Adsorptive removal of methylene blue from aqueous solution onto koh-activated carbons derived from saba banana (m. Acuminata balbisiana) peel

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Abstract. Organic pollutants in water are an increasingly prominent problem. Given this challenge, this study reported the high adoptive removal of methylene blue (MB) onto potassium hydroxide (KOH)-activated carbon. To prepare activated carbon, saba banana peel that are local organic waste were carbonized at 400 °C and activated using various KOH concentrations, e.g.(0.5, 1 and 1.5 M). Physical and microstructural properties of activated carbon were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), and Fourier Transform Infrared (FTIR). The effect of KOH concentrations on the adsorption performance of MB on KOH-activated carbon were further investigated. The adsorption process occurred more easily after KOH (1.5 M) of concentration and the adsorption capacity of activated carbon improved by more than 23 %. These results indicate that preparing Banana fruit peels-derived activated carbon using KOH activation is an effective way to reduce pollution and utilize a waste resource.

1. Introduction

Water is a basic requirement for human survival. There are problems that often found in water resources at this time, namely the quality of water that does not meet the quality standards of clean water. Some of the causes for the decreased in water quality are caused by industrial, domestic, and other activities that have a negative impact on the quality of water resources [1].

One of the industrial activities that has an impact on water quality is the textile industry. According to the Ministry of Industry of the Republic of Indonesia, in the first quarter of 2019 the textile industry in Indonesia experienced an significant increase of 18.98% in production compared to the first quarter of 2018 of 8.73%. However, the increasing number of textile industries in Indonesia is not balanced with proper processing of liquid waste generated during the production activities. One of the important components in the textile industry is dyes. Dyes used in the textile industry have a negative impact on environmental sustainability, where dye waste is an organic compound that is difficult to decompose,
and poisonous [2]. One of the most common dyes found in textile industry waste is methyl blue. Methyl blue (MB) is a very important basic dye and is relatively cheap compared to other dyes. Methyl blue can cause irritation to the digestive organs if consumed, cause cyanosis if inhaled, and skin irritation if touched by skin [3]. Based on the potential hazardous, the methyl blue that allowed in the environment is relatively low. According to the Ministry of Environment, in 1995 regarding the quality standard of liquid waste, the maximum permissible concentration of methylene blue is 5-10 mg/L. Therefore, a method is needed to overcome the water contamination caused by textile industry waste such as methyl blue, by using the wastewater treatment method, one of which is by using activated carbon.

Activated carbon can adsorb certain gases and chemical compounds, depending on the size or volume of pores or porosity and surface area of the activated carbon. The absorption in the gas phase is influenced by the micropore structure (<20 Åo) while the liquid phase by the mesoporous structure (20-500 Åo). The size of this macropore is what used to purify drinking water, treatment of liquid waste, decolorizing food and chemicals. The use of activated carbon as an absorber is influenced by the surface area, pore distribution and surface chemical properties of activated carbon [4]. Activated carbon is an amorphous compound consisting of flat plates of carbon atoms arranged and bonded covalently in a hexagonal lattice. However, based on observations with X-ray diffraction, it shows that there is a very small crystalline form with a graphite structure on activated carbon as shown in Figure 1.

![Figure 1](image_url) The physical structure of activated carbon [4].

Activated carbon is produced from materials that contain carbon (or charcoal), for example, organic materials such as plants. This is because plants contain “lignocellulose”, where lignocellulose itself is divided into three components, namely cellulose, hemicellulose, and lignin which have high carbon content, so that lignocellulose is a good material to produce charcoal [5].

To produce charcoal, an organic material will go through a thermal treatment called "carbonization" [6]. During the carbonsization process, organic materials will be heated at a temperature between 400°C - 600°C in conditions or an atmosphere without oxygen [7]. During this heating, water desorption occurs from the organic material, depolymerization of cellulose, hemicellulose, and lignin and leaving a black solid material which is an element that does not come out or is released from organic material during the heating process called "fixed carbon" [8].

One source of charcoal is saba banana peels. According to Suhartini's, 2013 research has proven that banana peels can be used as adsorbents and in a study conducted, banana peels consist of a number of components including cellulose and lignin (table 1) [9]. With the presence of cellulose and lignin, banana peels can potentially act as carbon source, through the carbonization process.

| Element          | Composition (%) |
|------------------|-----------------|
| Water content    | 11,09           |
| Ash content      | 4,82            |
| Component                  | Value  |
|----------------------------|--------|
| Fat Content                | 16.47  |
| Protein Content            | 5.99   |
| Crude fiber content        | 20.96  |
| Carbohydrate levels        | 40.74  |
| Cellulose content          | 17.04  |
| Lignin levels              | 15.36  |

However, Saba banana peel charcoal is only carbon and not activated carbon with high porosity, so it cannot be applied as an adsorbent (because the poros structure does not develop) without additional activation.

Activation is a treatment of charcoal which aims to enlarge the pore and its surface area to increase its adsorption properties, by breaking hydrocarbon bonds or oxidizing surface molecules, so that the charcoal becomes activated carbon due to increased adsorption properties [10].

In the research conducted by Teng, the activation process using an activation solution of Potassium Hydroxide (KOH) produces activated carbon with a surface area of 3000 m$^2$ / g and the results also show that the porous structure formed from KOH activation is more thermally stable compared to activation with H$_3$PO$_4$ or ZnCl$_2$ [11]. And according to Wang, chemical activation using KOH is very promising because only requiring a low activation temperature will get high results, and the micropore size will be well distributed and the specific surface area is very high up to 3000 m$^2$ / g. From these results, KOH is a good activator solution for use in making activated carbon. The chemical reactions that occur upon activation using the KOH solution are as follows;

$$4\ KOH + C \rightleftharpoons 4\ K + CO_2 + 2\ H_2O$$
$$6\ KOH + 2C \rightleftharpoons 2\ K + 3\ H_2 + 2\ K_2CO_3$$
$$4\ KOH + 2\ CO_2 \rightleftharpoons 2K_2CO_3 + 2\ H_2O$$

The potassium carbonate compound (K$_2$CO$_3$) is formed from a chemical reaction between the activator and the carbon sample, but it is also caused by the reaction between the activator and the CO$_2$ gas obtained during chemical activation. Potassium carbonate or K$_2$CO$_3$ compounds is not expected to be present or formed on activated carbon and this compound should be lost when washing is done when the chemical activation process is complete. Figure 2 is an illustration of the pore formation on activated carbon through KOH activation.

![Figure 2 Illustration of pore formation of activated carbon through KOH activation](image)

2. Research Methodology

2.1. Equipments and Materials
The equipment used in the manufacture of banana peel activated carbon waste samples consists of: oven, propane furnace, hot plate stirrer, analytical balance, whatman filter paper, thermometer, thermocouple, crucible, beaker glass, glass spatula, iron spatula, litmus paper, 100 mesh sieve, measuring cup, dropper pipette, measuring pipette, cuvette, breast milk bottle, glass funnel, aluminum foil, mortar and pestle, petri dish, watch glass, and a ruler. The sample testing equipment consists of three tests, namely FTIR (Fourier Transform Infrared), XRD (X-Ray Diffraction), and SEM (Scanning Electron Microscopy). And the materials used in this research include: saba banana peels, methylene blue, filter paper, KOH (Potassium Hydroxide), aluminum foil, and distilled water.

2.2 Fabrication of activated carbon

The first stage before the carbonization process of saba banana peel waste is washed to remove impurities that stick to the banana peel waste. Clean banana peel waste is cut to a size of 2 cm x 4 cm, then dried using an electric oven. Furthermore, the carbonization process using a propane furnace, which is carried out for 30 minutes with a temperature of approximately 400°C. Banana peel waste that has become activated carbon. Then mashed using a pestle and mortar, then sieved the banana skin carbon using a 100 mesh sieve. The banana peel carbon that has been sieved is in the form of powder, then activated. The activation process carried out in the form of chemical activation with KOH using a hot plate stirrer, for 2 hours with a temperature of 80°C and a speed of 200 rpm, the variables in this study were the KOH activator concentration as follows: banana peel carbon without the activation process hereinafter abbreviated as "C", banana peel carbon activated with KOH 0.5 M hereinafter abbreviated as "CA0,5", banana peel carbon activated with KOH 1 M hereinafter abbreviated as "CA1". And the banana peel carbon activated with KOH 1.5 M, hereinafter abbreviated as "CA1,5" (Table 2). After the activation process, the filtering process is carried out using Whatman filter paper, then rinsed using distilled water until it reaches normal pH. And the last step is drying the activated carbon that has been activated using an electric oven for 12 hours with temperature of 120°C. The activated carbon that has been made is then analyzed by FTIR, XRD, SEM and UV-Vis to determine the differences in the characteristics of activated carbon before and after activation.

| Sample name | Explanation                      |
|-------------|----------------------------------|
| C           | Carbon non-activation            |
| CA0,5       | Carbon -Activation KOH 0.5 M     |
| CA1         | Carbon -Activation KOH 1 M       |
| CA1,5       | Carbon -Activation KOH 1,5 M     |

2.3. Characterization

In this study the morphology of activated carbon samples was analyzed by scanning electron microscopy (Scanning Electron Microscopy) with various magnifications, functional group analysis by using FTIR (Fourier Transform Infrared Spectroscopy), and crystal structure analysis by using XRD (X-Ray Diffraction).
3. Result and Discussion

3.1. FTIR analysis

The FTIR results in Figure 3 and Table 3 indicate the presence of C-O, C = O, C-H, and O-H bonds, indicating that these bonds are derived from cellulose, hemicellulose, and lignin [12]. In addition, there are aromatic bonds which indicate the possibility of graphite being formed [13]. Based on the results of the FTIR spectrum pattern on the banana peel activated carbon sample, it appears that the KOH activation process affects the absorption intensity in the wavelength region and results in changes to the functional group structure. This shows that the surface structure of activated charcoal still contains bonds in the form of C-O and C-H and the formation of aromatic C = C. The aromatic functional groups are the main functional groups that make up the graphite structure on carbon. In wastewater treatment, carbon has a function to increase or accelerate the surface adsorption ability of activated carbon so that carbon acts as a catalyst [14]. Based on this, the alcohol, carbonyl, and aromatic functional groups are important functional groups in wastewater treatment applications.

FTIR testing is not sufficient to prove the existence of graphite, because FTIR testing only knows the functional groups that make up the graphite structure on carbon. In wastewater treatment, carbon has a function to increase or accelerate the surface adsorption ability of activated carbon so that carbon acts as a catalyst [14]. Based on this, the alcohol, carbonyl, and aromatic functional groups are important functional groups in wastewater treatment applications. However, FTIR testing is not sufficient to prove the existence of graphite, because FTIR testing only knows the functional groups that make up graphite in the form of aromatics. Meanwhile, the graphite structure cannot be detected by FTIR testing. Therefore, XRD testing is to determine the formation of graphite in the sample.

![Figure 3 FTIR testing results](image)

**Table 3 FTIR functional group**

| No | C (cm\(^{-1}\)) | CA0.5 (cm\(^{-1}\)) | CA1 (cm\(^{-1}\)) | CA1.5 (cm\(^{-1}\)) | Functional Group          |
|----|----------------|----------------------|------------------|---------------------|--------------------------|
| 1  | 3366           | 3366                 | *                | *                   | Stretching O-H            |
|    |                |                      |                  |                     | Hydroxyl                 |
| 2  | *              | *                    | 1054             | 1054                | Stretching C-O            |
|    |                |                      |                  |                     | Hydroxyl                 |
3.2. XRD analysis

The saba banana peels charcoal without activation showed the formation of the formed phase according to the journal [15]. In Figure 4, banana peels charcoal without activation shows that the peak of 2θ = 26 °, 28.4 °, and 34.2 ° is a structure of K$_2$CO$_3$ and K$_2$O with a field value of 2θ, namely 112, and 111, while peak 45.3 ° is graphite with a field value of 2θ, which is 100. Banana peels charcoal before activation, banana peels show that there are impurity elements that cover the pores of the activated carbon of banana peel waste, such as SiO$_2$, K$_2$O, and K$_2$CO$_3$. However, after activation with KOH, the impurity elements such as K$_2$O and SiO$_2$ were lost, as evidenced by the XRD results in Figure 4, but at the activation of 0.5 M and 1 M, there were still impurities in the form of K$_2$CO$_3$. This is due to the washing process of the activated carbon is not truly clean the impurities from the activated carbon [16] The XRD pattern of the all activated carbon sample shows the same XRD

|   |   |   |   |   |
|---|---|---|---|---|
| 3 | * | * | 1222 | 1222 |
| 4 | * | * | 2920 | 2920 |
| 5 | * | * | 1739 | 1739 |
| 6 | 1620 | 1620 | 1442 | 1442 |
| 7 | 1397 | 1397 | 1364 | 1364 |
| 8 | 825, 780 | 780 | * | * |

* Not detected

Figure 4 The diffraction pattern of banana peel activated carbon
pattern, where there are two main peaks in the XRD analysis results, namely located at peak $2\theta = 26^\circ$ and $44^\circ$, as for both peaks correspond to graphite [17]. FTIR test proves, where the aromatic functional group shows the possibility of graphite formation, and in the results of the XRD pattern on variables without activation and activation there are graphite and amorphous graphite. When organic material undergoes carbonization and activation, amorphous graphite begins to form, which initially only graphite. Combustion (carbonization) and activation processes can remove impurities from activated carbon by evaporating oxygen, hydrogen, nitrogen, and so on.

3.3. SEM Analysis

![Figure 5 Morphological structure](image)

In the Figure 5, the surface morphology of the saba banana peels charcoal that is not activated and activated has a difference, where the banana peels charcoal without activation is known to have pores and there are still impurities on the surface. On banana peels charcoal activated by KOH the pores look cleaner. It can be seen that there is an effect of giving KOH activation on the banana peels charcoal, where the addition of KOH activation can remove the impurities that are formed and this is also supported by XRD results which show the loss of impurities when the banana peels charcoal is given KOH activation [18]. Table 4 shows the average pore size of banana peel activated carbon, and it can be seen that there is an increase in pore size. The larger the pores of activated carbon, also increases the surface area of the activated carbon. This increase in surface area can result in an increased adsorption ability of activated carbon [19].

| No | Sample | Average Porosity Size (μm) |
|----|--------|---------------------------|
| 1  | C      | $0.193 \pm 0.11\mu m$    |
| 2  | CA0.5  | $0.31 \pm 0.19\mu m$     |
| 3  | CA1    | $0.709 \pm 0.27 \mu m$   |
| 4  | CA1.5  | $0.79 \pm 0.32 \mu m$    |
3.4. Methylene blue degradation analysis

![Image of Methylene blue degradation analysis](image)

**Figure 6** The results of visual removal of Methylene blue (a) 0 hours (b) 2 hours (c) 5 hours and (d) 24 hours

As for the visual testing of the removal of Methylene blue (figure 6), it can be concluded that the activated carbon of banana peel waste can adsorb Methylene blue and the KOH 1.5 M variable is the variable that degrades Methylene blue the fastest, followed by KOH 1 M, then 0.5 M and last or the longest to degrade Methylene blue, is the banana peels charcoal without activation. The visual results can be supported by the results of the methyle blue degradation test using a UV-Vis spectrophotometer, while the percentage of degradation can be seen in table 5 and figure 7.
The higher the KOH concentration given to charcoal activation, increasing the adsorption ability of methylene blue, this statement is in accordance with the results obtained using the UV-Vis spectrophotometer in Table 5. In addition, the above statement proves the average surface area of activated carbon 1,5 M higher than the other samples in the SEM test, it can be concluded that the higher the KOH concentration on carbon activation, increase the surface area of the activated carbon thereby increasing the adsorption ability of Methylene blue [20]. The adsorption ability of activated carbon was due to the presence of oxygen-surface group on the surface of activated carbon by KOH which was proven in FTIR testing, where the functions of oxygen-surface group is to adsorb adsorbate. In addition, the presence of carbon in the form of graphite which is proven by XRD testing functions to accelerate the adsorption process on the surface of activated KOH charcoal. Therefore, the role of carbon in wastewater treatment is referred to as a catalyst [11]. The results of this test prove that the activated carbon of banana peel waste can degrade Methylene blue, and it is known that the variable with KOH activation of 1,5 M degrades faster than the other variables.

4. Conclusion
The optimum KOH activator concentration for activated carbon from saba banana peels against the removal of Methylene blue, is shown by sample CA1,5 which had been activated with 1,5 M KOH.
Where based on observations with a UV-VIS spectrometer sample CA1.5 can degrade methyl blue up to 66.47% and 80.87% within 30 minutes and 120 minutes.

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