Optimization of Lead Ion Adsorption Capacity by Biomass Mixture of Palm Bunches and Rice Husks after Activated with Citric Acid

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Abstract. Optimization of lead ion adsorption rate by biomass mixture of palm bunches and rice husks (PB-RS) after activated with citric acid was carried out with the Design-Expert 6.0.8 software. The purpose of this study was to obtain an optimal response (adsorption rate) which was influenced by several dependent variables (biomass weight ratio, activator concentration, and contact time). Biomass mixture was carbonized in the tube furnace at 500 °C for 2 hours followed chemically activated using citric acid as an activator. The activated carbon formed was contacted with water containing Pb(II) ion. Pb removal rate was measured to observe the biomass performance on Pb(II) ion absorption with various variables including biomass ratio, citric acid concentration, and contact time. Pb(II) ion concentration was analyzed using Atomic Absorption Spectrophotometry, Shimadzu AA-6300 while the optimum adsorption of Pb ion was analyzed using Design Expert 6.0.8 software with Central Composite Design (CCD). The results showed that the variable of mass ratio, activator concentration, and contact time influence the rate of Pb(II) ion adsorption from the water phase. Base on the optimization analysis, the optimum condition of Pb(II) ion adsorption achieved at 30 g of activated PB-RS biomass, activator concentration (citric acid) of 0.6 mol/L, at 99.88 minutes contact time, and at a Pb(II) initial concentration of 99.42 mg/L. In this optimum condition, Pb(II) ion adsorption capacity obtained was 3.01 mg/g.

1. Introduction

Heavy metal pollution is very dangerous for the environment, and many reports provide the fact how dangerous environmental pollution, especially by heavy metals ion in the waters, both due to the use of water for daily consumption and when consuming freshwater biota that lives in polluted waters [1,2]. One of the dangerous heavy metals and worldwide pollution issue is lead.

In nature, native lead is rare. Currently lead is could be found in ore with silver, copper, and zinc and it is extracted together with these metals. The main lead mineral in Galena (PhS) and there are also deposits of cerussite and anglesite which are mined. Lead occurs naturally in the environment. However, human activities cause most lead concentrations that are found in the environment. Due to the addition of lead in gasoline, an unnatural lead-cycle has consisted. In vehicle engines lead is burned, so that lead salts will originate. These lead salts enter the environment through the exhausts of vehicles. The larger
particles will drop to the ground immediately and pollute surface waters or soils, while the smaller particles will travel long distances through air and remain in the atmosphere. When it is raining, part of this lead will fall back on earth. This human production lead cycle is much more extended than the natural lead-cycle. Therefore, it has caused lead pollution to be a worldwide issue.

To overcome the problems mentioned above, it is necessary to handle heavy metal waste, especially Pb before being discharged into the environment. Many studies have been carried out in handling heavy metal waste [3,4,5,6]. The use of biomass adsorbent as a low-cost heavy metal absorption material has been carried out in various studies, so in this study, a mixture of biomass as adsorbent and citric acid was used as an activator [7]. Citric acid is a hydrophilic (polar) protic solvent, similar to water and ethanol. Citric acid has a moderate dielectric constant of 6.2. So that it can dissolve both polar compounds such as inorganic salts and sugars and non-polar compounds such as oils and elements such as sulfur and iodine (including the lead in them). In this study also used a mixture of biomass as an adsorbent where the use of palm bunches and rice husks (PB-RS) as an absorbent that can produce high absorption. The purpose of this study was to obtain an optimal response (Pb(II) ion adsorption rate) which was influenced by several dependent variables (PB-RS biomass weight ratio, activator concentration, and contact time).

2. Materials and Method

2.1. Materials and Equipment

The main material used this study was mixed biomass from palm bunches and rice husk. Palm bunches (PB) was collected from the palm oil mill in Nagan Raya District, while rice husk (RS) was collected from Cot Yang rice mill, Tungkop village, Aceh Besar District, Aceh Indonesia. All analytical-reagent grade chemicals used (citric acid, 99.5%; NaOH, 99.9%; and Pb(NO\textsubscript{3})\textsubscript{2}; 99.9%) were obtained commercially from Sigma-Aldrich Chemical Company. These solutions were further prepared to suitable concentrations on the day of use. The equipment used for this study include: Muffle Furnace (Line Thermolyne, model: FB1410M-33 at 1100°C), Oven Dryer (Memmert UF-55), Shaker (SLM-OS-250-Digital), Buchner Funnel (Pyrex), Digital Scales (ACIS, BC-500), Filter Paper 3M), Desiccators (Pyrex), Atomic Absorption Spectrophotometry; Shimadzu AA-6300. Also, supporting tools for testing were 250 mL Erlenmeyer (Pyrex), 1000 mL (Pyrex) flask, thermometer (Yenaco), 100 mL (Pyrex), pH meter (Ohaus, Starter 300), and dropper (Pyrex).

2.2. Active Carbon Preparation

Preparation of activated adsorbent from PB-RS was carried out as shown in our previous work [8,9]. The preparation was conducted in three stages, consisting of preparation, activation, and adsorption. Palm bunches and rice husk were washed with aquadest to remove impurities. After drying at 40°C, the pyrolysis reaction was conducted in muffle furnace (Line Thermolyne, model: FB1410M-33 at 1100°C), Oven Dryer (Memmert UF-55), Shaker (SLM-OS-250-Digital), Buchner Funnel (Pyrex), Digital Scales (ACIS, BC-500), Filter Paper 3M), Desiccators (Pyrex), Atomic Absorption Spectrophotometry; Shimadzu AA-6300. Also, supporting tools for testing were 250 mL Erlenmeyer (Pyrex), 1000 mL (Pyrex) flask, thermometer (Yenaco), 100 mL (Pyrex), pH meter (Ohaus, Starter 300), and dropper (Pyrex).

2.3. Lead ion Adsorption and Analysis

The adsorption of lead [Pb(II)] ion was conducted in a batch experiment. An aqueous solution (100 ml) containing a suitable concentration of Pb(II) ion was shaken (at 100 rpm for 100 min) with a suitable amount of activated adsorbent PB-RS at room temperature (30°C). Suitable volume of acid (hydrochloric acid) or base (sodium hydroxide) solution was added to adjust pH that was measured with a digital pH meter (Ohaus, Starter 300). After removal of the adsorbent by centrifugation, the concentration of Pb ion remaining in the supernatant was determined by atomic absorption spectrophotometry (Shimadzu AA-6300). The optimum adsorption of Pb(II) ion was analyzed using Design Expert 6.0.8 software with Central Composite Design (CCD).
3. Results and Discussion

3.1. Effect of Citric Acid on Pb(II) Adsorption
The absorption process occurred at the biomass ratio of 1:5; 1:1; and 5:1 with the weight of each PB-RS biomass was 15 grams, 20 grams, and 25 grams. The absorption process took place starting from 40 minutes, 60 minutes, 80 minutes and 100 minutes at concentrations of citric acid used as activators were 0.4 N and 0.6 N, respectively. The ability of PB-RS biomass to adsorb Pb(II) ion was tabulated in Table 1. Based on the research and observations that have been carried out (Table 1), the highest absorption occurred at the PB-RS biomass ratio of 1:5 with initial concentrations was 80 mg/L and 100 mg/L, respectively. After the absorption process occurred, the PB-RS biomass adsorption was 45.36% at 100 minutes and 41% at 60 minutes, respectively. These results indicated that contact time affects the adsorption kinetics performance. Adsorption kinetics described the solute concentration profile during the adsorption process before equilibrium was reached, the adsorption kinetics were influenced by the following factors: (1) surface area, (2) particle diameter of the adsorbent, (3) initial concentration, (4) solubility of adsorbate, (5) molecular weight adsorbate, (6) temperature, (7) stirring speed, (8) pH, and (9) contact time [1]. Adsorption kinetics also function to determine the rate of reduction of heavy metal ions by adsorbents in the water phase at a certain time.

| No. | Biomass Ratio (weight) | Citric Acid Concentration (mol/L) | Time (minutes) | Concentration of Pb(II) (mg/L) | % Adsorption |
|-----|------------------------|----------------------------------|----------------|--------------------------------|--------------|
| 1   | 5:1                    | 0.6                              | 40             | 40                             | 21.45        | 18.55        |
| 2   | 5:1                    | 0.6                              | 80             | 80                             | 43.39        | 36.61        |
| 3   | 1:1                    | 0.4                              | 60             | 100                            | 43.39        | 41.00        |
| 4   | 1:1                    | 0.4                              | 100            | 80                             | 34.64        | 45.36        |
| 5   | 1:5                    | 0.6                              | 80             | 40                             | 23.47        | 16.53        |
| 6   | 1:5                    | 0.6                              | 80             | 80                             | 43.93        | 36.07        |

3.2. Optimization of Pb(II) Adsorption
The optimum conditions of adsorption time and the concentration of Pb(II) adsorbed using PB-RS biomass obtained from the optimization function of Design Expert 6.0.8 Software, and the results were tabulated in Table 2. Table 2 shows that the largest adsorption capacity of Pb(II) shown at run 16 was 4.07 mg/g, while the lowest adsorption capacity of Pb (II) shown 0.08 mg/g at the run of 29.

| Run | Biomass ratio (gram) | Citric Acid Concentration (mol/L) | Adsorption time (minutes) | Initial concentration (mg/L) | Adsorption capacity (mg/g) |
|-----|----------------------|----------------------------------|---------------------------|-----------------------------|-----------------------------|
| 1   | 15                   | 0.6                              | 80                        | 80                          | 3.06                        |
| 2   | 20                   | 0.2                              | 80                        | 80                          | 3.06                        |
| 3   | 20                   | 0.4                              | 60                        | 60                          | 2.43                        |
| 4   | 20                   | 0.4                              | 60                        | 60                          | 2.54                        |
| 5   | 20                   | 0.4                              | 60                        | 60                          | 2.88                        |
| 6   | 20                   | 0.8                              | 40                        | 40                          | 1.53                        |
| 7   | 20                   | 0.8                              | 60                        | 60                          | 2.59                        |
| 8   | 20                   | 0.4                              | 60                        | 60                          | 2.36                        |
| 9   | 25                   | 0.6                              | 80                        | 80                          | 2.83                        |
| 10  | 25                   | 0.4                              | 60                        | 60                          | 1.33                        |
| 11  | 25                   | 0.6                              | 80                        | 80                          | 2.71                        |
| 12  | 20                   | 0.4                              | 60                        | 60                          | 2.61                        |
| 13  | 20                   | 0.4                              | 60                        | 60                          | 2.50                        |
| 14  | 20                   | 0.2                              | 80                        | 40                          | 1.46                        |
| 15  | 25                   | 0.6                              | 80                        | 40                          | 1.22                        |
| 16  | 25                   | 0.2                              | 40                        | 80                          | 4.07                        |
| 17  | 15                   | 0.6                              | 40                        | 80                          | 2.78                        |
A summary of the statistical model provides suggestions for selecting the right model and in line with experimental data. The CCD design (Central Composite Design) that was used provides an actual mathematical model that was used to predict the adsorption capacity of Pb(II) ion based on the suggested model. Based on the quadratic model, the mathematical model equation provided for Pb(II) ion adsorption capacity as follows.

\[ Y = -1,98402 - 0,066090 \times X_1 + 0,77521 \times X_2 + 0,026328 \times X_3 + 0,095094 \times X_4 + 2,11828E-003 \times X_1^2 + 0,79268 \times X_2^2 + 9,94199E-006 \times X_3^2 - 5,92607E-004 \times X_4^2 - 0,053917 \times X_1 \times X_2 - 1,08883E-003 \times X_1 \times X_3 + 1,37333E-03 \times X_1 \times X_4 - 4,09569E-003 \times X_2 \times X_3 - 6,29167E-003 \times X_2 \times X_4 - 1,25332E-004 \times X_3 \times X_4 \] .........................................................(1)

Based on the equation model (1), each variable consists of biomass ratio (X₁), citric acid concentration (X₂), contact time (X₃) and initial concentration (X₄). These four variables have a very important influence where the use of these four variables will increase the adsorption capacity of Pb(II) ion. The most influential variable was biomass ratio based on the largest coefficient value in the equation, namely the coefficient on X₁. From equation (1), results of the predicted and actual values for Pb(II) ion adsorption capacity were obtained and tabulated in Design expert prediction column in Table 2. The prediction column shows the relationship of the predictive value based on the equation proposed by the response surface design and the actual value generated from the experiment. This condition can determine the accuracy of the model obtained.

ANOVA is one factorial of CCD which is useful to generate interaction between process variables with response variable [9]. The components in ANOVA will be used to calculate the F-ratio that serves to determine the effectiveness of a model. ANOVA results for the adsorption of Pb(II) ion by PB-RS biomass were shown in Tables 3. Table 3 shows that in this case the concentration variable (variable D) shows a significant effect on Pb(II) ion adsorption capacity which has a value (probability > F) < 0.05 that was equal to 0.0001.

3.3. Response Analysis Surface Against Pb(II) ion Adsorption Capacity
The model suggested by the software to calculate the adsorption capacity in this study is a quadratic equation. Model selection based on several factors, such as R² value. From this model, based on the response surface analysis two types of plots were used, namely contour plots and 3D plots. This plot was used to facilitate the description of the effect of variables on the response. The contour plot was a 2D plot which is a cross section of the 3D plot. The plot contour useful for analyzing the effects of interaction between factors on the response (Hasan, et al., 2009). The 3D plot shows the effect of two variables on the response in which variables were created in a fixed condition. The model equation suggested by software design expert version 6.0.8 for Pb(II) ion adsorption analysis was a quadratic model equation. To analyze this model, three-dimensional plots and contour plots can be used. The relationship between the three independent variables to the response can be seen in Figure 1 to 3.
Table 3. ANOVA results for surface quadratic model of Pb(II) ion adsorption capacity.

| Source  | Sum of Squares | DF  | Mean Square | F Value | Prob. > F |
|---------|----------------|-----|-------------|---------|-----------|
| Model   | 18.3           | 14  | 1.31        | 7.95    | 0.0001    | Significant |
| A       | 0.19           | 1   | 0.19        | 1.16    | 0.2990    |
| B       | 0.11           | 1   | 0.11        | 0.67    | 0.4245    |
| C       | 0.15           | 1   | 0.15        | 0.94    | 0.3480    |
| D       | 12.23          |     | 12.23       | 74.35   | <0.001    |
| A²      | 0.078          | 1   | 0.078       | 0.47    | 0.5014    |
| B²      | 0.028          | 1   | 0.028       | 0.17    | 0.6859    |
| C²      | 2.415E-004     | 1   | 2.415E-004  | 1.468E-003 | 0.9699 |
| D²      | 1.56           | 1   | 1.56        | 9.51    | 0.0076    |
| AB      | 0042           | 1   | 0042        | 0.26    | 0.6195    |
| AC      | 0.17           | 1   | 0.17        | 1.01    | 0.3316    |
| AD      | 0.27           | 1   | 0.27        | 1.67    | 0.2169    |
| BC      | 3.748E-003     | 1   | 3.748E-003  | 0.023   | 0.8820    |
| BD      | 9.21E-003      | 1   | 9.21E-003   | 0.056   | 0.8161    |
| CD      | 0.035          | 1   | 0.035       | 0.21    | 0.6507    |
| Residual| 2.47           | 15  | 0.16        | 0.16    |            |
| Lack of Fit | 1.02 | 8   | 0.13        |         |            |
| Pure Error   | 1.45 | 7   | 0.21        | 0.61    | 0.7458    | Not significant |
| Cor. Total   | 2.47 | 29  |             |         |            |

Figure 1 Contour and 3D graphics for the effect of biomass ratio and citric acid concentration on Pb(II) ion adsorption capacity.

Figure 2 Contour and 3D graphics for the effect of citric acid concentration and contact time on Pb(II) ion adsorption capacity.
In this research, the optimization process was conducted by adjusting the ratio of PB-RS biomass, citric acid concentration, and contact time. The response variable was Pb(II) ion Adsorption Capacity. The optimization solution of Pb(II) ion adsorption capacity calculated by Design Expert 6.0.8 Software in this study was shown in Table 4.

| No. | Ratio Biomass (gr) | Citric acid conc. (mol/L) | Contact time (minutes) | Initial concentration (mg/L) | Adsorption capacity (mg/g) | Desirability |
|-----|-------------------|----------------------------|------------------------|-------------------------------|---------------------------|--------------|
| 1   | 30.00             | 0.60                       | 99.88                  | 99.42                         | 3.01                      | 0.95         |

Figure 4 shows the optimization of Pb(II) ion Adsorption Capacity by PB-RS biomass. This result showed that the optimum conditions of the process would be achieved at 30 g of activated PB-RS biomass, citric acid concentration of 0.6 mol/L, contact time of 99.88 minutes, and at a Pb(II) initial concentration of 99.42 mg/L.

4. Conclusion
This research concludes that variables of mass ratio, activator concentration, and contact time influence the rate of Pb(II) ion adsorption from the water phase. Based on the optimization analysis using quadratic regression model, the optimum condition of Pb(II) ion adsorption achieved at 30 g of activated PB-RS biomass, the citric acid concentration of 0.6 mol/L, 99.88 minutes contact time, and at a Pb(II) initial concentration of 99.42 mg/L. In this optimum condition, Pb(II) ion adsorption capacity obtained was 3.01 mg/g.
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