Preparation of Activated Carbon from Mangrove Waste by KOH Chemical Activation

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Abstract. In this study, Mangrove (Rhizophora mucronata) fruit waste which was generated from water-based extraction of natural dyes from this fruit was used as raw material in activated carbon preparation. Carbonization of chopped Mangrove fruit waste was conducted in a batch pyrolyzer for slow pyrolysis at temperature range of 300°C to 335°C and atmospheric pressure. The produced carbon was then soaked with potassium hydroxide (KOH) solution for 24 hours before activation process in an electrical furnace at 400°C for an hour. Effect of KOH concentration on physical characteristics of activated carbon was investigated in terms of moisture content, ash content, surface area, pore diameter, iodine number, and surface morphology. It was observed that the surface area and pore diameter increased with increasing the KOH concentration. Soaking the carbon in 2.5 M KOH provided the highest surface area and pore diameter of activated carbon, which were 1,920.6 m²/g and 5.52 µm, respectively. Also, the iodine number of 1,540.13 mg/g was obtained in correspond to the adsorption capacity.

1. Introduction
Activated carbon has been well known as good absorbent for wide applications including wastewater treatment, air pollution control, and gas purifying due to high adsorption capacity, large surface area, and low cost [1]. Typically, agricultural waste such as rice husk, sawdust, bamboo, coconut shell [2], palm shell [3], and also urban organic waste [4] are used as raw material of activated carbon production.

In Indonesia, transplantation of Mangrove especially Rhizophora mucronata are used to reduce the land erosion by sea water waves [5]. The mangrove forest has been long utilized by society for construction materials, firewood, and charcoal [4]. Nowadays, the fruit of this mangrove species is used as natural dyes resources due to high tannin content (15–36%.wt) that produce reddish brown dyes [6]. Unfortunately, the significant amount of solid residue is generated in water-based tannin extraction of natural dyes production that it is only disposed without proper treatments. The production of one kg of concentrated natural dyes solution from this chopped fruit will generate 0.5 kg of fruit waste. Due to high density and carbon content of this solid residue, it is possibly to be used as a precursor in preparation of activated carbon in order to produce more valuable product.

Basically, the activated carbon is possibly be synthesized by physical and/or chemical activation process. Physical activation involves the carbonization under the inert atmosphere or using either steam, air, and CO₂ as activating agent [3, 7, 8, 9]. While, chemical activation involves the presence of chemicals such as; alkaline metal [10], zinc chloride [11], phosphoric acid [12] in an inert condition.
Due to higher carbon yield, larger surface area and lower operating cost, the chemical activation is preferred after physical activation [2, 13]. Many researchers have been observed that activated carbon produced by KOH activation from carbonaceous materials has a high surface area, good porosity, and well-developed pore distribution [2, 10, 11, 14]. However, sufficient literatures are not available about the utilization of mangrove fruit waste as an activated carbon precursor followed by KOH solution activation.

In this study, activated carbon was prepared from mangrove fruit waste using KOH solution as activating agent. The process includes carbonization followed by impregnation of the carbon (char) and activation process were employed to develop high-quality of activated carbon. The yield and specific energy consumption were investigated in order to evaluate the performance of carbonization process. Furthermore, the physical characteristics of activated carbon were analyzed including moisture content, ash content, surface area, pore diameter, iodine number, and surface morphology.

2. Experimental section

2.1. Materials
In this study, Mangrove (Rhizophora mucronata, see figure 1) fruit was obtained from Bontang district, Kalimantan Timur province, Indonesia. The fruit was then chopped into 2 cm of length and then boiled in water by ratio 10:1 (L/kg) at 100°C for an hour. The solid was then filtered and separated from the solution of natural dye. This solid (mangrove fruit waste) was then dried at 105°C for 24 hours before carbonization process. The proximate and ultimate analysis of mangrove fruit waste is shown in Table 1. The high-purity (more than 85% wt) of potassium hydroxide (KOH) was used in this study. This solution was then mixed with certain quantities of aquadest to make some KOH solution which then act as activating agents.

![Figure 1](image_url)

**Figure 1.** (a) Mangrove (Rhizophora mucronata); (b) magrove fruit; (c) chopped mangrove fruit

| Table 1. The proximate and ultimate analysis of mangrove fruit waste |
|---------------------------------------------------------------|
| **Proximate analysis (dry basis-%.wt)** | **Ultimate analysis (dry basis -%.wt)** |
| Fixed carbon | 48.56% | Carbon, C | 62.00% |
| Volatile matter | 41.91% | Hydrogen, H | 4.79% |
| Ash | 3.05% | Oxygen, O | 26.36% |
| | | Nitrogen, N | 1.20% |
| | | Sulfur, S | 0.03% |
| | | LHV, (MJ/kg) | 5,523 |

2.2. Methods
The precursor or carbon (char) was produced by carbonization process in a batch pyrolyzer with one kg of capacity. The carbonization was conducted by slow pyrolysis at temperature range of 300°C to 335°C for an hour. The heat requirement of carbonization was supplied by the combustion of liquid petroleum
gas fuel. After carbonization, the precursor was crushed and sieved into 0.01 mm, and then cleaned by using deionized water. The pre-dried char was then fully soaked with KOH solution for 24 hours. The KOH solution was varied at different concentration of 0.5 M, 1 M, 1.5 M, 2 M, and 2.5 M. Samples were then filtered and dried in electric oven at 110°C for two hours. Subsequently, samples were then spread separately into a glass plate as a thin layer for the activation process. The activation process was carried out in an electrical furnace at temperature of 400°C for an hour. In order to remove the remaining activator and impurities, the produced activated carbon was then washed by using deionized water until neutral pH reached.

2.3. Analytical Methods
In order to evaluate carbonization process, the yield of char and specific energy consumption are defined as follows:

\[ \text{Yield(%)} = \frac{m_{\text{char}}}{m_{\text{nw}}} \times 100\% \]  

(1)

\[ \text{Spesific energy consumption (MJ/kg)} = \frac{m_{\text{gas fuel}} \times \text{LHV}_{\text{gas fuel}}}{m_{\text{char}}} \]  

(2)

Where, \( m_{\text{char}} \) is the weight of produced char (kg) and \( m_{\text{nw}} \) is the weight of dried mangrove fruit waste (kg). The specific energy consumption is defined as the ratio of energy requirement of carbonization to the quantity of produced char. The energy requirement is calculated by multiplying the consumed fuel gas (kg) and its heating value (MJ/kg).

In this study, the physical characteristics of activated carbon are defined as moisture content, ash content, surface area, pore diameter, iodine number, and surface morphology. According to the Standard National Indonesia (SNI 06-3730-1995), the maximum moisture content and ash content are 15%.wt and 10%.wt, respectively. The Brunauer Emmet, and Teller (BET) method is used to measure the pore characteristics of the activated carbon by using Quantchrome Instrument Nova 3200e. Iodine number was analyzed in order to evaluate the adsorption capacity of activated carbon. The iodine number represents the porosity of the activated carbon which is defined as the milligrams of iodine absorbed per gram of carbon. The pore diameter and surface morphology of activated carbon was analyzed by using Scanning Electron Microscope (SEM) JEOL 650 apparatus.

3. Results and Discussion

3.1. The preparation of char by carbonization process
The effect of carbonization temperature was investigated in order to evaluate the yield of char and the specific energy consumption. As shown in Figure , the yield of char decrease with increasing of carbonization temperature. The higher temperature promotes gases formation while the char yield becomes decrease. The volatile matter in the biomass is released during the carbonization process [15]. The carbonization of hemicellulose and cellulose is quickly occurred at a temperature range of 220°C-315°C and 315°C-400°C, respectively. However, the decomposition of lignin is more difficult which is happened in the range of 160°C-900°C [16]. Char yield were found about 30%–45%.wt of dried mangrove fruit waste. Due to the endothermic reaction of carbonization, the heat requirement should be considered. The specific energy consumption of carbonization increase with increasing temperature and it’s ranged from 5.99×10^4 to 14.27×10^4 MJ/kg in correspond to fuel gas consumption during combustion.
3.2. The effect of KOH concentration on the activated carbon properties

In this study, activated carbon was prepared from char of mangrove fruit waste by using several concentrations of KOH solution as activating agent. Activation temperature in furnace was kept constant at 400°C. The previous studies have been reported that optimum activation temperature is in the range of 400°C to 500°C [1, 12, 17]. The effect of different concentration of KOH on the surface area of activated carbon and iodine number is shown in figure 3a. An increase of surface area of activated carbon is observed with increase in the concentration of KOH. The surface area of activated carbon with KOH 2.5 M is obviously larger than without KOH, with the value of 1,920.6 m²/g and 1,200.7 m²/g, respectively. In general, the larger surface area of activated carbon will promote good adsorption performance.

Iodine number is used to estimate the surface area of activated carbon. Iodine number increase with increasing surface area of activated carbon, this is closely related to the increase in adsorption capacity. It was found to attain 1.540,13 mg/g at 2.5 M of KOH concentration. In addition, the pore diameter is also an important property of activated carbon. It can be seen in figure 3b that the pore diameter significantly increased from 0.93 nm to 5.52 nm with the increase of KOH concentration. It was observed that KOH activation led to a porous formation of the activated carbon which has microporous and mesoporous structures. Similar trends were also reported by Ma [11] and Kawano [14] in their studies on the preparation of activated carbon by chemical activation.

![Graph](image-url)
The surface morphology of activated carbon are shown in figure 4. The increasing of concentration of KOH encouraged the alteration of pores, indicating that the volatile matter was released during the activation process. The releasing of volatile matter enhanced the pore structures of activated carbon \[18\]. Moreover, a higher concentration of KOH not only produce pores but also dramatically destroys the carbon structure as reported by Budi et.al \[2\]. During the activation process, the reaction mechanisms are given as follows \[10, 11\].

\[
\begin{align*}
C + KOH & \rightarrow 2K + CO_2 + H_2 \quad (3) \\
C + KOH & \rightarrow 2K + H_2O + CO \quad (4) \\
CO_2 + 2KOH & \rightarrow K_2CO_3 + H_2O \quad (5)
\end{align*}
\]

The mesoporous and microporous are formed in correspond to the consumption of carbon by KOH, that is acts as a dehydrating agent. Furthermore, the use of KOH promote the formation of microporous and transformation of lignin \[2\]. The pores distribution has to gain considerable attention due to activated carbon applications, but no analysis was made in this study. And also, due to the use of KOH as an activating agent, the point of zero charge (PZC) should be determined due to its next applications, but no measurement was made in this point. Based on the pore diameter range of activated carbon, the possible application of this activated carbon is as adsorbent of synthetics dyes in wastewater treatment.

\[\text{Figure 4. The SEM images of activated carbon}\]
According to Standard National Indonesia (SNI), the moisture content of activated carbon and ash content must lower than 15% and 10%, respectively. As shown in Table, both moisture content and ash content of produced activated carbon meet the requirements of SNI 06-3730-1995. All the biomasses contain ash minerals which are formed in organic or inorganic compounds [19]. In this case, the higher content of ash may reduce the adsorption capacity of activated carbon due to the presence of minerals such as potassium, calcium, magnesium, sodium in the pores.

Table 2. Moisture content and ash content of produced activated carbon

| Concentration of KOH (M) | Activation temperature (°C) | Moisture content (%.wt) | Ash content (%.wt) |
|--------------------------|----------------------------|-------------------------|--------------------|
| 0                        | -                          | 6.6                     | 8.1                |
| 0.5                      | 400                        | 3.2                     | 7.9                |
| 1                        | 400                        | 4.6                     | 7.8                |
| 1.5                      | 400                        | 6.1                     | 7.7                |
| 2                        | 400                        | 7.7                     | 7.5                |
| 2.5                      | 400                        | 8.5                     | 7.1                |

4. Conclusion

The activated carbon was prepared from Mangrove (Rhizophora mucronata) fruit waste that was generated from water-based extraction of natural dyes from this fruit by KOH activation. The effects of KOH concentration were investigated in order to evaluate the physical characteristic of produced activated carbon. The specific energy consumption of carbonization process were obtained from 5.99×10⁻⁵ to 14.27×10⁻⁵ MJ/kg with the yield of char from 30%.wt to 45%.wt. Increasing the KOH concentration in activation process improved the specific surface area, pore diameter and iodine adsorption capacity of produced activated carbon. The highest specific surface area and pore diameter were obtained at KOH concentration of 2.5 M, which are 1,920.6 m²/g and 5.52 µm, respectively, and the adsorption capacity was obtained at 1,540.13 mg/g of iodine number.

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References

[1] Shafieeyan M S, Daud W M W A, Houshmand A and Shamiri A 2010 J. Anal. Appl. Pyrolysis 89 (2) 143-151.
[2] Budi E, Umiatin, Nasbey H, Bintoro R A, Wulandari F and Erlina 2016 AIP Conference Proceedings 1712 (American Institute of Physics, Melville, NY) p 1-6.
[3] Herawan S G, Hadi M S, Ayob M R and Putra A 2013 Sci. World J. 6
[4] Ahmed I, Jangswang W and Gupta A K 2012 Appl. Energy 91 (1) 173-179.
[5] Nguyen T P, Luom T T and Parnell K E 2017 Ocean. Coast. Manage. 149(Supplement C) 12-21.
[6] Punrattanasin N, Nakpathom M, Somboon B, Narumol N, Rungruangkitkrai N and Mongkholrattanasit R 2013 Ind. Crop. Prod. 49 (Supplement C) 122-129.
[7] Hoseinzadeh Hasas R, Arami-Niya A, Daud W M A W and Sahu J N 2013 Chem. Eng. Res. Des. J. 91 (12) 2447-2456.
[8] Tan I A W, Ahmad A L and Hameed B H 2008 Chem. Eng. J. 137 (3) 462-470.
[9] Yang K, Peng J, Srinivasakannan C, Zhang L, Xia H and Duan X 2010 Bioresour. Technol. 101 (15) 6163-6169.
[10] Wang J and Kaskel S 2012 J. Mater. Chem. 22 (45) 23710-23725.
[11] Ma Y 2017 Waste Biomass Valori. 8 (3) 549-559.
[12] Srinivasakannan C and Abu Bakar M Z 2004 Biomass Bioenerg 27 (1) 89-96.
[13] Ahmadpour A and Do D D 1996 Carbon 34 (4) 471-479.
[14] Kawano T, Kubota M, Onyango M S, Watanabe F and Matsuda H 2008 Appl. Therm. Eng. 28 (8) 865-871.
[15] Chun Y N, Ji D W and Yoshikawa K 2013 J. Mec. Sci. Technol. 27 (1) 263-272.
[16] Yang H, Yan R, Chen H, Lee D H and Zheng C 2007 Fuel 86 (12–13) 1781-1788.
[17] Alam M Z, Muyibi S A, Mansor M F and Wahid R 2007 J. Environ. Sci. 19 (1) 103-108.
[18] Budi E, Nasbey H, Yuniarti B D P, Nurmayatri Y, Fahdiana J and Budi A S 2014 AIP Conference Proceedings 1617 (American Institute of Physics, Melville, NY) p 130-133.
[19] Werther J, Saenger M, Hartge E U, Ogada T and Siagi Z 2000 Prog. Energ. Combust. Sci. 26 (1) 1-27.