Microwave-assisted CO$_2$ activation preparation of *ceiba pentandra* seed based activated carbon for Cu(II) adsorption

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Abstract. This study involves producing activated carbon from Ceiba Pentandra seed by using a physical activation method to adsorb Cu(II) from synthetic wastewater. *Ceiba Pentandra* seed was carbonized and activated using CO$_2$ using a microwave heating process. The process was optimized using Design-Expert version 11. The interactions between different process conditions towards the Cu(II) adsorption were analyzed. The optimum radiation power, radiation time and CO$_2$ flow were found out 264 Watt, 4 minutes and 100 cm$^3$, respectively for the maximum Cu(II) removal.

1. Introduction

Heavy metal produced by industrial and agricultural activities become severe than before due to the increment of activities in these two sectors. Once the amount of heavy metal more than it supposed to be, it would directly seep into the soil and water and becomes dangerous to human and other living organism’s safety. Researchers state that there are several methods in reducing these heavy metals such as filtration, electrochemical treatment, ion exchange and adsorption[1]. Among these methods, adsorption based on activated carbon (AC) is the most effective and economical methods[2]. Recently, microwave-assisted activation process has overcome the problems via conventional activation. It includes the faster process, selective, uniform, precise and the contact between the heating elements and the precursor[3]. The allowable copper in wastewater according to Standard A and Standard B are 0.20 mg/L and 1.0 mg/L, respectively[4]. In this adsorption method, an agricultural waste will be used, which then will be transforming in the form of activated carbon. In this paper, the performance of *Ceiba Pentandra* (Kapok Tree) Seed as the activated carbon in removing the Cu (II) in the synthetic wastewater that prepared. Kapok tree or in its scientific name, *Ceiba Pentandra* is a tropical tree under family *Malvacea ae* which is widely distributed in a hot climate like Malaysia[5]. The potential of *Ceiba Pentandra* seed as a precursor for activated carbon has not been explored.
Current preparation process The optimization preparation condition for activated carbon is analyzed using Design Expert version 11.

2. Material and Methods

2.1 Activated Carbon and Synthetic Wastewater Preparation

_Ceiba Pentandra_ seed (CPS) used for the preparation of activated carbon was obtained from the local fields in the state of Sabah, Malaysia. The CPS were washed with distilled water to remove dirty and unnecessary things that stick on it. This seed then oven-dried at 105°C for about 24 hours. The dried seed then crushed by using a grinder and sieved to the desired mesh size (1.18-2 mm). The carbonization process using nitrogen gas was carried out by ramping the temperature from room temperature to 500 cm³ and hold for 30 minutes. The produced char then activated by using microwave irradiation process by allowing the flow of CO₂. Various preparation conditions were observed and analyzed by using Design Expert Version 11. The synthetic wastewater was prepared by mixing the solution of Cu (II) with the distilled water and diluted to the desired concentration. The percentage of heavy metal removal can be determined by using Equation 1 below. The initial concentration is set to be 2mg/L.

\[
\text{Heavy metal removal (\%) = \frac{C_o - C_e}{C_o} \times 100}
\]  

(1)

2.2 Design of Experiments

A standard Response Surface Methodology (RSM) design, which is called a central composite design (CCD) was applied in this work to study the variables the activated carbon. Generally, in this CCD consists of a 2^n factorial runs with 2n axial runs and n_c center runs which means there will be 6 replicates. For each of the variables, a 23 full factorial CCD means three variables take into consideration, wherein this case three variables are radiation power, radiation time and CO₂ flow which consists of 8 factorial points and 6 replicates at the center points. This indicated that all together, there would be 20 experiments were required based on the calculation from Equation 2 below.

\[
N = 2^n + 2n + n_c
\]  

(2)

Where N is the total number of experiments required, and n is the number of factors in the experiment.

2.3 Model Fitting and Statistical Analysis

Design Expert software version 11(STAT-EASE Inc., Minneapolis, US) was used for regression analysis and evaluation of the experimental data to fit the equations developed and for the statistical significance of the equations, respectively.

3. Results and Discussion

The complete preparation design, together with the values of both the responses obtained from the experiment, is given in Table 1. CCD was used to evaluate the correlation between carbon yields and Cu (II) removal.
Table 1. Preparation design of activated carbon and results.

| Radiation Power (Watt) | Radiation Time (min) | CO₂ (cm$^3$) | Carbon Yield (%) | Copper, Cu (II) Removal (%) |
|------------------------|----------------------|--------------|------------------|-----------------------------|
| 1                      | 264                  | 8            | 100              | 61.59                       | 59                           |
| 2                      | 264                  | 8            | 500              | 62.25                       | 43.5                          |
| 3                      | 264                  | 4            | 100              | 60.67                       | 46.5                          |
| 4                      | 264                  | 6            | 300              | 60.00                       | 57.5                          |
| 5                      | 264                  | 4            | 500              | 63.33                       | 63.5                          |
| 6                      | 440                  | 6            | 300              | 61.59                       | 58                            |
| 7                      | 440                  | 6            | 300              | 61.59                       | 58                            |
| 8                      | 440                  | 6            | 300              | 61.59                       | 58                            |
| 9                      | 440                  | 6            | 300              | 61.59                       | 58                            |
| 10                     | 440                  | 6            | 300              | 61.59                       | 58                            |
| 11                     | 440                  | 6            | 300              | 61.59                       | 58                            |
| 12                     | 440                  | 4            | 300              | 62.91                       | 51.5                          |
| 13                     | 440                  | 8            | 300              | 63.33                       | 62.5                          |
| 14                     | 440                  | 6            | 500              | 62.67                       | 51                            |
| 15                     | 440                  | 6            | 100              | 62.00                       | 62.5                          |
| 16                     | 616                  | 4            | 100              | 64.00                       | 61                            |
| 17                     | 616                  | 8            | 100              | 66.67                       | 39                            |
| 18                     | 616                  | 4            | 500              | 64.67                       | 57.5                          |
| 19                     | 616                  | 8            | 500              | 64.00                       | 53.5                          |
| 20                     | 616                  | 6            | 300              | 66.00                       | 52.5                          |

From the results in Table 1, it is shown that the carbon yield varies from 60% to 66.67% while for the percentage of Cu (II) removal varies from 39 % to 63.5%. The models were selected based on the highest order polynomials, where the models were significant. These two responses have different regression model where, the quadratic regression models is suggested for the carbon yield, while for the Cu (II) removal, a mean regression model was suggested. In terms of coded factors, the final empirical models for both responses are given by Equation 3 and 4, respectively.

Carbon yield ($Y_1$) = $+61.91 + 1.75A + 0.23B + 0.13C + 0.27AB – 0.66 AC – 0.67 BC + 0.61 A^2 + 0.73B^2 + 0.28 C^2$             (3)

Copper removal ($Y_2$) = +55.45                                                         (4)

The closer the correlation coefficient, $R^2$ values to the unity and the smaller the standard deviation value, the more accurate the response could be predicted by the model. The $R^2$ of the $Y_1$ is 0.8852. These values indicate that 60.35% and 55.45% of the carbon yields and percentage Cu (II) removal respectively. The standard deviation for Equation (2) and (3) was 0.79 and 6.47, respectively. This shows that the predicted value for carbon yield is more accurate compared to the percentage of Cu (II) removal. The adequacy of the models was further justified through analysis of variance (ANOVA).

The effect of that factor for the preparation of AC from CPS is represented by the coefficients with radiation power (A), radiation time (B) and carbon dioxide, CO₂ flow (C). It has been stated that a
positive sign in front of the terms indicates the synergistic effect, whereas a negative sign indicates the antagonistic effect [6].

3.1 Analysis of Variance (ANOVA)
With respect to RSM, values of Prob > F less than 0.0500 indicate model terms are significant while the values which are greater than 0.1000 indicate the model terms are not significant. Table 2 and Table 3 shows the ANOVA values for both responses, which are carbon yield and copper removal, respectively. It suggested that the linear term is significant to the carbon yields model, and the mean term is significant to the copper removal model.

Table 2 shows the analysis of variance for responses, carbon yield of the CPSAC surface generated by using the quadratic model. The Model F-value of 8.57 implies the model is significant. Approximately 0.12% chance that a Model F-value this large could occur due to noise. Previous studies mostly stated, values of Prob > F less than 0.0500 indicate model terms are significant. According to the result of this study, A, AC and BC are significant model terms. Values which are greater than 0.10000 indicate the model terms are not significant, which means that B, C, AB, A\(^2\), B\(^2\), and C\(^2\) are not significant model term.

### Table 2. ANOVA for response surface quadratic model for carbon yield of activated carbon.

| Source | Sum of Squares | Degree of Freedom, df | Mean Square | F Value | Prob > F |
|--------|----------------|-----------------------|-------------|---------|----------|
| Model  | 48.67          | 9                     | 5.41        | 8.57    | 0.0012   |
| A-Power| 30.62          | 1                     | 30.62       | 48.53   | < 0.0001 |
| B-Time | 0.51           | 1                     | 0.51        | 0.81    | 0.3895   |
| C-CO\(_2\) | 0.17  | 1                     | 0.17        | 0.28    | 0.6107   |
| AB     | 0.58           | 1                     | 0.58        | 0.92    | 0.3591   |
| AC     | 3.54           | 1                     | 3.54        | 5.61    | 0.0394   |
| BC     | 3.56           | 1                     | 3.56        | 5.65    | 0.0388   |
| A\(^2\) | 1.01           | 1                     | 1.01        | 1.60    | 0.2349   |
| B\(^2\) | 1.45           | 1                     | 1.45        | 2.29    | 0.1609   |
| C\(^2\) | 0.21           | 1                     | 0.21        | 0.33    | 0.5780   |
| Residual | 6.31          | 10                    | 0.63        | -       | -        |

The analysis of variance for responses, copper removal of the CPSAC surface generated by using the mean model. The values of Prob > F less than 0.0500 indicate model terms are significant.

3.2 Effects of Process Parameters
The parameter that has the greatest effect on the carbon yield for the AC from the CPS is the radiation power (A) whereas the radiation time (B) and carbon dioxide, CO\(_2\) flow (C) shows the least significant effect on the carbon yield for the activated carbon. The ANOVA result in Table 2 states that the radiation power (A) was found having the highest value of F value, which is 48.53 on the carbon yield. The relationship between the parameters and response, carbon yield can be shown in Figures 1, 2, and 3.

The parameters that give effect on the Cu (II) removal in synthetic wastewater for the AC from the CPS are the radiation time and radiation power. The relationship between the parameters and response, copper removal can be shown in Figures 4 and 5 for three-dimensional response surface plot and contour surface plot, respectively. Based on the result, it can be seen that there are equal effects of radiation time and radiation power to the removal of Cu (II).

3.3 Optimization
High product yield is a significant contributory factor to the development of the good performance of
AC, which then expected to have better adsorption capacity for economic viability purposes. AC that is produced should have high carbon yield and high efficiency of removing heavy metal. The low and high level that used is 264 Watt and 616 Watt, respectively. The medium radiation power is 440 Watt. The radiation time and carbon dioxide, CO\textsubscript{2} flow that used are 4 minutes, 6 minutes and 8 minutes, and 100 cm\textsuperscript{3}, 300 cm\textsuperscript{3}, and 500 cm\textsuperscript{3} respectively. Table 3 shows the predicted and experimental value of carbon yield and Cu (II) removal of the suggested AC. According to the result obtained from the experiment, the performance of the prepared AC in removing the Cu (II) in the synthetic wastewater is satisfactory with the removal efficiency of 74% for a solution concentration of 2 mg/L. The experimental value of carbon yield was found at 61.202%. The study found that the predicted model can be used for further study in removing the copper in the synthetic wastewater.

Figure 1. Three-dimensional response surface plot of yield power (A) and time (B).

Figure 2. Three-dimensional response surface plot of yield time (B) and, CO\textsubscript{2} flow (C).

Figure 3. Three-dimensional response surface plot of yield power (A) and carbon dioxide, CO\textsubscript{2} flow (C).

Figure 4. Three-dimensional response surface plot of copper removal of radiation power (A) and radiation time (B).
Figure 5. Contour response surface plot of copper removal of power (A) and time (B).

Table 3. Model validation based on the predicted value and experimental value of AC.

| Desirability | Radiation Power, Watt | Radiation Time, minutes | Carbon Dioxide, CO$_2$ flow, cm$^3$ | Carbon Yield % | Copper Removal % |
|--------------|-----------------------|-------------------------|-------------------------------------|----------------|-----------------|
|              | Predicted             | Experimental            | Error (%)                           | Predicted      | Experimental    | Error (%)       |
| 0.487        | 264.00                | 4.00                    | 100.00                              | 60.3477        | 61.202          | 1.396           |
|              | 61.202                | 74                      | 25.07                               | 55.45          |                |                |

4. Conclusion
This paper has investigated the optimum preparation of *Ceiba Pentandra* seed-based activated carbon by physical activation for the removal of Cu (II) in the synthetic wastewater. The optimum preparation condition, which is the radiation power, activation time and CO$_2$ flow was found out to be 264 Watt, 4 minutes and 100cm$^3$, respectively. The results revealed that *Ceiba Pentandra* seed as an excellent precursor to produce an efficient AC with high performance in removing the Cu (II) in the synthetic wastewater.

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