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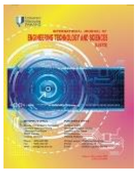

Rare Earth Extraction using Solvent Extraction: Which Factor Has the Most Significant Impact?

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Abstract- Using a two-level factorial design, a study was undertaken to change the parameters impacting the recovery of rare earth from rare earth mixture. The experimental design was used to screen and identify the major contributing aspects to rare earth recovery. The experiment aims to isolate samarium from a mixture of samarium, europium, and gadolinium using di-(2-ethylhexyl) phosphate as the extractant. Factors involved consist of pH (pH 1 and pH 6), acid type (nitric acid and hydrochloric acid) and concentration (1.0M and 5.0M), mixing duration (30 min and 120 min), feed composition (20% samarium and 80% samarium), type of diluent (hexane and chloroform), temperature (room temperature and 60°C) and organic to aqueous phase ratio (1:1 and 2:1). The results showed that the samarium recovery was in the range of 0.98% to 90.88%. Based on analysis variance (ANOVA), five factors significantly affect the samarium recovery out of eight factors explored. The five factors according to the most significant order are pH> feed composition> organic to aqueous phase ratio>acid concentration>acid type>mixing duration>type of diluent> temperature. Statistical analysis shows that the linear model is significant, with the value of R^2 is 0.9886. Based on the statistical data, five significant variables influence the separation of samarium. This research shows that two-level factorial design can anticipate significant variables impacting rare earth separation, particularly samarium, in the solvent extraction process.

Indexed Terms- rare earth extraction, two-level factorial design, samarium, screening, significant variable

I. INTRODUCTION

In exploring rare earth extraction, various factors such as pH of the medium, type of acid and diluent used, the concentration of the acid, temperature of the working process, feed composition, mixing duration, and organic to aqueous phase ratio have been investigated [1–3]. Generally, the optimum condition of these factors was preceded by screening experiments that were carried out by one-factor at a time (OFAT) method where the effect of one factor is assessed by varying the value of only one factor while all other independent variables remain constant [4]. However, due to a variety of high materials costs and a large number of trials, this traditional approach has been noted to be exceedingly costly and time-consuming [5]. Furthermore, because this technique can only analyze one element at a time, it is incapable of capturing the interactions between them [6].

Experimental designs, such as the full factorial designs, are useful for studying systems with a small number of factors as these experimental designs provide information concerning interactions between factors. A frequently stated advantage of factorial designs over OFAT designs is their high relative efficiency. However, when the number of parameters grows, the total number of experimental runs necessary becomes increasingly difficult, if not impossible. [7]. To save on costly runs, researchers usually perform the experiment based on factorial design. Factorial design can solve this problem as it usually requires less experimental running. As a result, its comparatively low cost and high efficiency in improving a process have become its main selling point. This method has been used in a wide range of rare earth applications, such as in the separation of yttrium using hollow fiber [8], extraction of uranium from yellowcake [9], and extraction of rare from waste materials [10].

Nevertheless, so far, there is no work reported on the usage of fractional factorial design in screening the effect of several factors on the extraction of rare earth, especially samarium from mixed rare earth solutions using solvent extraction. In this work, eight parameters were screened to evaluate their effects on a response using a two-level fractional factorial design. Furthermore, analysis of variance (ANOVA) and predicted samarium extraction from the model at 95% confidence interval against the experimental result is used to examine the adequacy of the developed empirical relationship regression model.

II. EXPERIMENTAL WORK

2.1 Materials

Di-(2-ethylhexyl) phosphate (DEHPA) and chloroform were purchased from Sigma Aldrich (USA). Hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), and hexane were purchased from Fischer Scientific. Stock solutions of samarium, europium, and gadolinium mixed solution were prepared by dissolving its oxide (99.9%) in concentrated acid.

2.2 Extraction of samarium from the samarium-europium-gadolinium mixture

The extractant, DEHPA, was dissolved in the hexane or chloroform based on the experiment requirement. 5 mL of aqueous phase containing a mixture of samarium, europium, and gadolinium and 5 mL of organic phase containing extractant were mixed and shaken at 200 rpm. The duration of mixing and the temperature of the process were depended on the experiment. The pH of the solution was adjusted either at pH 1 or pH 6 using sodium salt (either NaCl or $NaNO_3$). The mixture is then centrifuged for 5 min at 8000 rpm to enhance the aqueous and organic layer separation. The efficiency of samarium extraction from the feed was calculated using Equations 1:

$$\text{Samarium extraction (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

Where C_i is the initial concentration of samarium, and C_f is the equilibrium concentration of samarium.

2.3 Design of Experiment

2.3.1 Two-level factorial design

Factors influencing the extraction of samarium were screened using a two-level factorial design created by Design-Expert software (State-Ease Inc., Statistics made easy, Minneapolis, MN, USA, Version 7.1.6). This design contains a total of 32 experiments. The variables used were pH (A), mixing duration (B), acid type (C), acid concentration (D), diluent type (E), temperature (F), feed composition (G), and organic to aqueous phase ratio (H) variables were coded as -1 (low coded) and +1 (high coded) (Table 1). In the design matrix, the effects of eight variables on the extraction of samarium were evaluated. A total of 32 experimental runs were randomized for statistical purposes. The statistical significance of each factor and their combinations at a 5% significance level was evaluated using the Statistica Version 7.1.6 software.

Table 1: The range of variables and their coded levels independent

Factor	**Name**	**Low coded (-1)**	**High coded (+1)**
A	pH	1	6
B	Mixing duration	30 min	120 min
C	Acid type	HNO_3	HCl
D	Acid concentration	1.0M	5.0M
E	Diluent type	Hexane	Chloroform
F	Temperature	30°C	80°C
G	Feed composition	20%	80%
H	Organic to aqueous phase ratio	20%	80%

2.3.2 Analysis of variance (ANOVA)

The adequacy of regression models obtained in fitting the observed data was examined by the analysis of variance (ANOVA) and coefficient of determination (R^2). ANOVA evaluates the significance of regression by determining whether there is a relationship between the response variable and a subset of the regression variables via Fisher's statistical test (F-test). R^2, which has a value from 0 to 1, measures the global fit of a model. However, adding a variable to a model will always increase its R^2 value regardless of whether the additional variable is statistically significant or not [5].

III. RESULTS AND DISCUSSION

3.1 Screening of factors affecting the extraction of samarium

The design matrix used in the fractional factorial design to screen the factors affecting the extraction of samarium from mixed rare earth solution is shown in Table 2. In this study, a total of 32 runs of the experiment were conducted under consistent conditions in one block of measurements, and the experimental sequence (standard order) was randomized so that the effects of uncontrollable factors are minimized. The results showed that the extraction percentage of samarium was found to be in the range of 3.29% to 90.88%. This indicates the factors used in this study will either improve or worsen the extraction process. Next, all critical factors that significantly affect the samarium extraction were evaluated based on a half-normal probability plot of standardized effects, t-value, and p-value and a Pareto chart at a 5% significance level using the Statistica Version 7.1.6 software.

Table 2: Design Matrix for 2xx factional design and samarium extraction percentage as the response

Standard order	Run order	Variables								Extraction %
		A	B	C	D	E	F	G	H	
22	1	+1	-1	+1	-1	1	-1	1	1	50.98
12	2	1	1	-1	1	-1	-1	1	1	30.87
7	3	-1	1	1	-1	-1	-1	1	1	90.88
1	4	-1	-1	-1	-1	-1	-1	-1	1	51.66
9	5	-1	-1	-1	1	-1	-1	1	-1	42.46
13	6	-1	-1	1	1	-1	1	1	1	72.95
19	7	-1	1	-1	-1	1	1	1	1	78.06
4	8	1	1	-1	-1	-1	-1	-1	-1	15.97
16	9	1	1	1	1	-1	1	1	-1	34.62
28	10	1	1	-1	1	1	-1	1	-1	14.17
26	11	1	-1	-1	1	1	1	-1	1	7.98

24	12	1	1	1	-1	1	1	-1	-1	27.08
32	13	1	1	1	1	1	1	1	1	41.23
18	14	1	-1	-1	-1	1	1	1	-1	27.48
25	15	-1	-1	-1	1	1	-1	1	1	57.11
17	16	-1	-1	-1	-1	1	-1	-1	-1	34.96
8	17	1	1	1	-1	-1	1	-1	1	46.78
20	18	1	1	-1	-1	1	-1	-1	1	23.37
30	19	1	-1	1	1	1	-1	-1	-1	6.14
15	20	-1	1	1	1	-1	-1	-1	-1	40.07
3	21	-1	1	-1	-1	-1	1	1	-1	63.41
11	22	-1	1	-1	1	-1	1	-1	1	49.91
6	23	1	-1	1	-1	-1	-1	1	-1	41.32
27	24	-1	1	-1	1	1	1	-1	-1	29.22
5	25	-1	-1	1	-1	-1	1	-1	-1	51.37
29	26	-1	-1	1	1	1	1	1	-1	56.83
10	27	1	-1	-1	1	-1	1	-1	-1	3.29
23	28	-1	1	1	-1	1	-1	1	-1	71.29
31	29	-1	1	1	1	1	-1	-1	1	55.72
14	30	1	-1	1	1	-1	-1	-1	1	23.98
2	31	1	-1	-1	-1	-1	1	1	1	42.17
21	32	-1	-1	1	-1	1	1	-1	1	66.02

3.1.1 Half-Normal probability of standardized effects

The half-normal probability plot of all variables was presented in Figure 1 shows the absolute values of the estimated effects from the largest effect to the smallest effect. In general, the estimated effects of an inconsequential variable will appear to be near zero and will tend to be on or close to a near-zero line in the plot, whereas the estimated effects of an essential factor will appear to be off the line and well-displaced from zero. Hence, the larger the important effects, the further they are from the zero lines in the plot [11].

Figure 1 clearly showed that parameters A, C, D, G, and H stirred away from the linear line, showing that those variables are important in this work. The farthest variable from the linear half-normal plot indicates that the factor strongly impacts the response. The sequence of the significant main effects with respect to decreasing influence on extraction of samarium is found to be A>G>D>H>C.

According to the plot, the system's pH is the most significant effect on samarium extraction due to the difference of interaction between rare earth in low pH (such as pH1) compared to higher pH medium (such as pH 6). In the study by Eunyoung and Osseo using the Eh-pH diagram, they evaluated the interaction of acid-rare earth. They found that the stability of rare earth is high in a low pH system (pH 0-1), as rare earth readily exists as RE(III) species. The rare earth needs to be in its RE(III) forms as these forms will interact with extractants in the organic phase. At high pH (>pH6), the rare earth exists as hydroxide, which in the form of precipitate [12].

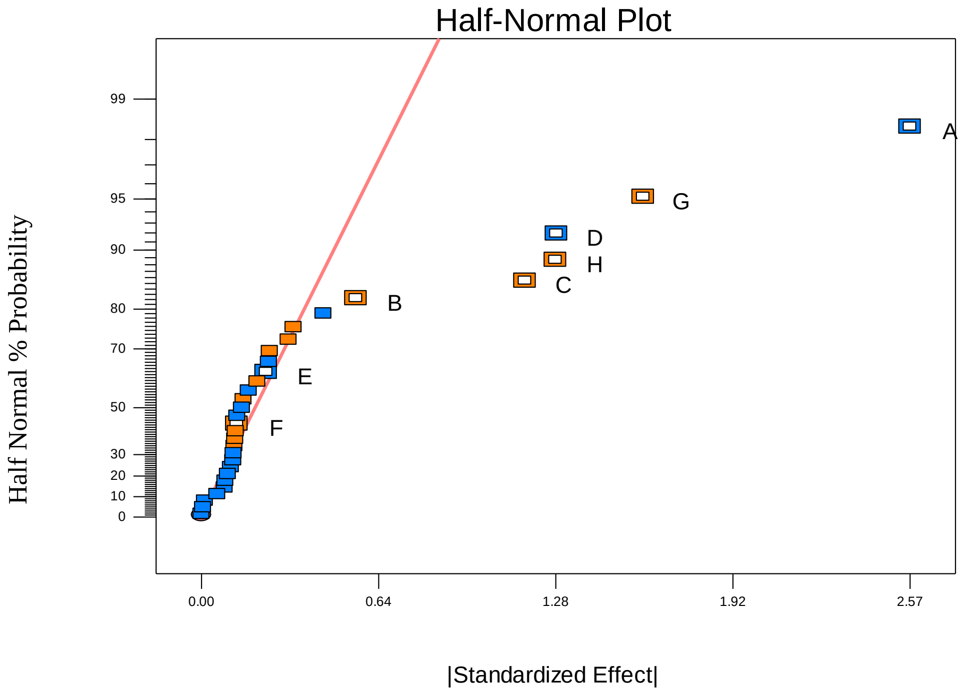

Figure 1: The plot of half-normal probability of A) pH, B) mixing duration C) type of acid D) concentration of acid E) type of diluent F) temperature G) feed composition, and H) organic to aqueous phase ratio

Meanwhile, the second most significant process variable was the feed composition. The higher feed composition of the targeted element leads to a higher possibility of the element to be extracted by the extractant. Suppose the amount of the targeted element is low in the feed (i.e., low feed composition). In that case, there will be high competition between the targeted and untargeted, therefore reducing the extraction percentage. In the low composition of the targeted element, some researchers need to introduce modifications to the extractant to reduce the competition reported by Fryxell and coworkers [13]. The same phenomena can be observed for the effect of the organic to aqueous phase ratio (the fifth most significant variable). Eventually, a higher volume of organic phase volume will increase the possibility of the targeted rare earth being extracted by the extractant.

On the other hand, acid type and acid concentration also significantly affect the extraction process. Different types of acid and concentration provide different mechanisms toward the extracted element and the extractant used. There could be various factors that are affecting the extraction behavior. One of the factors is the stability of the anion. In water, HCl and HNO_3 dissociate into Cl^-, and NO_3^- anion. These anions have different hydration abilities as known as the Hofmeister effect. The order in increasing value as follow: $SO_4^{2-} > Cl^- > NO_3^-$. The difference in anion stability could be the reason for the high samarium extraction in this study.

It should also be noted that the other three variables were not entirely unrelevent for the extraction process of the samarium. For example, increasing the mixing duration from 30 minutes to 120 minutes has a negligible effect on the extraction. However, the difference is too small compared to other variables.

3.1.2 Pareto chart

Another quick way to screen the significant factors is by analyzing the Pareto chart of the estimated effects. To validate the results obtained from the half-normal probability plot of effects in Figure 1, a Pareto chart was generated and tabulated as shown in Figure 2. The p-value serves as a tool for checking the significance of each coefficient and can be used to indicate the strength of interaction between variables. Across the Pareto chart, two horizontal lines in red and blue may be seen. The Bonferroni limit is represented by the red line at a higher level, while the blue line represents the t-value limit. For each bar in the Pareto chart, the Bonferroni limit and t-value limit are statistically based acceptance limits (equivalent to 95 percent confidence intervals)[14]. Parameters above the Bonferroni limit were more significant than those above the t-value limit. Parameters above the t-value limit had 95% significance; parameters below the t-value limit were not likely to be significant. Pareto chart analyses revealed that there are five statistically significant factors and have a much larger effect than the other factor. The five factors are A, which is the pH of the medium, G, which is the feed composition, D which is the acid concentration, H, the organic to aqueous phase ratio, and C, which is the acid type. Compared to the data gathered from the half-normal probability chart in Figure 1, the sequence of the significant main is similar.

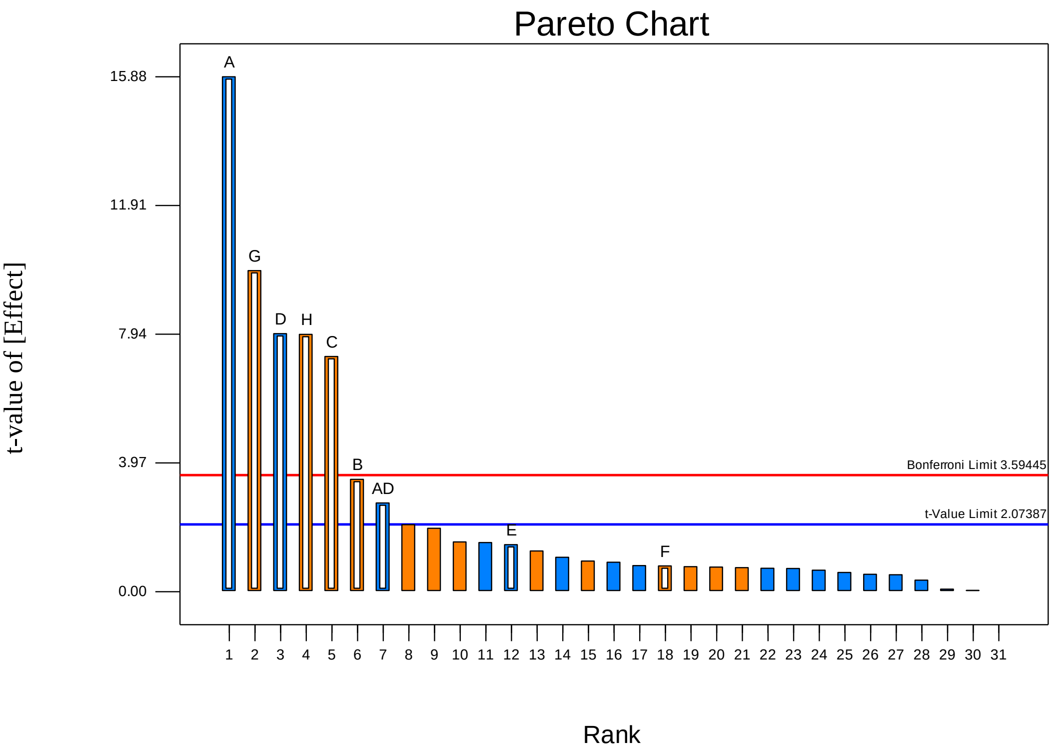

Figure 2: Pareto chart of each parameter coefficient for the extraction of samarium

3.2 Analysis of Variance (ANOVA)

In studying the extraction of samarium from samarium-europium-gadolinium mixture, the experimental design began with a screening experiment involving eight factors that were widely studied among rare earth researchers. Interpretation of the research was statistically analyzed using analysis of variance (ANOVA), and the probability values (P-values) of each term and factor interactions are as shown in Table 3. The P-value less than 0.005 means that the factors are significant to the responses studied. This is based on a confidence level set at 95%. The model used in this study portrayed a probability of <0.0001, which showed that the correlation between the factors and the extraction of the samarium is statistically significant. In this study, pH has the highest F value with 196.87 showed that pH is the most significant variable for this work. The order of the F value in decreasing order: pH>feed composition>acid concentration>organic to aqueous phase ratio>acid type. The mixing duration, diluent type, and temperature of the process have high P values, showing that the variables are not significant for the study.

Table 3: Analysis of Variance (ANOVA) for the extraction of samarium using two-level factorial design

Source	**Sum of squares**	**Degree of freedom**	**Min square**	**Value >F**	**P>F**
Model	113.51	8	14.19	53.06	<0.0001 significant
A	52.64	1	52.64	196.87	<0.0001 significant
B	2.50	1	2.50	9.36	0.1055
C	10.98	1	10.98	41.05	<0.0001 significant
D	13.21	1	13.21	49.42	<0.0001 significant
E	0.44	1	0.44	1.64	0.2132
F	0.13	1	0.13	0.49	0.4904
G	20.46	1	20.46	76.51	<0.0001 significant
H	13.14	1	13.14	49.13	<0.0001 significant
R^2	0.9886	Adjusted R^2	0.9707	Standard deviation	0.52

3.3 Extraction of samarium from mixed rare earth solution

One crucial part is whether the screened condition gives high efficiency on the samarium extraction using solvent extraction. Calculated to achieve the highest possible extraction, the software projected each variable's optimum value to achieve 93.42% of samarium extraction, as shown in Table 4. To confirm the prediction, a further experiment was carried out at the screening condition for the chromium removal, and the result shows that 96.44% of samarium able to extract. This result indicates that the separation of samarium from mixed rare earth solution (samarium-europium-gadolinium) could be done.

IV. CONCLUSIONS

A systematic experimental design approach has been applied to screen eight factors which are pH of the medium (A), mixing duration (B), acid type (C) and concentration (D), diluent type (E), the temperature of the system (F), feed composition (G) and organic to aqueous phase ratio (H) using two-level factorial design. The experiment aims to separate samarium from samarium-europium-gadolinium mixture using DEHPA as the extractant by solvent extraction process. The results reveal that the degree of significance of each independent variable in the order of decreasing significance with respect to the influence on samarium separation is A > G > D > H > C > B > E > F. A regression model for the samarium separation was developed and its R^2 (98.86%) and R^2 (adjusted) (97.07%) values were determined. The high R^2 values signify that the model obtained can give a reasonably good estimate of samarium separation for the system in the range studied.

Table 4: Optimum condition for extraction of samarium

Variable	Symbols	Optimum projected values	Samarium extraction (%)	
			Predicted value	Observed value
pH	A	pH 0.71	93.42%	96.44%
Mixing duration	B	114.85 min		
Type of acid	C	HCl		

Concentration of acid	D	1.56M
Type of diluent	E	Hexane
Temperature	F	62.80°C
Feed composition	G	79.98%
Organic to aqueous phase ratio	H	79.07

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