Utilization of Palm Kernel Meal (PKM) as activated charcoal to remove organic pollutants

A G Fahmi¹, Z Abidin², C Kusmana² and E Noor³

¹ Department of Natural Resources & Environment Management, IPB University, Bogor 16680, Indonesia
² Department of Chemistry, Faculty of Mathematics and Natural Science, IPB University, Bogor 16680, Indonesia
³ Department of Silviculture, Faculty of Forestry and Environment, IPB University, Bogor 16680, Indonesia
⁴ Department of Agro-Industrial Technology, Faculty of Agriculture Technology, IPB University, Bogor 16680, Indonesia

E-mail: abindizael@apps.ipb.ac.id, achmad_gusfahmi@apps.ipb.ac.id

Abstract. Palm kernel meal (PKM) is a waste product from the palm oil industry. The objectives of this study are to synthesize activated charcoal from palm kernel meal and apply its ability to adsorb organic matter in water. Charcoal was prepared and activated by pyrolysis without the flow of the inert gasses method and characterized by Fourier-Transform Infrared (FT-IR), estimation surface area, and their adsorption of organic compounds such as oxalic acid and methylene blue. The product has polar and basal sites with hydroxy and carboxyl groups on the surface. The highest estimation surface area is 523 m²/g with 350 °C temperature pyrolysis. Adsorption data fit the Freundlich isotherm model for oxalic acid and Langmuir isotherm model for methylene blue that indicates interaction of active site on the surface charcoal with adsorbates. The absorption capacities of activated charcoal were 38.03 mmol/g absorbent and 12.49 mmol/g absorbent against methylene blue and oxalic acid, respectively. Therefore, PKM waste can be used to be a potentially viable activated charcoal for removing organic pollutants from aqueous solutions.

Keywords: Methylene blue, oxalic acid, waste.

1. Introduction
In the world, the increasing human population is the reason for freshwater availability. Guppy and Anderson[1] predict, in 2035, about 40% of the world's population will experience a lack of clean water. Everyone needs 150 L of fresh water per day[2]. Some of the Indonesian people, use freshwater from the river, for daily activity. However, the condition of rivers in Indonesia is highly polluted. As much as 21% of pollutants in the river are organic matter such as dyes, organic solvents, domestic liquid waste, and others[3].

Organic contaminants function as ligands that increase the amount of dissolved metals in solution such as oxalic acid which has two carboxylic functional groups as ligands [4]. So, the contaminants will become more complex. In addition, organic contaminants can also be carcinogens for living things such as methylene blue [5]. In the past, organic pollutants have been removed by different adsorbent [6] such as magnetic-biochar [7], clay [8], goethite [9], volcanic ash [10] metal composite [11], and another modified carbon-based adsorbent [12]. Besides, many different adsorbents have been prepared using agricultural waste and applied to absorb organic matter from wastewater [13,
But activated charcoal is still the main choice. Activated charcoal is an adsorbent that is widely used including for organic contaminants [15,16]. Activated charcoal has a high absorption capacity with abundant raw materials. So that activated charcoal is highly recommended for solving this problem [16, 17, 18]. Besides, to produce activated charcoal using the pyrolysis method requires, more than 1000 °C of temperature and uses inert gases [19]. A simple low-temperature method for making activated charcoal has been developed. However, the activated charcoal product has a low surface area, because volatile compounds close the pores [20]. In this study, we used palm kernel meal as a raw material for making activated charcoal to absorb organic contaminants. Palm kernel meal is waste that is used for feed because it still contains high protein, so its use as activated charcoal has not been developed much.

2. Method

2.1. Preparation of Activated Carbon
PKM 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. A total of 5 grams sample was put into the pyrolysis reactor that had been made. The temperatures used are 150, 250, and 350 °C using 47900 Thermocline furnace for 3 hours. The obtained charcoal was calculated its yield and characterized by using Perkin-Elmer Spectrum One FTIR (Fourier Transform Infrared) to identify the functional groups [20].

2.2. Analysis of Adsorption Capacity
Methylene blue and oxalic acid are a model of organic matter. 5 ml of organic contaminant was added to 50 mg activated charcoal 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 Libra S11 at a maximum wavelength of 664 nm for methylene blue and permanganate titration for oxalic acid. 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 an 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 weigh of activated charcoal (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:

\[ S = \frac{x_m \times A_m \times N_A}{MW} \] (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 (m²) and \( N_A \) is the Avogadro number (mol/g⁻¹), \( MW \) is the adsorbate molecular weight [21, 22, 23].
3. Results and Discussion

3.1. Activated Charcoal product and characteristics

Activated charcoal products in this method tend to reduce weight by 21.2% until temperatures reach 350 °C. A significant reduction in weight is influenced by excessive oxidation so that in the pyrolysis process, inert gas is usually added to suppress it. In this method, the use of inert gas is replaced by using a glass wool as in the previous method [20]. According to Masyhur and Setiono [24], pyrolysis at a temperature of 300–400 °C is a slow pyrolysis with a yield of 35% charcoal. The weight loss occurs due to the evaporation of volatile compounds and the oxidation of biomass to carbon dioxide. If the pyrolysis temperature is increased, the weight reduction that occurs is not very significant (ramps). However, if the temperature increased continuously, the charcoal will become ash. Also, we use a coconut shell as a comparison in the carbonization process (Figure 1).

![Figure 1. The pyrolysis process at various temperatures with a percentage yield of activated charcoal from PKM (blue line) to scan the yield stability comparison with coconut shell sample (orange line).](image)

Observations during the pyrolysis process can be stated that the process of releasing colorless gases occurs at 170–220 °C. All the smoke comes out at 220–330 °C, physical activation at 330–350 °C, and after 350 °C the activated charcoal is formed. These results are in line with Lewis's statement [25]. So, we used the optimum temperature of the pyrolysis process is 350 °C with the yield percentage is 10–20 %. This is the temperature that we use to synthesize activated charcoal.

![Figure 2. The FTIR spectrum of the wavenumber of 400–4000 cm⁻¹ with resolution 4 cm⁻¹. (a) PKM biomass (b) PKM activated charcoal at temperature of pyrolysis are 150 °C (b) 250 °C (c) and 350 °C (d).](image)
Characterization using FTIR can detect functional groups on the surface of activated charcoal. All activated charcoal has a hydroxyl group (O-H) at 2900–3200 cm\(^{-1}\) with broad shape and carboxyl group (C=O) at 1350 cm\(^{-1}\) with sharp shape (Figure 2). It shows that the pyrolysis method used can maintain the loss of active functional groups on the surface of activated charcoal. In addition, it can be seen that activated charcoal products have a spectrum similar to biomass raw materials (PKM waste). Although there are similarities, there are still differences in other characters such as adsorption capacity and specific surface area that indicate a structural change in the activated charcoal product obtained.

![Figure 3. Estimation of activated charcoal surface area with calculations based on the Langmuir adsorption isotherm model.](image)

The specific surface area plays an important role in the adsorption ability of activated charcoal. According to Suhas et al.,[26] Activated charcoal has a surface area of about 500–2000 m\(^2\)/g, a high adsorption capacity, and can absorb various types of waste. The irregularity of the pore shape and the high surface area make activated charcoal low in adsorbate selectivity. In addition, the raw material and pyrolysis method are the most decisive steps to produce activated charcoal with a large surface area.[18, 27]

The standard method for determining surface area is the Brunauer-Emmett-Teller (BET) method, which determines the surface area based on the amount of gas absorbed. However, most of the activated charcoal applications are used to absorb contaminants in water, especially in this study. So we use a specific approximate surface area calculation. This method estimates the surface area by utilizing the size of the adsorbate molecule, so this calculation can only be used for adsorbents that follow the Langmuir adsorption isotherm model.[19, 20]. Although this method has a high bias, it can provide an overview of the specific surface area of activated charcoal. Based on the research results, the surface area of synthetic activated charcoal is 100–500 m\(^2\)/g (figure 3). The specific surface area of activated charcoal at carbonization temperatures of 150, 250, and 350 were 147, 325, and 523 m\(^2\)/g, respectively. The higher the pyrolysis temperature, the higher the surface area.

3.2 Adsorption Capacity of Organic Contaminants
In this study, we use methylene blue (as a model of organic contaminants with a positive charge) and oxalic acid (as a model of organic contaminants with a negative charge). The adsorption capacity of oxalic acid is 12.49 mmol/g adsorbent. This value is smaller than the adsorption capacity of methylene blue which is 38.30 mmol/g adsorbent (figure 4).
The adsorption isotherm model fits the Freundlich adsorption isotherm model for oxalic acid and Langmuir for methylene blue. This is very interesting because the same material has different tendencies to different adsorbates. The difference in adsorbate charge indicates an interaction between charcoal and the adsorbate with a negative or positive charge. So it will be more difficult to absorb the negatively charged adsorbate with a low adsorption capacity because of the repulsion force on the activated charcoal surface which is also negatively charged.

Table 1. Isotherm adsorption model for carbon fitted with Freundlich and Langmuir model.

| Adsorbates      | R² Freundlich | R² Langmuir |
|-----------------|---------------|-------------|
| Methylene blue  | 0.9939        | 0.9989      |
| Oxalic acid     | 0.9877        | 0.9627      |

3.3 Adsorption mechanism

Adsorbate which has a negative charge will be absorbed in the pores of activated charcoal, but not as much because the surface of activated charcoal still has functional groups, it is possible to cover some of the macropores of activated charcoal. However, adsorbate with a positive charge will be absorbed on the outer surface of activated charcoal and interact with active functional groups such as hydroxyl and carboxyl. Besides, some of the adsorbates with a positive charge can also enter the pores of activated charcoal but not dominant.

Figure 4. The adsorption capacity of the organic contaminant at the room temperature.

Figure 5. Mechanism illustration of adsorption of organic contaminants against activated charcoal. The orange one is anionic organic contaminants and the blue one is the cationic organic contaminants.
4. Conclusions
Activated charcoal from PKM has been synthesized as activated charcoal at low temperatures. The characterized of activated charcoal product is polar sites with hydroxyl and carboxyl functional groups on the surface area. PKM waste can remove organic contaminants in surface water, it's the potential to be developed further using activated charcoal from PKM waste for other organic contaminants.

References
[1] Guppy and Anderson 2017 Water Crisis Report.
[2] Suoth A E, Purwati S U and Yuriska A 2018 Ecolab 2 53
[3] Badan Pusat Statistik 2017 Statistik Kelapa Sawit Indonesia
[4] Ash C, Tejnecký V, Luboš Borůvka and Drábek O 2016 J. Contam. Hydrol. 187 18
[5] Miculescu A and Wiklund L 2010 RJAIC 17 35
[6] Zhou Y, Zhang L and Cheng Z 2015 J Mol Liq. 212 739
[7] Saleh S, Kamarudin KB, Ghani K and Kheang S 2016 Procedia Eng 148 228
[8] Ray J R, Shabtai I A, Teixido M, Mishael Y G and Sedlak D L 2019 Water Res 157 454
[9] Kharisma D, Abidin Z, and Kusmana C 2019 IOP Conf. Series EES 399 012013
[10] Prajaputra V, Abidin Z and Widiatmaka 2019 IJSTR 7 706
[11] Garcia A M, Torres-Palma R A, Garcia H, Troya A H and Galeano L A 2020 J Water Process Eng. 39 101755
[12] Van H T, Bui T T P and Nguyen L H 2019 Water Air Soil Pollut 229 292
[13] Foya H, Mdoe J E G, and Mkayula L L 2014 IJERT 4 1035.
[14] Ratan JK, Kaur M, and Adiraju B 2018 Mater Today 5 3334.
[15] Xiao F, Bedane AH, Zhao JX, Mann MD, and Pignatello JJ 2018 Sci Total Environ 618 276.
[16] Jiao Y, Wan C, and Li J 2016 Mater Des 107 26.
[17] Li X 2012 Colloids and Surface A: Physicochem Eng Aspects. 4 79.
[18] Bansal RC and Goyal M 2005 Activated Carbon.
[19] Tadda MA, Ahsan A, Shitu A, ElSergany M, Arunkumar T, Jose B, Razzaque MA, and Daud N 2016 JACEPR 2 7.
[20] Fahmi A G, Abidin Z, and Kusmana C 2019 IOP Conf. Series EES 399 012015.
[21] Itodo A U, Itodo H U, dan Gafar M K. 2010 J. Appl. Sci. Environ Manage. 4 141.
[22] Okeola O F, Odebunmi E O, dan Ameen O M 2012 Bull Chem Soc Ethiop. 2 171.
[23] Marsh H and Rodriguez-Reinoso F 2006 Activated Carbon.
[24] Masyhur I A and Setiyono 2018 Prosiding KITT 1 141.
[25] Lewis 1982 Carbon 30 519.
[26] Suhas, Carrot P J M, Carrot M M L 2007 Bioresource Technol. 98 2301.
[27] Bergna D, Varila T, Romar H and Lassi U 2018 J Carbon Res. 4 41