Synthesis and Characterization of Coffee Based-Activated Carbon with Different Activation Methods

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Abstract. Activated carbon (AC) is used in many applications because it has many strengths such as high adsorption ability, inexpensive, and not hazardous. The use of agricultural waste in AC production has become a popular topic in recent years. One of the waste materials that can be utilized is coffee wastes. Indonesian have a high rate of coffee consumption which results in a high number of wastes. In general, the AC generation was done by three main steps; carbonization at 400°C, chemical activation using KOH and physical activation using CO₂ with a 100 ml/minute flow rate. The obtained results showed that AC has the highest iodine number of 443.58 mg/g and a surface area of 399.05 m²/g. The SEM results indicated the pore had formed on the carbon surface. The carbon mass percentage was known at 67.5% from the EDX test. These results showed that coffee waste can be used as an alternative raw material and can be used for several needs.

1. Introduction

Adsorbents such as activated carbon is always an interesting topic to be developed. Activated carbon is an adsorbent with large internal pores and a wide area. But the main challenge is to find adsorbents with high storage performance at low pressures and ambient temperatures that allow for desorption under mild conditions [1]. AC already used in previous research, such as to remove metal from the aqueous environment [2], removal of organic pollutants [3], water purification [4], etc.

Nowadays, biomass waste became a popular raw material due to its renewable properties [5]. Coffee waste is one of the lignocellulosic residues produced in large numbers throughout Indonesia with a total plantation area of 1.3 million hectares (ha). Indonesia can produce at least 748 thousand tons per year or 6.6% of world coffee production in 2017. Therefore, research using coffee grounds to make activated carbon has good prospects because of its lignocellulosic content and large amount.

In this study, activated carbon producing was done with chemical, physical, and the combination of both activation process. Coffee waste as the material was carbonized in a furnace. KOH solution mixed with carbon serves as an activating agent that will oxidize carbon and damage the inner surface of carbon so that it will form pores and increase adsorption power [6]. The optimum condition such as temperature was controlled and monitored. The physical activation was done using CO₂ under high temperatures. This study aims to produce high quality activated carbon with good performance for adsorption or desorption that can be used for further research.
2. Materials and Methods

2.1 Activated Carbon Synthesis
Preparation was done with the dehydration process of coffee solution at 100 °C for 3 hours. Carbonation of coffee grounds was carried out at 400 °C for 2 hours using Furnace Vulcan A-550. There were two steps for activation, chemical and physical. Chemical activation used KOH as an activating agent. After activation using KOH, then the physical activation process was carried out by the thermal activation method, by heating activated carbon at high temperatures, above 600 °C with the help of gas carbon dioxide (CO₂). The activation process used a temperature of 600 °C with a CO₂ gas flow rate of 100 ml/minute with a heating rate of 5.75 °C /minute for 1 hour.

Then the samples were washed with HCl for 1 hour and rinsed with distilled water until the neutral pH. The AC next was dried in the oven for 1 hour with a temperature of 110 °C.

2.2 Characterization Process
There were 3 types of characterization used in this study. Iodine number test to calculate the surface area of AC, Field emission scanning electron microscopy (FESEM) to analyze the surface structure which integrated with Energy Dispersive X-Ray Spectroscopy (EDX) to identify the component of AC, and BET to measure the actual surface area of the AC using Micromeritics ASAP 2020 V.4.02

Iodine adsorption was obtained by measuring the volume of a titration between Na₂S₂O₃ and I₂. From this volume, iodine (mg/g) was calculated using equation 1.

\[
\text{Adsorbed Iod (mg/g)} = \frac{(V_{\text{titrat}} - v \times N)}{W} \times 12.69 \times 2
\]

Where:
- \(V_{\text{titrat}}\): I₂ volume which mixed with the AC (5 ml)
- \(v\): natrium thiosulphate solution used (ml)
- \(N\): sodium thiosulphate solution concentration (N)
- \(W\): the weight of AC used (gr)

3. Results and Discussion

3.1 Carbonization of Material
The carbonization process would remove unwanted and volatile components [7]. The final yield from the carbonization process was listed in table 1.

| No | Coffee waste initial mass (gram) | Final mass (gram) | Yield (%) |
|----|----------------------------------|-------------------|-----------|
| 1  | 100.36                           | 28.54             | 28%       |
| 2  | 100.21                           | 30.17             | 30%       |
| 3  | 100.25                           | 30.38             | 30%       |
| 4  | 100.12                           | 30.05             | 30%       |
| 5  | 100.45                           | 32.14             | 32%       |
| 6  | 100.22                           | 31.12             | 31%       |
| 7  | 100.05                           | 28.18             | 28%       |
| 8  | 100.24                           | 29.35             | 29%       |
Volatile contaminants can be defined by the mass loss after the carbonization process (burn-off). The functional groups of raw material were also removed in this process \[8\]. The value of mass lost can be seen in Table 2.

| No | Removed mass (gram) | Burn Off (%) |
|----|---------------------|--------------|
| 1  | 71.82               | 72%          |
| 2  | 70.04               | 70%          |
| 3  | 69.87               | 70%          |
| 4  | 70.07               | 70%          |
| 5  | 68.31               | 68%          |
| 6  | 69.1                | 69%          |
| 7  | 71.87               | 72%          |
| 8  | 70.89               | 71%          |
| 9  | 69.95               | 70%          |
| 10 | 70.3                | 70%          |

The average percentage of burn off was 70% which means over 70% of the total component removed from samples.

The carbon activation process was carried out with two steps, chemical followed by physical activation. For this reason, before the activated process, samples were crushed and sieved with 150 mesh size. The adsorption ability of AC was very affected by its size. The smaller size of samples will give a higher contact area in the adsorption process. After being crushed, carbon is activated chemically using a KOH solution. The results of activation using the KOH solution can be seen in table 3.

| No | Carbon mass (gr) | KOH concentration (M) | KOH volume (ml) | Carbon mass after activation (gr) | Yield |
|----|------------------|------------------------|-----------------|-----------------------------------|-------|
| 1  | 10.06            | 5                      | 100             | 8.1279                            | 81%   |
| 2  | 10.11            | 6                      | 100             | 8.2041                            | 81%   |
| 3  | 10.08            | 7                      | 100             | 8.1133                            | 80%   |
| 4  | 10.07            | 8                      | 100             | 8.1937                            | 81%   |

In chemical activation, carbon was mixed using a KOH solution at 65 °C and stirred using a magnetic stirrer for four hours. KOH solution mixed with carbon serves as an activating agent that will oxidize carbon and damage the inner surface of carbon so that it will form pores and increase adsorption capability. Also, activating agents will inhibit the formation of tar and reduce the formation of acetic acid, methanol and so on \[8\]. The reaction occurred in the activation process are:

\[
\begin{align*}
6 \text{KOH} + \text{C} & \leftrightarrow 4\text{K} + \text{CO}_2 + \text{H}_2\text{O} \\
6\text{KOH} + \text{C} & \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \\
4\text{KOH} + 2\text{CO}_2 & \leftrightarrow 2\text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}
\end{align*}
\]
The chemical activation was followed by physical activation using CO$_2$. The main purpose of this process was to increase the pore volume of AC. The gases used for gasification were used to remove volatile substances which were impurities on the AC. The results were shown in table 4.

| No | Initial mass (gr) | Final mass (gr) | Yield % |
|----|------------------|----------------|---------|
| 1  | 5.006            | 3.542          | 71%     |
| 2  | 5.011            | 3.76           | 75%     |
| 3  | 5.007            | 3.742          | 75%     |

The temperature chosen for this process was 600 °C as this was the optimal temperature for physical activation. If the temperature is too low then the activation process will not run optimally, while the temperature is too high will cause damage to the carbon structure (sintering), thereby reducing the surface area. The higher the CO$_2$ flow rate used; the more carbon atoms react to carbon monoxide (CO) gas. As a result of the reaction and carbon erosion, the yield of activated carbon will also decrease compared to the chemical activation process as in Table 3. The reaction between CO$_2$ gas and carbon (C) is stated in Equation 3.

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad (5)
\]

Reactions that occur in the physical activation will remove the mass to form active carbon pores but if the reaction is excessive then the pore structure will be damaged [9]. Besides the nature of coffee grounds that are very sensitive to heat causes reduced surface area because it is easily oxidized by CO$_2$.

After that, AC was washed using a 1M HCl solution to remove K+ ions which were still attached to the carbon. The main goal was to clean impurities and reduce the ash content. Washing with HCl was done for 1 hour by immersing activated carbon in the HCl solution. After that, the AC was washed using distilled water to neutralize the remaining acid solution in the AC.

### 3.2 Characterization process

#### 3.2.1 Iodine number calculation

The surface area of AC as an adsorbent is an important parameter. AC can be said as a good adsorbent if it has a high surface area. Iod number test is a method for determining surface area by performing sodium thiosulfate titration with an iodine solution that has been mixed with activated carbon [10]. The value of the iod number obtained is the absorption capacity of milligrams of iod per gram unit of activated carbon (mg/g). Iod number testing was carried out on AC which had done carbonization, chemical activation with variations in KOH molarity, and physical-chemical activation.

The results of the iodine number calculation could be seen in figure 1. It can be concluded that the surface area value is inversely proportional to the volume of the titration. The lower the titration volume, the greater the surface area.

The activation process of Physical Chemistry had failed because this process damages the pores of AC. It could be seen that this process damages the parts of the pores that have formed in carbonization and chemical activation. This caused the test result of the physical-chemical activation iod number was lower because of the reduced pores to absorb iodine.
3.2.2 SEM, EDX and BET characterization. The characterization of AC using SEM aims to see the morphological structure of activated carbon that has been made [5]. Characterization is carried out on only carbonization samples and activated carbon which has undergone chemical activation and physical-chemical activation.

The carbonization process forms the mesoporous part as shown in figure 1. The SEM test also conducted to the carbon which activated with KOH 5 M. From figure 2, it can be seen that the pores were much smaller than the first one. The structure of the pore is also more visible.
Figure 3. SEM Characterization of Chemically activated carbon: (a) 500x magnified, (b) 2000x magnified, (c) Pore size with 500x magnified.

From figure 3c, it can be seen that the pore size distribution was different from figure 2c. In figure 3c, the pore size distribution was smaller. This indicated that the chemical activation broke the carbon wall and made some new pores. Although from figure 2a, the surface area of the AC was still uneven.

Energy Dispersive X-ray (EDX) test was also done in this study. This test aims to determine the composition of a material by firing x-rays at the material. The (EDX) test results can be seen in table 5.

| Elements | Mass percentage (%) | Atom percentage (%) |
|----------|---------------------|---------------------|
| Carbon   | 67.5                | 72.88               |
| Nitrogen | 7.66                | 7.09                |
| Oxygen   | 24.54               | 19.89               |
| Aluminum | 0.21                | 0.1                 |
| Sulfur   | 0.06                | 0.02                |
| Chlorine | 0.03                | 0.01                |

The carbon components in AC was relatively high. Nitrogen, Aluminum, and Sulfur are elements that are already contained in coffee beans. Chlorine was obtained from the washing process of activated carbon using 1M hydrochloric acid (HCl).

BET testing was done once using the sample with the best activation method previously tested with the iod number method, i.e. Chemical Activation of 5 M KOH. BET surface area characterization was carried out using Micromeritics ASAP 2020 V4.02. The surface area results obtained from chemical
activation are 399.0507 m$^2$/g. This number is still low compared to other studies, so further research is needed to obtain optimal condition operation and activation process modification.

4. Conclusion
Coffee wastes had a potential future to replace the current AC raw materials. The AC production with chemical activation using KOH 5 M resulted in the highest surface of 399.05 m$^2$/g. But the physical activation ruined the pore structure in the carbon surface which decreases the iodine number of AC. The SEM Characterization showed that some mesopore had already created although the pore surface was still disorganized and the EDX test exhibited the high number of carbon present in the AC produced.

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