0	3.5	7.3	57.5	4.01	4.11
14	2.0	25.0	3.5	6.6	25.0	1.97	2.21
15	2.0	57.5	3.5	6.6	57.5	1.65	1.83
16	2.0	25.0	3.0	6.6	57.5	1.70	1.54
17	2.0	25.0	3.5	5.9	57.5	0.97	1.12
18	2.0	57.5	3.5	5.9	25.0	1.46	1.32
19	2.0	25.0	4.0	6.6	57.5	1.75	1.55
20	3.0	57.5	3.5	6.6	90.0	1.31	1.42
21	2.0	57.5	3.5	6.6	57.5	1.68	1.92
22	2.0	57.5	3.5	7.3	25.0	4.02	4.31
23	2.0	57.5	4.0	6.6	25.0	2.32	2.55
24	2.0	57.5	3.5	7.3	90.0	3.76	3.54
25	3.0	57.5	3.5	6.6	25.0	1.94	2.01
26	1.0	57.5	3.0	6.6	57.5	2.38	2.33
27	1.0	57.5	3.5	7.3	57.5	3.71	3.23
28	2.0	57.5	3.0	6.6	25.0	1.74	1.56
29	1.0	57.5	3.5	5.9	57.5	1.05	1.33
30	3.0	57.5	4.0	6.6	57.5	1.16	1.28
31	1.0	57.5	3.5	6.6	25.0	0.95	1.09
32	2.0	57.5	3.0	5.9	57.5	1.13	1.38
33	1.0	90.0	3.5	6.6	57.5	2.18	2.01
34	2.0	90.0	3.0	6.6	57.5	1.76	1.66
35	3.0	90.0	3.5	6.6	57.5	1.54	1.75
36	2.0	57.5	3.5	6.6	57.5	1.93	1.76
37	2.0	57.5	3.0	7.3	57.5	4.21	3.91
38	2.0	90.0	3.5	6.6	25.0	2.43	2.61
39	1.0	25.0	3.5	6.6	57.5	1.96	2.07
40	2.0	57.5	3.5	6.6	57.5	1.13	1.32
41	3.0	25.0	3.5	6.6	57.5	2.04	1.98
42	2.0	57.5	3.5	6.6	57.5	1.72	1.43
43	2.0	90.0	3.5	5.9	57.5	1.05	1.27
44	2.0	25.0	3.5	6.6	90.0	2.13	1.89
45	2.0	57.5	3.5	5.9	90.0	1.01	0.88
46	2.0	90.0	3.5	5.9	25.0	3.20	2.97

Table 5b. Arrangement Experimental Design with Coded Factor of Rare Earth Element Separation Using Precipitation Method by Box Behnken Design

Run	Oxalic acid concentration (X_1)	Precipitation temperature with oxalic acid (X_2)	Precipitation pH of REE heavy group (X_3)	Precipitation pH of REE medium group (X_4)	Precipitation temperature of REE medium group (X_5)	Response % REEs (medium-group)	
						Exp.	Pred.
1	0	0	1	1	0	3.83	3.33
2	0	1	1	0	0	1.80	2.18
3	0	0	1	-1	0	0.97	1.19
4	0	0	1	0	1	2.80	2.44
5	0	0	0	0	0	1.82	1.66
6	-1	0	0	0	1	1.89	2.14
7	0	1	0	1	0	4.09	3.87
8	1	0	-1	0	0	1.63	1.77
9	-1	0	1	0	0	1.78	1.99
10	0	0	-1	0	1	2.96	2.70
11	1	0	0	1	0	4.18	3.91
12	1	0	0	-1	0	1.02	0.89
13	0	-1	0	1	0	4.01	4.11
14	0	-1	0	0	-1	1.97	2.21
15	0	0	0	0	0	1.65	1.83
16	0	-1	-1	0	0	1.70	1.54
17	0	-1	0	-1	0	0.97	1.12
18	0	0	0	-1	-1	1.46	1.32
19	0	-1	1	0	0	1.75	1.55
20	1	0	0	0	1	1.31	1.42
21	0	0	0	0	0	1.68	1.92
22	0	0	0	1	-1	4.02	4.31
23	0	0	1	0	-1	2.32	2.55
24	0	0	0	1	1	3.76	3.54
25	1	0	0	0	-1	1.94	2.01
26	-1	0	-1	0	0	2.38	2.33
27	-1	0	0	1	0	3.71	3.23
28	0	0	-1	0	-1	1.74	1.56
29	-1	0	0	-1	0	1.05	1.33
30	1	0	1	0	0	1.16	1.28
31	-1	0	0	0	-1	0.95	1.09
32	0	0	-1	-1	0	1.13	1.38
33	-1	1	0	0	0	2.18	2.01
34	0	1	-1	0	0	1.76	1.66
35	1	1	0	0	0	1.54	1.75
36	0	0	0	0	0	1.93	1.76
37	0	0	-1	1	0	4.21	3.91
38	0	1	0	0	-1	2.43	2.61
39	-1	-1	0	0	0	1.96	2.07
40	0	0	0	0	0	1.13	1.32
41	1	-1	0	0	0	2.04	1.98
42	0	0	0	0	0	1.72	1.43
43	0	1	0	-1	0	1.05	1.27
44	0	-1	0	0	1	2.13	1.89
45	0	0	0	-1	1	1.01	0.88
46	0	1	0	-1	-1	3.20	2.97

Table 5. Characteristics of the Constructed Models

Regression equation		Coefficient	Value	Coefficient	Value
$Y = \beta o + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_5X_5 + \beta_{1.1}X_1^2 + \beta_{1.2}X_1X_2 + \beta_{1.3}X_1X_3 + \beta_{1.4}X_1X_4 + \beta_{1.5}X_1X_5 + \beta_{2.2}X_2^2 + \beta_{2.3}X_2X_3 + \beta_{2.4}X_2X_4 + \beta_{2.5}X_2X_5 + \beta_{3.3}X_3^2 + \beta_{3.4}X_3X_4 + \beta_{3.5}X_3X_5 + \beta_{4.4}X_4^2 + \beta_{4.5}X_4X_5 + \beta_{5.5}X_5^2$		βo	1.88	$\beta_{2.3}$	0.020
R	0.877	β_1	-0.067	$\beta_{2.4}$	-0.0007
R^2	0.769	β_2	0.091	$\beta_{2.5}$	0.15
Adj-R^2	0.740	β_3	-0.064	$\beta_{3.4}$	-0.052
Standard error	0.505	β_4	1.45	$\beta_{3.5}$	-0.19
		β_5	0.14	$\beta_{4.5}$	0.051
		$\beta_{1.1}$	-0.21	$\beta_{2.2}$	0.11
		$\beta_{1.2}$	-0.18	$\beta_{3.3}$	0.050
		$\beta_{1.3}$	0.033	$\beta_{4.4}$	0.61
		$\beta_{1.4}$	0.12	$\beta_{5.5}$	0.22
		$\beta_{1.5}$	-0.39		

the model. The response functions with the determined regression coefficients for recovery percentage the medium REEs group was presented by a final equation in terms of coded factor (Eq. (3)).

$$Y\ (\%\text{Medium REEs group}) = 1{,}88 - 0.067X_1 + 0.091X_2 - 0.064X_3 + 1.447X_4 + 0.137X_5 - 0{,}206X_1^2 - 0{,}178X_1X_2 + 0.033X_1X_3 + 0.124X_1X_4 - 0.393X_1X_5 + 0{,}107X_2^2 + 0.018X_2X_3 - 0.0001X_2X_4 + 0.153X_2X_5 + 0.050X_3^2 - 0.052X_3X_4 - 0.194X_3X_5 + 0.606X_4^2 + 0.051X_4X_5 + 0{,}221X_5^2 \quad (3)$$

Based on Eq. (3), the output data can be interpreted as if all independent variables (X_1, X_2, X_3, X_4 and X_5) have a value of 0, then the constant value is 1.88, which means that the REE recovery of the medium group has a value of 1.88%. Regression coefficients of precipitation temperature with oxalate (X_2), medium group REEs precipitation pH (X_4), medium group REEs precipitation temperature (X_5), interactions between variables X_1 and X_3, X_1 and X_4, X_2 and X_3, X_2 and X_5, and X_4 and X_5 are positive, this indicates that if all of these variables have increased, the recovery percentage of medium group REEs will increase by the value of the regression coefficient of the variable. The regression coefficient of oxalate concentration (X_1), pH of heavy group REEs precipitation (X_3), the interaction between variables X_1 and X_2, X_1 and X_5, X_2 and X_4, X_3 and X_4, and X_3 and X_5 are negative, this indicates that all these variables experienced an increase, the recovery percentage REEs of the medium group will decrease by the value of the regression coefficient of the variable. The positive factors would provide additional responses, while negative factors would impact the resulting reduced response [17].

Table 6. Independent Variable Partial Test (t-Test)

Variable	Standard error	b_i	t-Statistic	t-Table	Sig.
X_1	0.06593	-0.067	-1.0162	2.014103	Y
X_2	0.00203	0.091	44.8570	2.014103	N
X_3	0.13186	-0.064	-0.4854	2.014103	N
X_4	0.09419	1.45	15.3947	2.014103	Y
X_5	0.00203	0.14	69.0108	2.014103	N

Partially, the effect of variable x is tested by t-test, this is to determine the effect of each variable x on the targeted response, as shown in Table 7.

According to the table, showed that of the five independent variables, when tested partially, only variable X_4 (the pH of medium group REEs precipitation) has a

Table 7. Analysis of Variance for the Response Surface Quadratic Model

Source	Sum of square (SS)	Degrees of freedom (DF)	Mean of square (MS)	Variance source (F)	Probability of error significant (P) Probe > F	Explaination
Model	40.84	20	2.04	11.53	< 0.0001	Significant
X_1	0.072	1	0.072	0.41	0.5300	
X_2	0.15	1	0.15	0.84	0.3684	
X_3	0.073	1	0.073	0.41	0.5253	
X_4	33.48	1	33.48	189.03	< 0.0001	
X_5	0.31	1	0.31	1.74	0.1993	
$X_1 X_2$	0.13	1	0.13	0.72	0.4047	
$X_1 X_3$	4.25×10^{-3}	1	4.25×10^{-3}	0.024	0.8781	
$X_1 X_4$	0.061	1	0.061	0.35	0.5612	
X_1X_5	0.62	1	0.62	3.49	0.0734	
X_2X_3	2.51×10^{-5}	1	2.51×10^{-5}	1.42×10^{-4}	0.9906	
$X_2 X_4$	1.54×10^{-6}	1	1.54×10^{-6}	8.73×10^{-6}	0.9977	
X_2X_5	0.093	1	0.093	0.52	0.4756	
X_3X_4	0.011	1	0.011	0.061	0.8063	
$X_3 X_5$	0.14	1	0.14	0.77	0.3884	
X_4X_5	0.010	1	0.010	0.058	0.8117	
X_1^2	0.081	1	0.081	0.46	0.5048	
X_2^2	0.44	1	0.44	2,.9	0.1272	
X_3^2	0.25	1	0.25	1.43	0.2433	
X_4^2	4.47	1	4.47	25.22	< 0.0001	
X_5^2	0.97	1	0.97	5.48	0.0275	
Residual	4.43	25	0.18			
Lack of fit	4.04	20	0.20	2,63	01437	Not significant
Pure error	0.38	5	0.077			
Cor total	45.27	45				

strong influence on the response of REEs recovery in the medium group, while the other variables cannot be proven to affect the results. This can be seen from the significance of X_4, the X_4 t-test value is higher than the t-table value. Although partially only the X_4 variable affects the response, simultaneously all the independent variables will affect the desired response, this can be seen from the F test.

The adequacy of the model was tested by Fisher's statistical test for the analysis of variance (ANOVA) using Design-Expert software [18]. ANOVA quadratic regression model shows that the model is significant with a calculated F value of 11.53, the calculated f value is greater than the F table value (2.59), this shows that simultaneously all x variables will affect the response. The model also generates the value of P>F value lower than 0.05, if the value of coefficient variation is lower then suggests higher readability of the experiment. ANOVA tests were also conducted for each response and presented in Table 8. Indicating the fact that the predictability of the model was at 95% confidence level [17]. To consider the relationship between the predicted values from the model calculated from Eq. (2) and the observed values, the data obtained

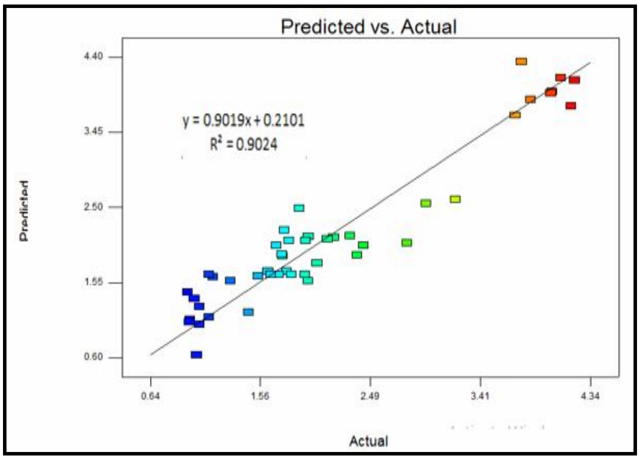

Fig. 1. Linear regression curve between the actual response value and the predicted response value.

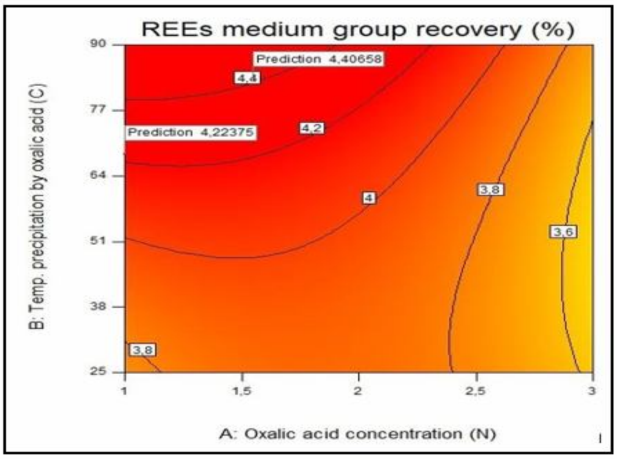

Fig. 2. Response surface (2D), the effect of precipitation temperature and concentration of oxalic acid on the separation of the REEs group.

were very close to linear, indicating that both values were accurate and reliable, as shown in Fig. 1.

The Effect of Variables on REEs Group Separation

Figure 2 to Fig. 9 presents the two-dimensional (2D) response surface plots of yields as a function of the independent variables. The 2D surface explained the relationship between the dependent variables (Y) and independent variables (X_1, X_2, and X_3). With regard to these three variables, one of them remained constant at its zero levels, while the two others were analyzed separately.

The 2D contour plots in Fig. 2 to Fig. 9, which are simulations from Eq. (3) described the effect of the process variables on the separation of REEs group efficiencies. As shown in Fig. 2 to Fig. 9, the highest percentage recovery of the medium REEs group obtained from the optimization

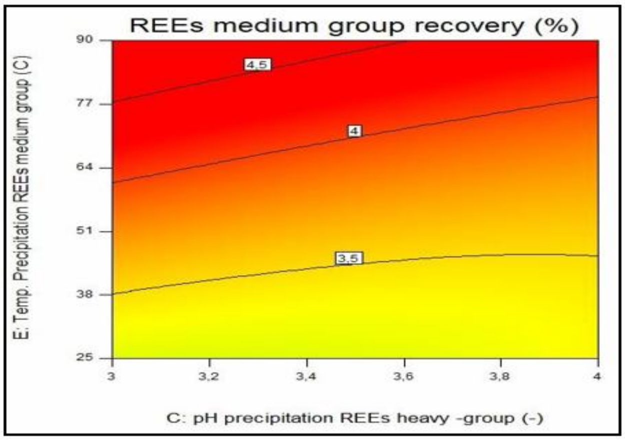

Fig. 3. Response surface (2D), the effect of REEs heavy group precipitation pH and REEs medium group temperature precipitation on the separation of the REEs group.

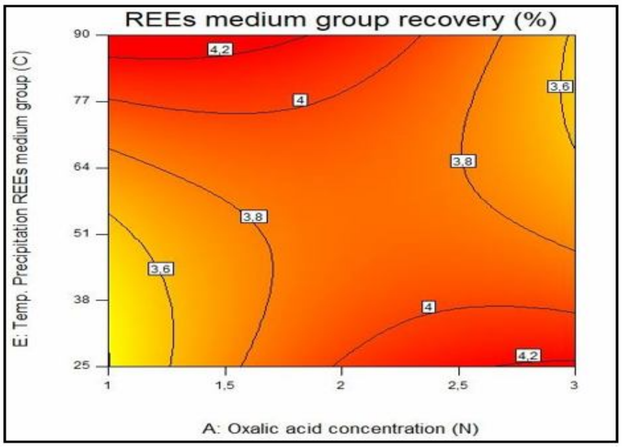

Fig. 4. Response surface (2D), the effect of oxalic acid concentration and REEs medium group temperature precipitation on the separation of the REEs group.

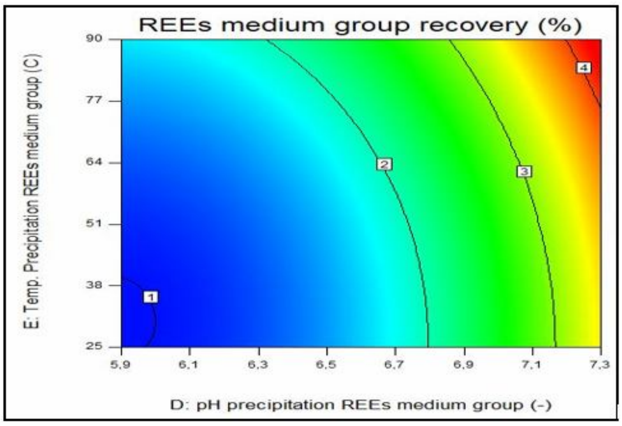

Fig. 5. Response surface (2D), the effect of REEs medium group precipitation pH and REEs medium group temperature precipitation on the separation of the REEs group.

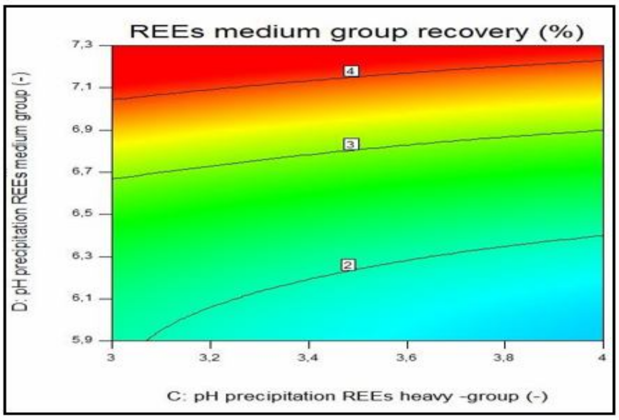

Fig. 7. Response surface (2D), the effect of REEs heavy group precipitation pH and REEs medium group precipitation pH on the separation of the REEs groups.

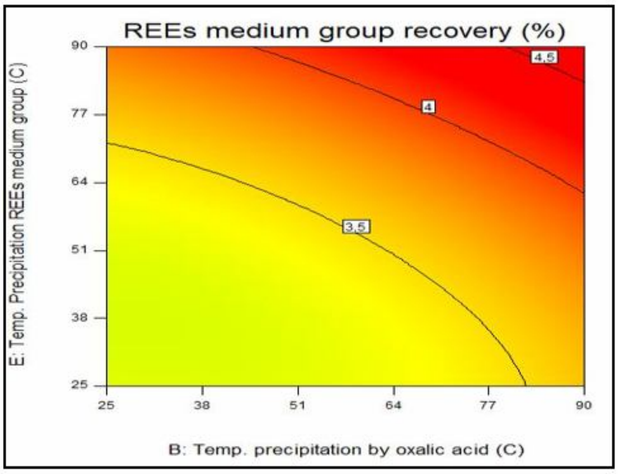

Fig. 6. Response surface (2D), the effect precipitation temperature oxalic acid precipitate and REEs medium group temperature precipitation on the separation of the REEs group.

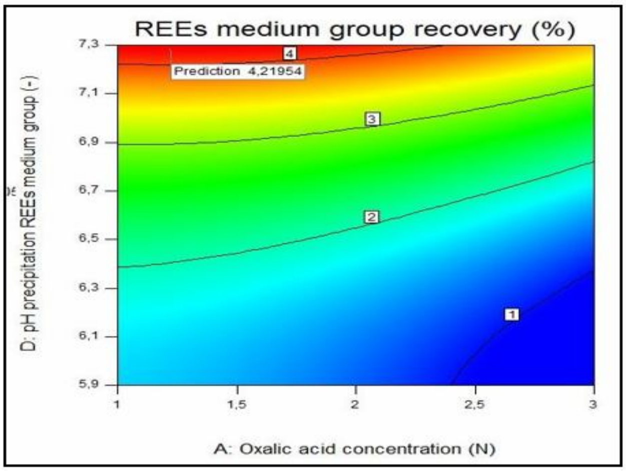

Fig. 8. Response surface (2D), the effect of oxalic acid concentration and REEs medium group precipitation pH on the separation of the REEs group.

results (4, 2-4, 4%) achieved in precipitation temperature by oxalic acid (80-90 °C), oxalic acid concentration (1-1, 5 N), precipitation pH of the heavy REEs group (3.0-3.5), precipitation pH of medium REEs group (7.3) and precipitation temperature of REEs medium group (80-90 °C).

The REEs have the same physical and chemical properties, but based on previous research could be separated into groups by deposition based on differences in pH according to Table 2. The determination of pH for each REEs group was obtained from the Ksp value data for each REEs element. separation by precipitation based on differences in pH is difficult because the pH adjustment of each group is not too far apart. Based on the response

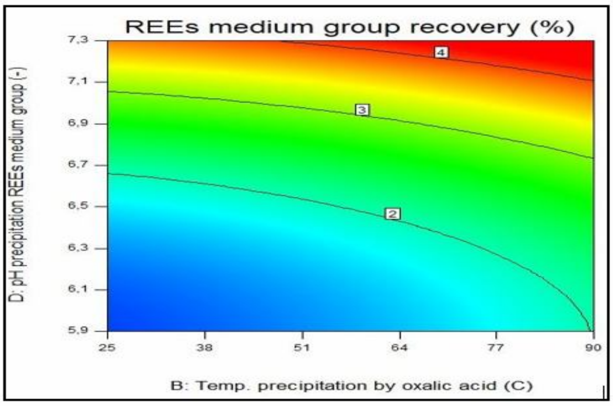

Fig. 9. Response surface (2D), the effect of temperature precipitation with oxalic acid and REEs medium group precipitation pH on the separation of the REEs group.

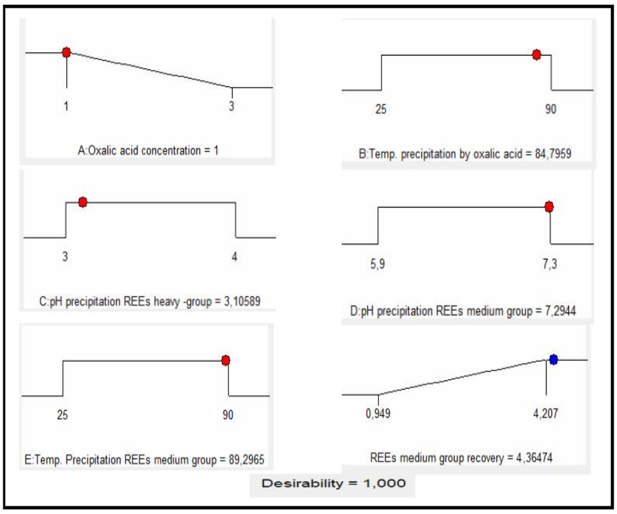

Fig. 10. Parameter optimum level formula of separation REEs group base Box-Behnken Design.

surface contour plot in Fig. 2 to Fig. 9, the optimum pH for precipitating the heavy REEs group was (3.0-3.5) and medium REEs group was (7.3), If the pH was lower or upper than the optimum level, the results would not have been optimal.

Temperature is one of the important factors in the precipitation reaction. When the solute content is fixed, the supersaturation of the solution usually decreases with increasing temperature according to the relationship between supersaturation and temperature. The supersaturation may be larger at a very low temperature, but the rate of formation of crystal particles may be low due to the low energy of the solute molecules. With an increase in temperature, the crystal particle generation can reach maximum. If the temperature continually increases, on the one hand, the supersaturation of solution may decrease; on the other hand, the crystal particles of generation speed tend to decrease because the molecular kinetic energy increases too quickly to inhibit forming stable crystal particles [19]. Based on the response surface contour plot on Fig. 2 to Fig. 9 to obtain the expected target yield, as follow the maximum recovery of the medium REEs group, the optimum temperature for precipitation was in the range of 80-90 °C. If the temperature was lower, the results would not have been optimal.

Optimization and Model Validation

Response surface graphs were plotted by the quadratic regression equations obtained from the BBD method to understand the interaction effects of variables and for identifying the optimal levels of each parameter for attaining the optimum condition of REEs separation and to get maximum recovery percentage of the medium REEs group. For each response, the desired goal was to recommend maximum, maximum, minimum, target, in range, and none.

In the design of BBD, there were 30 alternative formula optimization results suggested with different DF (desirability function) levels. In this research the formula chosen was the one with the highest DF value based on the setting of variable criteria and the targeted response, as follows: the smallest concentration of oxalic acid, pH, and precipitation temperature within the minimum and maximum limits, with the target response to the minimum REEs recovery of heavy and light groups and the maximum REEs medium group. This criterion was chosen to scale up the separation as effectively as possible, where the maximum possibility of the medium REEs group recovery percentage was obtained, but the costs involved in the separation could be minimized. The alternative formulas suggested by the Box-Behnken program could be seen in Fig. 10.

Based on the BBD design, the formula was chosen with the highest DF value and the highest target response, the formula with the following optimum factor conditions, as follows: oxalic acid concentration 1 N, precipitation temperature with oxalic acid (85 °C), precipitation pH of the heavy REEs group (3.1), precipitation pH of the REEs medium group (7.3) and the precipitation temperature for the precipitation of medium REEs group (90 °C) as described on Fig. 10. The REEs medium group content of the initial REE hydroxide sample was 6.01%, while the REEs of the medium group resulted from the separation by the method of deposition based on the BBD design was 4.36%, so that the efficiency of this separation was = 72.55%.

CONCLUSIONS

This work was mainly focused on the preparation of the REEs group separation with the precipitation method. Besides, it included modeling and optimization of parameter levels. The effects of the five parameters, namely Oxalic acid concentration, precipitation temperature with oxalic acid, precipitation pH of the heavy and medium REEs group, and precipitation temperature of the medium REEs group, were studied using the Box-Behnken experimental design.

The ANOVA data for the quadratic model revealed that pH precipitation for medium REEs group parameter was the most significant factor influencing the response, and the quadratic models using the Box-Behnken design expressed a high coefficient of determination R^2 (0.769).

Optimal conditions after regression analysis were achieved the oxalic acid concentration of 1 N, precipitation temperature with oxalic acid at 85 °C, precipitation pH of the heavy REEs group 3.1, precipitation pH of the medium REEs group 7.3, and precipitating temperature for precipitating of the medium REEs group at 90 °C with efficiency separation of 72.55%. Furthermore, this strategy was an interesting economic approach to obtain the targeted information in a short time, with a minimum number of experiments.

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