Optimization adsorption of lead (II) using Aceh natural-bentonite by response surface methodology

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Abstract. Response Surface Methodology was employed for the removal of lead on synthetic water. The process parameters including bentonite mass (0.5; 1.25; 2.0 g), lead concentration (10; 55; 100 mg/L), and agitation time (5; 17.5; 30 minutes) were optimized using statistical Box-Behnken Design. The experimental data were obtained and analyzed by analysis of variance (ANOVA) and fit to a quadratic polynomial equation (Regression Analysis, $R^2 = 0.9996$) for 17 runs experiment and 5 runs of the central-point (confidence level at 95%). The numerical optimization was used to identify the optimum condition for maximum removal of lead. The maximum adsorption efficiency expressed as the adsorption capacity, which was found to be 7.42 mg/L, at agitation time 17.5 minutes and adsorbent dosage 2.0 g.

1. Introduction
Heavy metal contamination of water is a relevant issue in the context of water resources protection. The industrial activities such as paint, pesticide, mining, textile, lead batteries and the manufacturing release a large number of heavy metal ion to aquatic ecosystem. Among the heavy metal ion, lead is one of most dangerous pollutant in industrial wastewater even at low concentration. Lead are non-biodegradable ions and known as a toxin with effect on several organ systems. According to the World Health Organization (WHO), the safe level for lead ions is $0.1 \text{gm}^{-3}$[1-8].

In order to handle the heavy metal ion on waste water, several methods has been developed to eliminate it from waste water before disposal, such as chemical precipitation, membrane filtration, solvent extraction and adsorption. Among these methods, adsorption is a common and effective method for heavy metal ions removal, due to its features of easy operation, eco-friendly, strong practicability, high efficiency, and low cost [9-13]

In recent years, the used of bentonite as adsorbent have been carried out in handling heavy metal waste on waste water, but the used of bentonite (especially Aceh natural bentonite) as adsorbent has not been utilized optimally. It has a different composition with other natural bentonite. So in this study, Aceh natural bentonite was used as adsorbent to remove lead ions from waste water (lead aqueous solution). However, the adsorption capacity of natural bentonite is low because it still contains impurities [14-16]. Therefore, before being used in industry, it must be purified. The natural bentonite is modified by physical process. The modification results are to remove the impurities ($\text{CO}_2$) and to enhance the adsorption capability [17-22].

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The most important stages in an environmental process are modeling and optimization to improve the system and increase the efficiency of the process [23]. The main objective in this study is to evaluate of Aceh natural bentonite adsorption capacity as adsorbent in lead (Pb) removal through the application of Response Surface Methodology (RSM). In order to have a better understanding of the optimization of adsorption at various operating parameters were studied.

2. Experimental

2.1. Materials
Bentonite was obtained from Blang Karing, Aceh. The Pb(NO₃)₂ and acetate-buffer solution (Merck, Germany) and distilled water were purchased from Rudang Jaya Company, Medan Indonesia.

2.2. Adsorbent Preparation
Firstly, the bentonite was grinded and sieved to work particle size (200-mesh) using ball mill grinder. After that, the bentonite was heated at 105°C for 2 h and kept in desiccator. The sifted and heated bentonite was added in 250 mL acetate-buffer solution (pH = 4.8) and stirred for 5 h until no CO₂(g) formed. Furthermore, the mixture was separated by centrifugal for 10 minutes.

2.3 Adsorption Experiment
The adsorption of lead onto bentonite was investigated in stirred-batch experiment [10]. Purified natural bentonite of 25 g was put into a flask, and added by 500 mL water. It was stirred by magnetic stirrer for 24 h at 70°C. The mixed solution was separated by decantation. The precipitated was dried at 105°C. After that, 100 mL of lead aqueous solution with different concentration and bentonite dose was placed in a flask. Then, the mixture was agitated at 200 rpm and filtered to analyze the residual of lead. The lead adsorption onto natural bentonite was calculated according to the following equation [24]:

\[ \frac{q_t}{m} = \frac{(C_0 - C_t)V}{m} \]

Where, \( C_0 \) is the initial lead concentration ; \( C_t \) is the remaining lead concentration at any time ; \( V \) is the volume of the lead solution ; and \( m \) is the weight of bentonite.

| Run | Bentonite (g) | Time (minutes) | Concentration of Pb (mg/l) | Ion Pb adsorption (mg/l) |
|-----|---------------|----------------|---------------------------|-------------------------|
| 1   | 1.25          | 17.50          | 55.00                     | 3.94                    |
| 2   | 0.50          | 17.50          | 10.00                     | 1.12                    |
| 3   | 2.00          | 5.00           | 55.00                     | 4.33                    |
| 4   | 1.25          | 5.00           | 100.00                    | 3.05                    |
| 5   | 1.25          | 17.50          | 55.00                     | 3.94                    |
| 6   | 0.50          | 5.00           | 55.00                     | 1.08                    |
| 7   | 1.25          | 30.00          | 100.00                    | 5.22                    |
| 8   | 1.25          | 5.00           | 10.00                     | 1.92                    |
| 9   | 2.00          | 30.00          | 55.00                     | 7.42                    |
| 10  | 1.25          | 30.00          | 10.00                     | 3.30                    |
| 11  | 0.50          | 30.00          | 55.00                     | 1.85                    |
| 12  | 1.25          | 17.50          | 55.00                     | 3.94                    |
| 13  | 1.25          | 17.50          | 55.00                     | 3.94                    |
| 14  | 2.00          | 17.00          | 100.00                    | 7.11                    |
| 15  | 1.25          | 17.50          | 55.00                     | 3.94                    |
| 16  | 0.50          | 17.50          | 100.00                    | 1.78                    |
| 17  | 2.00          | 17.50          | 10.00                     | 4.49                    |
2.4. *Box Behnken Experimental Design and Optimization by Response Surface Methodology*

Response surface methodology is a statistical method for optimizing the independent factors to achieve the desirable response by carrying out a set of experiments [9].

In this study, a three factor - Box-Behnken design (Design Expert Vers. 6.0.8) as associating with response surface methodology to determine and to predict the optimum condition of adsorption. In this study obtained 17 run-experiments in a factorial design and 5 run of the central-point.

3. Results and Discussions

3.1 *Box-Behnken Design and Model Evaluation.*

The Box-Behnken method was analyzed and the results of the analysis of variance (ANOVA) from regression coefficient are presented in Table 2 and Table 3.

| Source                  | Sum of Square | DF | Mean Square | F Value | Prob>F   | Characteristic |
|-------------------------|---------------|----|-------------|---------|-----------|----------------|
| Model                   | 53.43         | 9  | 5.94        | 174862  | <0.0001   | Significant    |
| A - Natural Bentonite (g) | 38.66        | 1  | 38.37       | 13149.65| <0.0001   | Significant    |
| B - Times (minutes)     | 6.86          | 1  | 6.86        | 2352.24 | <0.0001   | Significant    |
| C - Concentration of Pb (mg/L) | 5.01       | 1  | 5.01        | 1716.54 | <0.0001   | Significant    |
| A2                      | 0.0069        | 1  | 0.0069      | 2.35    | 0.1688    | Non-Significant|
| B2                      | 0.32          | 1  | 0.32        | 111.32  | <0.0001   | Significant    |
| C2                      | 0.39          | 1  | 0.39        | 135.34  | <0.0001   | Significant    |
| AB                      | 1.35          | 1  | 1.35        | 461.16  | <0.0001   | Significant    |
| AC                      | 0.96          | 1  | 0.96        | 329.15  | <0.0001   | Significant    |
| BC                      | 0.16          | 1  | 0.16        | 53.47   | 0.002     | Significant    |
| Residual                | 0.02          | 7  | 0.00292     |         |           |                |

From Table 2, it can be seen that the analysis interaction of variables and the effect of individual quadratic were significant. Respectively, it was deduced that the adsorption of lead (Pb) were significant at 95% of confidence level which is an indication of the validity of the model. The significance of each term (variables) were evaluated using second order model and determined by P-value (Prob>F) which is listed in Table 2 and Table 3 (Design Expert Software 6.0.8). The statistic models are feasible and valid for the present work. The resulting of Response Surface Methodology model equation is following:

\[
Y = 3.94 + 2.19X_1 + 0.93X_2 + 0.79X_3 - 0.00875X_1^2 - 0.26X_2^2 - 0.31X_3^2 \ldots \\
+ 0.58X_1X_2 + 0.49X_1X_3 + 0.20X_2X_3 
\] (2)

From Equation (2), It can be seen that the factor of each variables (\(X_1 = \) Bentonite (g), \(X_2 = \) Agitation time (minutes), \(X_3 = \) Concentration of Lead (mg/L), \(X_1X_2 = \) interaction of \(X_1\) and \(X_2\) as well as \(X_1X_3\) and \(X_2X_3\) is the effect of the interaction of these two variables) have a positive effect on the adsorption, the positive value represents an effect of optimization. As seen in Table 3, this models is very appropriate because the value of \(R^2\) close to 1.00 (\(R^2 = 0.9996\); Adj-\(R^2 = 0.9990\); Pre-\(R^2 = 0.9989\).
0.9929). So that, the correlation between actual and prediction is almost same and the suggested mathematical model in this study is quadratic model equation.

### Table 3. Statistical Result Model

| Response                  | Source  | Std Dev | R-Square | Adj-R² | Pre-R² |
|---------------------------|---------|---------|----------|--------|--------|
| Concentration of Pb (mg/l)| Linier  | 0.50    | 0.9391   | 0.9251 | 0.8793 |
|                           | 2 FI    | 0.27    | 0.9859   | 0.9774 | 0.9546 |
|                           | Quadratic | 0.058  | 0.9996   | 0.9990 | 0.9929 |

#### 3.2 Effect of interactive variable

The effect of interactive variables can be seen at Figure 1. Figure 1 present the plots of experimental and predicted (responses surface). The predicted value that is proposed by design response surface equation has high accusation and low standard deviation. It can be seen from the distribution point spread above the prediction line. To obtain the decent model, that needs to check the accusation of normal probability value (%). As seen in Figure 2, the proposed equation model is suitable for adsorption (lead) by using bentonite. So that, the suitability indicates the analysis of variance were used for this study.

![Figure 1](image_url)

**Figure 1.** (a) Plot of experimental and predicted responses surface ; (b) plot of studentized residual and normal % probability

#### 3.3 Response Surface Analysis.

The interactive effect of any two of three independent variables on the dependent variable was shows graphically by contour and 3-D response surface. 3-D plot describes the relation between dependent and independent variable as well as to analyze the interaction effect (response surface). Based on the polynomial regression, the suggested equation is Quadratic Model, Box-Behnken (Design Expert Software). The relation between adsorbent (Bentonite mass), agitation time, and adsorbent concentration were shown in (Figure 2 to 4). (Figure 2 to 4) indicated that with an extended of agitation time, the adsorption uptake was increased and then remained to the saturated value. This phenomenon indicated the adsorption reached equilibrium at a certain time [25].
Figure 2. Response Surface – The effect of bentonite mass and agitation time on Pb(II) ion adsorption capacity (a) Contour (b) 3D Graphics

Figure 3. Response Surface – The effect of bentonite mass and adsorbate concentration on Pb(II) ion adsorption capacity (a) Contour (b) 3D Graphics

Figure 4. Response Surface – The effect of agitation time and adsorbate concentration on Pb(II) ion adsorption capacity (a) Contour (b) 3D Graphics
4. Conclusion
The statistical methodology, Box-Behnken Response Surface Method is demonstrated to be effective and reliable in finding the optimal conditions for the adsorption of Lead (Pb) onto bentonite. The response surface plots were used for estimating the interactive effect of variables (bentonite mass, agitation time, adsorbate concentration) on the response (adsorption capacity). The results showed that, the quadratic equation mathematical model was developed by regression analysis ($R^2 = 0.9996$) of the experimental data obtained for 17 runs. Optimization of adsorbent (bentonite) dose 2.0 g and agitation times 17.5 minutes gave a maximum uptake (ion) of 7.42 mg/L.

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