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Effect of temperature and acid concentration on lanthanum extraction from spent catalyst using organic acid

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Abstract. Rare earth elements (REE) are nowadays being used widely in many industries from electronics to petroleum industries as catalysts. However, their disposal caused serious problems to the environment. With the sharp growth in its usage, there is a better way to use and utilize REE from secondary sources such as their disposal rather than using new raw materials. The aim of this work is to study the potential of citric acid as a leaching agent to extract one of REE (i.e. lanthanum) in various acid concentrations and leaching temperatures. The raw material used in this work is spent catalyst from Pertamina Refinery Unit VI, Balongan, Indonesia. The spent catalyst is decarbonized with a heat treatment at 725°C for 10 minutes before the leaching process. The leaching process used 0.1; 1; and 2 M of citric acid with a varied temperature of 30, 60, and 80°C. The lanthanum recovery was calculated by comparing the mass percentage of lanthanum before leaching process and after leaching process using Energy Dispersive X-Ray Spectroscopy (EDX). The results were analyzed by response surface methodology (RSM) and are proved to be a reliable method to depict and analyze the leaching characteristics. The independent variables used in the research show significant effect on the response, especially the acid’s concentration. A second order polynomial equation was used to correlate response and independent variables. The coefficient of determination (R²) shows a satisfactory result of 86.53% and the normal probability plot ensure the model’s adequacy.

1. Introduction

The sharp growth in information technology such as tablet PCs, smart phones, and other gadgets in the last years leads to a huge demand for REE (Rare Earth Elements). On the other hand, due to their special characteristics, rare earth materials are also nowadays important part of the catalysts used in petroleum chemical industries[1]. However, aligned with its frequent use, the waste is also rising by a significant amount. Disposal by land filling is the oldest and was the most widely used method years ago. Due to increased environmental consciousness and regulations, land filling is, fortunately, less and less used. The issue is that liability still belongs to the waste producer as long as this waste has not
been destroyed, and thus lasts on long term[2]. Today the wastes are becoming a serious global threat[3]. This is because spent catalysts are composed of heavy metals and REE such as iron, chromium, nickel, palladium, manganese, and lanthanum. Instead of using new raw materials, there is a wiser choice that is extracting REE from secondary raw materials such as their disposal.

The special characteristics of REE make them considered as highly valuable metals. Nowadays, their price and presence have become a serious concern to many countries which also led to the rapid studies and researches for their extraction from secondary sources[4, 5, 6]. One of the most widely used REE which is still lacking studies of its extraction from secondary sources is lanthanum. Lanthanum is a ductile and soft metal which easily tarnishes when exposed to air.

Lanthanum extraction from industrial wastes becomes important because any disposal may affect the environment. Previous research by Jinxia et al. (2018), stated that Lanthanum may affect the soil ecosystems at a concentration slightly above natural condition level (6.6-50.0 mg La/kg dry soil)[7]. A study by Abhilash et al. (2014), found that the maximum recovery of lanthanum (99.9%) from Indian red mud in sulfuric acid extraction can be achieved in 3 M of H₂SO₄ and 35°C temperature[8]. Another study by Kuang et al. (2017), stated that among inorganic acids such as H₂SO₄, HNO₃, HCl, HCl was the most effective stripping solvent[9]. In addition, a work by Wei et al. (2011), stated that lanthanum can be easily stripped–reaching 95% recovery from chloride medium with organic acetic acids when the acidity is more than 0.03 M[10]. Astuti et al. (2017) also found that approximately 90% of lanthanum can be leached from hydro-processing spent catalyst by inorganic acid (HNO₃, HCl, H₂SO₄) with 4M acid concentration at 90°C temperature[5].

However, there is still lack of study in terms of REE extraction, especially lanthanum, from spent catalyst using organic acid. Because so, this work was done to study the effect of temperature and acid concentration on lanthanum extraction from spent catalyst using citric acid.

2. Experimental

2.1. Raw material characterization

The spent catalyst was obtained from PT. Pertamina Refinery Unit VI, Balongan, Indramayu, Indonesia. The spent catalyst was covered with carbon and it has to be decarbonized using a muffle furnace. The de-carbonization process was carried out at 725°C for 10 minutes. The spent catalyst was then analyzed using Energy Dispersive X-ray spectroscopy (EDX). The result is shown in Table 1.

| Constituents | %Mass |
|--------------|-------|
| Al           | 50.66 |
| Si           | 40.17 |
| La           | 3.56  |
| Ni           | 2.66  |
| Pr           | 0.77  |
| Fe           | 0.59  |
| Ca           | 0.49  |
| S            | 0.47  |
| P            | 0.33  |
| K            | 0.20  |
| Co           | 0.09  |
| Zr           | 0.01  |
| Sr           | 0.01  |

2.2. Leaching process

The de-carbonized spent catalyst was leached by citric acid with a concentration of 0.1; 1; and 2 M. As much as 10 grams of de-carbonized spent catalyst were put in a 50 ml of acid in an Erlenmeyer flask.
The process was carried out for 4 hours in a laboratory water bath (Fig. 1) at a temperature of 30, 60, and 80°C.

![Laboratory water bath as a reactor for leaching process](image)

**Figure 1.** Laboratory water bath as a reactor for leaching process (1. Temperature display; 2. On/off button; 3. Temperature controller; 4. Erlenmeyer flask; 5. Leached spent catalyst; 6. Water level)

### 2.3. Recovery analysis
After 4 hours of leaching, the leachate was separated from the spent catalyst using filter paper. The remaining solid was dried in an oven at 50°C for 5 hours to remove its moisture. The dried spent catalyst was then analyzed again using EDX to determine its metal contents. The overall process is shown in figure 2.

![Overall experimental process](image)

**Figure 2.** Overall experimental process

The spent catalyst’s REE content after leaching process will be surely reduced. Therefore, the recovery calculation must be carried out with constant denominator instead of the total mass. Silica is considered to be one of the most inert constituents in this research. Previous studies show that silica can only be leached by a strong acid such as hydrochloric acid[11]. Furthermore, acid leaching
methods are widely used as silica purification from heavy metals[12]. The formulated equation can be seen below:

\[ \% R = \frac{W_0 - W_t}{W_0} \times 100 \]  

(1)

Where, \( \% R \) is the recovery percentage; \( W_0 \) and \( W_t \) are the weight of lanthanum before and after leaching process, in mg.

2.4. Design of experiment and statistical analysis

Response surface methodology (RSM) was chosen to analyze the result of this research statistically. A full three-level factorial design was used with two independent variables, acid concentration and temperature. The dependent variables, of course, are the recovery percentage of lanthanum. The design is shown in Table 2.

| Independent variables | Range and level |
|-----------------------|-----------------|
| Acid Concentration, M (X₁) | 0.1 1 2 |
| T, °C (X₂) | 30 60 80 |

A second-order polynomial equation was used to match the response (dependent variable) and the factors (independent variables). The polynomial equation has a general form which written as follows[13]:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \]  

(2)

Where \( Y \) is the response; \( x_i \) and \( x_j \) are the factors (i and j are the range from 1 to k); \( \beta_0 \) is the constant coefficient; \( \beta_i, \beta_{ii}, \beta_{ij} \) are the coefficients for the linear; quadratic and interaction effect; and \( \varepsilon \) is the error. The model’s accuracy was analyzed using the coefficient of determination (\( R^2 \)). The \( R^2 \) has a value, ranged from 0 to 1. If \( R^2 \) is close to 1, the model is highly accurate[14].

3. Results and Discussion

3.1. Lanthanum recovery percentage statistical analysis

The experiment was done based on a full three-level factorial design to analyze the factors’ influence on the lanthanum recovery. In the result, it is clear that both acid concentration and temperature play a significant role in the recovery of the lanthanum. Lanthanum can reach 100% of recovery using 2 M of citric acid in all temperatures. However, in a 0.1 M of the citric acid solution, the maximum lanthanum recovery was 43.94% (at 80°C), making acid concentration as the most significant variable in the result.

On the other hand, there is a declining trend aligned with lower temperature. This phenomenon can be seen as an incomplete reaction as it is widely known that temperature affects the kinetics of chemical processes. But, it has to be proved in further study of leaching kinetic behavior of lanthanum in organic acids. The result is shown in Table 3 below.
Table 3. Lanthanum recovery result and the predicted value

| Temperature (°C) | Acid Concentration (M) | %R   | Predicted %R |
|------------------|------------------------|------|--------------|
| 30               | 0.1                    | 40.54| 29.89        |
|                  | 1                      | 53.25| 73.72        |
|                  | 2                      | 100.00| 90.69       |
| 60               | 0.1                    | 41.07| 47.29        |
|                  | 1                      | 100.00| 89.74        |
|                  | 2                      | 100.00| 105.18      |
| 80               | 0.1                    | 43.94| 49.39        |
|                  | 1                      | 100.00| 90.92        |
|                  | 2                      | 100.00| 105.34      |

Minitab software was used to process the data with the satisfactory result as it can be seen in Table 3 and Table 4. The empirical correlation between response (%R) and independent variables (acid concentration and temperature) are expressed in the equation 3 below.

\[
\%R = -11.3 + 68.6X_1 + 1.44X_2 - 16.7X_1^2 - 0.0095X_2^2 - 0.051X_1X_2
\]  

(3)

The data satisfactoriness and the model fitness were assessed by regression and analysis of variance (ANOVA), a statistical technique that distributes the total variability into several component parts associated with particular sources of variation for the testing of model parameters[15]. In addition, F-test and P value are also assessed to determine the statistically significant variables. The results can be seen in Table 4.

As it can be seen from the table, the P-value for all linear independent variables was practically smaller than the square or 2-way interaction mode. For a value lower than the level of significant, that is 0.05, the variable is considered as statistically significant for the proposed model[16] and in this case, X_1 (acid’s concentration) is the most significant variable.

Table 4. ANOVA Analysis Results

| Source         | DF | Adj. SS  | Adj. MS  | F-Value | P-Value |
|----------------|----|----------|----------|---------|---------|
| Model          | 5  | 5,970.93 | 1,194.19 | 3.86    | 0.148   |
| X_1            | 1  | 416.84   | 416.84   | 1.35    | 0.330   |
| X_2            | 1  | 5,067.17 | 5,067.17 | 16.36   | 0.027   |
| X_1^2          | 1  | 64.80    | 64.80    | 0.21    | 0.678   |
| X_2^2          | 1  | 450.90   | 450.90   | 1.46    | 0.314   |
| X_1,X_2        | 1  | 6.01     | 6.01     | 0.02    | 0.898   |
| Error          | 3  | 928.99   | 309.66   |         |         |
| Total          | 8  | 6,899.92 |          |         |         |

3.2. The validity of the model

To verify the proposed model, it is important to ensure the adequacy of predicted values with actual (experimental) values. In this case, the experimental and predicted values are fitted as it can be seen in Figure 3. The data points on this plot are considered close to the straight lines. The results suggest that the model used in this study is compatible to depict the conditions (with an R² value of above 0.86) with considerably high accuracies.

Figure 4 shows whether the data are normally distributed, other variables are affecting the responses, or outliers exist in the data. In addition, residual values explain the variation between
predicted and experimental values. A highly accurate model is characterized by its small residual value[17]. The results show that the data are normally distributed, as it visually visible because the data points are positioned close to the reference line and the outlier data are minimal.

**Figure 3.** Comparison between experimental and predicted value of %R

**Figure 4.** Normal probability plot of %R

4. Conclusion
In this study, a full three-level response surface design is proved to be a reliable method to depict and analyze the characteristics of lanthanum leaching from spent catalyst using citric acid. The independent variables used in the research show a significant effect on the response, especially the acid concentration. A second order polynomial equation was used to correlate response and independent variables. The coefficient of determination ($R^2$) shows a satisfactory result of 86.53% and the normal probability plot ensure the model’s adequacy.

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