Preparation and Characterization of Activated Carbon from Palm Kernel Shell at Low Temperature as an Adsorbent for Methylene Blue

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Abstract. The preparation of activated carbon as an adsorbent from biomass waste was usually conducted at high temperatures. In this research, activated carbon was prepared from palm kernel shell by the pyrolysis process at temperature under 400 °C to reduce excessive energy consumption. This study aims to identify the surface character of the formed activated carbon as an adsorbent for methylene blue. The pyrolysis process produced activated carbon which has a hydroxyl (3102–3423 cm⁻¹) and carboxyl (1650 cm⁻¹) functional groups, resulting in ionic interactions between activated carbon and methylene blue. The equilibrium data fit the Langmuir isotherm model with correlation efficient higher than 0.99. The highest adsorption capacity is 0.28 mmol/g adsorbent for activated carbon which is hydrolyzed at 350 °C with a surface area of 523 m²/g adsorbents.

Keywords: pyrolysis, Langmuir isotherm, palm kernel shell.

1. Introduction

Synthetic dyes are one of the organic pollutants in waters. This waste usually produced from the textile industry, such as methylene blue (MB). Methylene blue is positively charged (cationic) and is commonly used to dye cotton, wool, and silk [1]. It has effects of eye-burning in humans and animals, methemoglobinemia, cyanosis, seizures, tachycardia, dyspnea, skin irritation, and if swallowed, it causes digestive tract, nausea, vomiting, and diarrhea [2]. Methylene blue can be removed from the environment through the adsorption process. This method is still used in dealing with pollutants in water because it is more profitable, inexpensive and easy to apply [3]. The adsorbent that can be used is activated carbon.

Activated carbon is a porous material that can be used as an absorbent of various pollutants in the environment [4]. Activated carbon has a surface area of about 500-2000 m²/g, high adsorption capacity, and can adsorb various kinds of waste. High molecular weight compounds are usually adsorbed in the mesoporous whereas compounds with low molecular weight can be adsorbed up to the micropore[5]. The surface area, pore size, and functional groups on the surface of activated carbon determine the adsorption
characteristics that occur. The raw material and the activation process are the most decisive stages to obtain good activated carbon [6]. Activated carbon can be prepared from biomass by physical or chemical treatment or both [4,7].

As the largest palm oil producer in the world, Indonesia has a lot of biomass waste that has not been utilized, one of which is palm kernel shell waste. According to Devendra [8], palm kernel shells were produced about 2.5% of fresh fruit bunches (FFB). Over the past ten years, Indonesia's palm oil production has tripled [9]. The development of the palm oil industry will have an impact on increasing the waste generated from the production process [10]. So, this is a potential as a material source for activated carbon.

Activated carbon is produced by burning biomass at high temperatures in inert gas conditions such as Nitrogen [11] and water vapor [12,13] or without oxygen (pyrolysis). The process is carried out in a particular reactor furnace, making it difficult to apply. Therefore, a simple applicative method is needed and can be applied at a community scale. This study aims to identify and estimate the minimum temperature that can be used in synthesizing activated carbon as an adsorbent for dye waste with methylene blue as a model.

2. Method

2.1. Preparation of Activated Carbon

Palm kernel shell waste was obtained from Cikasungka, Bogor. The sample was dried in direct sunlight for approximately 3 days. The dried sample (moisture content <10%) was ground in Wiley mill (5000-6000 rpm) to get 100 mesh of size. 5 grams of sample was dried at low temperature (150, 250 and 350 °C) using 47,900 Thermocline furnace for 3 hours. The obtained carbon was calculated its yield and characterized by using Perkin-Elmer Spectrum One FTIR (Fourier Transform Infrared) to identify the functional groups.

2.2. Analysis of Adsorption Capacity

5 ml of methylene blue (100, 250, 500, 750, and 1000 ppm) were added to 50 mg activated carbon in vial respectively. The samples were shaken using Shaker batch at neutral pH for 24 hours at room temperature. The supernatant was separated by using a centrifuge and then its concentration was measured using spectrophotometer 20D+ at maximum wavelength of 254 nm. The adsorption isotherm was calculated by following equation:

Freundlich isotherm: \[ \log y = a \log x + b \] (1)

Langmuir isotherm: \[ y = ax + b \] (2)

where y is equilibrium concentration per adsorption capacity (g/L), x is equilibrium concentration (mg/L), a is curve slope and b is intercept.

The amount of adsorbed methylene blue at equilibrium, \( Q \) (mg/g) was calculated by

\[ Q = \frac{V(C_0 - C)}{m} \] (3)

Where \( Q \) is adsorption capacity (mg/g), \( V \) is the volume of solution (ml), \( C_0 \) is the initial of methylene blue concentration (mg/L), \( C \) is the equilibrium of methylene blue concentration (mg/L), and \( m \) is the weight of activated carbon (g).

2.3. The Measurement of Specific Surface Area

Semi-quantitative measurement was used to calculate the specific surface area of adsorbent which fits the Langmuir isotherm model. The equation can be written as:

\[ S = \frac{s_m \times A_m \times N_A}{MW} \] (4)
Where $x_m$ is the amount of solute adsorbed on the monolayer (mol/g), $A_m$ is the surface area occupied by the adsorbent in the form of molecules or aggregates (m$^2$) and $N_A$ is the Avogadro number (mol/g). $MW$ is the adsorbate molecular weight [14,15,16].

3. Results and Discussion

3.1. Activated Carbon

Activated carbon is produced in high thermal conditions to increase the surface area but loss of functional groups. These functional groups are commonly utilized for adsorbing and catalyzing in many chemical reactions. Generally, activated carbon can be prepared by using physical or chemical methods[17]. The previous research by Xiao et al.[7] has used the pyrolysis method to make the activated carbon property better by increasing the surface area, porosity, and absorptivity at a temperature of 300-700 ℃. In this work, we only focussed on the physical method to produce activated carbon from palm kernel shells. The carbonization process at low temperatures (below 400 ℃) has been successfully carried out to obtain activated carbon that has slightly hydrophobic characteristics (figure 1) as much as 61 ± 5%. The increasing carbonization temperature from 150 ℃ to 350 ℃ could reduce the amount of activated carbon produced. However, this condition can be anticipated by the pyrolysis method without the presence of oxygens.

Figure 1. The carbonization of palm kernel shells at low temperature (< 400 ℃).

Figure 2. The spectra of palm kernel shells waste (a), activated carbon at 150 ℃ (b), 250 ℃ (c) and 350 ℃ (d).

The functional groups in each sample which successfully identified could be seen in figure 2. All of the samples have hydroxyl groups (O–H) at 3102-3423 cm$^{-1}$ and carboxyl groups (C=O) at 1650 cm$^{-1}$. The FTIR spectra obtained is similar to the previous report [18]. Increasing the carbonization temperature reduced the absorbance of functional groups on their structure. The carbonization process
at 150 °C produces activated carbon with a physical form similar to the biomass (granule). Meanwhile, the carbonization process at 350 °C produced carbon with smooth shapes. Although all of the spectra (activated carbon and raw material) are significantly similar, we investigated the differences by looking at their adsorption ability. We assumed that the presence of hydroxyl and carboxyl functional groups in the raw sample did not function as sorbents (inactive).

3.2. Adsorption Capacity of Methylene Blue

The adsorption ability of each sample was tested to adsorb methylene blue dye in solution. Methylene blue was chosen as a model of dye in this work due to its specific color and easy to know the differences between before and after the adsorption process. The maximum wavelength (λ\text{max}) of methylene blue was found at 664 nm. The adsorption test was carried out by using different concentrations of methylene blue dyes (100, 250, 500, 750 and 1000 ppm). For the first step, the adsorption capacity of each sample was tested in a methylene blue solution of 100 ppm to identify the adsorption kinetic process. During the adsorption process, there were significant changes that occur between the beginning and after one-day treatment if we compare it from the intense color of solutions (figure 3). After a one-week adsorption process, methylene blue molecules were perfectly adsorbed by activated carbon from palm kernel shells. This condition also showed that the adsorption process by using raw materials was much longer than activated carbons generated from different thermal conditions.

![Figure 3](image-url)

**Figure 3.** The methylene blue adsorption process (100 ppm) by each sample

Many factors influence the adsorption capacity of activated carbons, such as the characteristics of the components absorbed, the nature of the solution and the contact system. According to the previous report, the ability of activated carbon as sorbents in aqueous or gas phases is affected by surface conditions and pore structure\cite{19}. The adsorption ability of activated carbon at 350 °C was higher than all activated carbon produced, but it was lower compared to commercial carbon. The methylene blue adsorbed by activated carbon at 350 °C and commercial carbon was 0.28 mmol/g and 0.43 mmol/g, respectively, for 24 hours (figure 4). On the other hand, the carbonization results at 150 and 250 °C still have a typical resemblance to the adsorption capacity for 24 hours because these temperatures were poorly activated the functional groups.
There are two isotherm models commonly used to investigate the adsorption characteristic of adsorbent materials, namely Langmuir and Freundlich models. Freundlich isotherm model indicates non-interacting sites with heterogenic surface and exponential adsorption \(^{20}\), while the Langmuir model is the opposite. Based on the results, the activated carbon and biomass followed the Langmuir isotherm model. However, the commercial activated carbon was more suitable for the Freundlich isotherm model (table 1) which indicates the presence of ionic bond between hydroxyl or carboxyl groups (negative charge) and methylene blue (positive charge) on the commercial activated carbon surface (figure 5).

![Figure 4](image)

**Figure 4.** Adsorption capacity of raw material (---), commercial activated carbon (--), activated carbon at 150 °C (---), 250 °C (---), and 350 °C (---).

| Adsorbents                  | \( R^2 \) Freundlich | \( R^2 \) Langmuir |
|-----------------------------|-----------------------|---------------------|
| Biomass                     | 0.9956                | 0.9979              |
| Commercial activated carbon | 0.9990                | 0.9960              |
| Activated carbon at 150 °C  | 0.9859                | 0.9970              |
| Activated carbon at 250 °C  | 0.9488                | 0.9980              |
| Activated carbon at 350 °C  | 0.9939                | 0.9989              |

3.3. Specific Surface Area

The specific surface area plays an important role in determining the physical and chemical properties of activated carbon. The standard method for determining the surface area is the Brunauer-Emmett-Teller (BET) method, which is to determine the surface area based on the amount of gas absorbed. Although the BET method is widely used in determining surface area, there are also other surface area measurement methods that have been reported using ethylene glycol monoethyl ether (EGME) material. Based on the results, the surface area of synthetic activated carbon was 100-500 m\(^2\)/g (table 2). The specific surface areas of activated carbon at carbonization temperatures of 150, 250, and 350 °C were 147, 325, and 523 m\(^2\)/g, respectively. The more increase carbonization temperature, the higher of surface area value.
Table 2. The surface area value of activated carbon based on the Langmuir isotherm model

| Adsorbents          | Langmuir constant | Estimation of surface area (m²/g) |
|---------------------|-------------------|----------------------------------|
| Biomass             | 0.063             | 236                              |
| Commercial activated carbon | 0.171             | 636                              |
| Activated carbon at 150 °C | 0.039             | 147                              |
| Activated carbon at 250 °C | 0.087             | 325                              |
| Activated carbon at 350 °C | 0.141             | 523                              |

Figure 5. Illustration of the mechanism of absorption of methylene blue against activated carbon.

4. Conclusions
Activated carbon from palm kernel shells was successfully synthesized by the pyrolysis method under minimum thermal conditions at 350 °C. The adsorption capacity of this activated carbon for adsorbing methylene blue dye was 0.28 mmol/g with the specific surface area as much as 523 m²/g. The appropriate adsorption isotherm model for the synthetic activated carbon was the Langmuir model which indicated there was an interaction on the surface of the activated carbon.

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