Effect of Phosphate species on biomass carbonization

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Abstract. Dye waste produced from industry causes environmental damage and harmful to living organism, so it is necessary to find a solution to reduce this problem. The dyes that are often used in industry are methylene blue and methyl orange. Methylene blue and methyl orange can be removed from the environment through the adsorption process. Adsorption process using activated carbon is an easy, effective, and efficient way to treat dye waste. Palm kernel shell as agricultural waste can be used as a raw material in preparing an activated carbon. This method used chemical activation to produce activated carbon. Some sample of palm kernel shell was mixed with different phosphate species, such as (NH₄)H₂PO₄, (NH₄)₂HPO₄, and H₃PO₄ with various concentration (1%, 5%, 10%, and 15%). The different phosphate species producing different yields because it has different roles in the carbonization process. Palm kernel shell is added with activating agent with a ratio 1:1 (w/v). Sample was put in a furnace at 600 °C for 1 hour. The sample was washed with distilled water until neutral pH, then dried in an oven at 105 °C for 1 hour. The phosphate acid is able to inhibit the combustion process and increase the yield. The highest yield was produced by the addition of H₃PO₄. The adsorption isotherm of the activated carbon follows the Langmuir isotherm.

1. Introduction

Dye waste produced from industry causes environmental damage and harmful to living organism, so it is necessary to find a solution to reduce this problem. The dyes are often used in industry are methylene blue and methyl orange. Methylene blue is a cationic dye commonly used as textile dye [1]. Methyl orange is an anion dye used in the textile, paper and printing industries [2]. These dyes can cause eyes, skin, and digestive tract irritation [3]. Methylene blue and methyl orange can be removed from the environment through the adsorption process. The adsorption process using activated carbon is an easy, effective and efficient way, making it suitable for use in waste treatment. Activated carbon has a high surface area and high adsorption power.

Activated carbon can be produced from raw materials that contain carbon. Agricultural waste is very important raw material because it is cheap, renewable, available in large quantities, easy to obtain, and has a high carbon content [4]. The conversion of agricultural waste to activated carbon can reduce waste disposal costs. Palm kernel shell is one of agricultural waste that can be used as a raw material for activated carbon [5]. In Indonesia palm kernel shell (Elaeis guineensis) is an abundant plantation crop. Palm kernel shell contains many carbon atoms making it suitable for activated carbon.

The methods for preparing activated carbon can be divided into two categories, physical activation and chemical activation. The chemical activation process requires a lower heating temperature, resulting in a higher yield and surface area. However, chemical activation needs for washing to remove impurities carried from the activating agent [6]. An example of an activating agent is H₃PO₄, which can oxidize carbon and wreck the carbon surface so that the pore diameter will enlarge, forming new pores, and
increasing adsorption power [7]. In addition, (NH₄)H₂PO₄ and (NH₄)₂HPO₄ can also act as activating agents. This study aims to make activated carbon from palm kernel shells with the addition of activating agent with different phosphate species and compare the yield that has never been investigated before, identify its effect on the carbonization process and adsorption capacity.

2. Method

2.1. Preparation of Activated Carbon
Dry palm kernel shell (PKS) is milled, then added with various concentrations of H₃PO₄ solutions, 1%, 5%, 10%, and 15% (w/v). Palm kernel shell is added with H₃PO₄ with a ratio 1:1 (w/v). The same step was repeated with (NH₄)H₂PO₄ and (NH₄)₂HPO₄ solutions. The sample was put in a furnace at 600 °C for 1 hour. The sample was washed with distilled water until neutral pH, then dried in an oven at 105 °C for 1 hour.

2.2. Analysis of Activated Carbon Yield
The weight of each sample of raw material and activated carbon is measured, then the percent yield is calculated by the following equation:

\[
\text{Yield (\%) = } \frac{b}{a} \times 100\% \quad (1)
\]

where a is initial raw material weight (g), b is activated carbon weight (g).

2.3. Analysis of Adsorption Capacity
This analysis begins with the preparation of 1000 ppm methylene blue and methyl orange stock solutions. Methylene blue and methyl orange stock solutions were diluted into five concentrations (100, 250, 500, 750, and 1000 ppm). A total of 20 mg of activated carbon (PKS+H₃PO₄ 5%) was added to 5 mL of a solution of methylene blue and methyl orange of various concentrations in different containers, then shaken every hour for 24 hours. The concentration of the filtrate was determined using a visible light spectrophotometer at maximum \( \lambda \). The adsorption capacity of the adsorption data was calculated and analyzed using the Freundlich and Langmuir equations:

Freundlich isotherm:

\[
\text{Log } y = a \text{Log } x + b \quad (2)
\]

Langmuir isotherm:

\[
y = ax + b \quad (3)
\]

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

Adsorption capacity:

\[
Q = \frac{V(C_0-C)}{m} \quad (4)
\]

where \( Q \) is adsorption capacity (mg/g), \( V \) is the volume of solution (mL), \( C_0 \) is the initial of methylene blue or orange meyhylene concentration (mg/L), \( C \) is the equilibrium of methylene blue or methyl orange concentration (mg/L), and \( m \) is the weigh of activated carbon (g).

3. Results and Discussion

3.1. Activated Carbon
Activated carbon is a flat hexagonal amorphous structure with a C atom at each corner (figure 1). Activated carbon is an adsorbent that is often used in the adsorption process of gases or liquids. Activated carbon contains hydrogen and oxygen which are bound in various functional groups. This
functional group plays a role in the adsorption process. Acid groups such as carboxylic, phenol, and anhydride act as a negative site. Conversely, base groups such as ketones and esters act as a positive site. The activation process removes hydrogen, gases, and water molecules from the carbon surface. The process will also increase the pore size and surface area of activated carbon.

Figure 1. Graphite activated carbon structure [8].

3.2. Yield of Activated Carbon
The yield of palm kernel shell activated carbon is ranged from 3.06–13.83%. The highest yield was obtained in PKS+H₃PO₄ 10%. The yield of the product will increase with increasing activating agent concentration (table 1). The yield in this study was lower than Lim’s research [9] which produced activated carbon from palm kernel shell with phosphoric acid which produced yield 50%. Activated carbon with the addition of H₃PO₄ is the best yield among the three phosphate species used. The addition of different phosphate species will affect the carbonization process, resulting in different yields. The addition of H₃PO₄ will increase the yield of the product because the combustion process is disrupted. Phosphoric acid promotes the depolymerization of hemicellulose and lignin at low temperature during the chemical activation of lignocellulosic materials, as well as promote cyclation and condensation reactions of the polymeric fragments at medium temperatures. This resulted in the release of tars and volatile matters during the carbonization process, thus increasing the yield [10].

The increasing yield also occurred when added (NH₄)H₂PO₄ or (NH₄)₂HPO₄ 5%. The addition (NH₄)H₂PO₄ can reduce the volatile matter, so the yield can increase. However, the addition of (NH₄)₂HPO₄ with a concentration of 1%, 10%, and 15% did not form activated carbon, but became ash. This is because (NH₄)₂HPO₄ can increase the quantity of functional groups containing acidic oxygen, carboxyl groups, and lactone groups as volatile matters in activated carbon [11]. The increasing volatile components caused complete combustion process and produce ash.

Table 1. The yield of palm kernel shell activated carbon.

| Activating Agent | Yield (%) |
|------------------|-----------|
| H₃PO₄ 1%         | 3.61      |
| H₃PO₄ 5%         | 10.66     |
| H₃PO₄ 10%        | 13.83     |
| H₃PO₄ 15%        | 13.45     |
| (NH₄)H₂PO₄ 1%    | 1.88      |
| (NH₄)H₂PO₄ 5%    | 5.26      |
| (NH₄)H₂PO₄ 10%   | 5.29      |
| (NH₄)H₂PO₄ 15%   | 5.69      |
| (NH₄)₂HPO₄ 1%    | ash       |
| (NH₄)₂HPO₄ 5%    | 4.41      |
| (NH₄)₂HPO₄ 10%   | ash       |
| (NH₄)₂HPO₄ 15%   | ash       |
| Without activating agent | 3.06 |
3.3. Adsorption Capacity of Methylene Blue and Methylene Orange

Adsorption consists of the process of absorption (adsorption) and release (desorption). In the initial stage of the reaction, adsorption will dominate desorption over time. The adsorption test aims to determine the optimum adsorption capacity and concentration of methylene blue and methyl orange. The maximum wavelength (λmax) of methylene blue was found at 664 nm and methyl orange 464 nm. The adsorption test was carried out by using different concentrations of methylene blue and orange methyl (100, 250, 500, 750 and 1000 ppm). During the adsorption process, there were significant changes that occur between the blank (Figure 2) and after 24 hours adsorption process (Figure 3) if we compare it from the intense color of solutions. Adsorption of dye solutions using activated carbon occurs due to the surface structure of activated carbon which has many pores. These pores can be entered by small molecules such as methylene blue and methyl orange. The greater porosity of activated carbon will increase the adsorption of the dye solution. Adsorption is also influenced by the electronegative interaction between adsorbent and adsorbate. The positive charge of dye solution will interact with the negative charge on the surface of the activated carbon, and vice versa.

Figure 2. Blank of methylene blue (a) and methyl orange (b) concentration 100, 250, 500, 750, and 1000 ppm.

Figure 3. Adsorption process after 24 hours of methylene blue (a) and methyl orange (b).

Figure 4 shows that the adsorption capacity increases with increasing concentrations of methylene blue and methyl orange and is constant when it reaches equilibrium. Equilibrium occurs when the adsorbent has reached a saturated state. The saturated condition indicates that all the active sites of activated carbon have bind to the adsorbate[12], so that the adsorption and desorption rates are the same. This causes the activated carbon surface to no longer bind to the adsorbate and the adsorption capacity changes constantly.

The adsorption isotherm shows the distribution of molecules between the liquid and solid phases. Solid-liquid phase adsorption generally refers to the Freundlich and Langmuir isotherm type [13]. Freundlich isotherm model indicates non-interacting sites with heterogenic surface and exponential adsorption [14], while the Langmuir model is the opposite. The analysis results show that the activated carbon obtained follows the Langmuir isotherm type. This is indicated by coefficient determination (R²) of the Langmuir isotherm which is higher than the Freundlich isotherm (Table 2). This shows that the adsorbent used in this study has a homogeneous surface [15].
Figure 4. Adsorption capacity curve of methylene blue (a) and methyl orange (b) by commercial activated carbon (■) and PKS+H₃PO₄ 5% (●).

Table 2. Isotherm adsorption model for carbon fitted with Freundlich and Langmuir model.

| Adsorbate       | Adsorbent                  | R²  | R²          |
|-----------------|----------------------------|-----|-------------|
|                 |                            | (Freundlich) | (Langmuir) |
| Methylene blue  | Comercial activated carbon | 0.9716 | 0.9994     |
|                 | PKS+H₃PO₄ 5%               | 0.9703 | 0.9960     |
| Methylene orange| Comercial activated carbon | 0.8796 | 1           |
|                 | PKS+H₃PO₄ 5%               | 0.824  | 0.9999     |

4. Conclusions
Activated carbon can be made from palm kernel shells through chemical activation. The different phosphate species, such as (NH₄)H₂PO₄, (NH₄)₂HPO₄, and H₃PO₄ producing different yields because it has different roles in the carbonization process. Activated carbon with the addition of H₃PO₄ is the best yield among the three phosphate species used. The H₃PO₄ can inhibit the ash formation process and increase the yield of activated carbon. The adsorption of activated carbon with the addition of H₃PO₄ follows the Langmuir isotherm.

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