Effect of Chemical Activation on the Physical Properties of Activated Carbon from Banana Empty Fruit Bunches as Heavy Metal Adsorbent

Awitdrus*, Rita Kartini Manulang, Agustino, Saktioto, Iwantono, Romi Fadli Syahputra, and Rakhmawati Farma

Department of Physics, University of Riau, Simpang Baru, Pekanbaru 28293

*awitdrus@lecturer.unri.ac.id

Abstract. Heavy metal pollution was a headline issue for environmental degradation, both in water and soil environments. Reducing efforts of heavy metal can be carried out through the green system, such as activated carbon from agriculture waste. This paper investigates the properties of activated carbon from banana empty fruit bunches (BEFBs) for heavy metal adsorption. The activated carbon was produced using chemical activation under microwave-assisted. Potassium hydroxide (KOH) is used as an activating agent for concentrations of 2, 3, and 4 M, each sample denoted AC-2M, AC-3M, and AC-4, respectively. The microwave irradiation was performed by a commercial microwave oven with output power up to 630 W for 15 minutes. X-ray diffraction characterization result shows the lower stack length \( L_c \) occurs in a sample of AC-2M with a value of 10.966. The surface morphology of all samples shows the presence of non-uniformed pores. The EDX analysis reveals that carbon content of AC-2M is higher than other samples up to 78.86\%, while the oxygen is lower (11.87\%). FTIR spectrum shown that the activated carbon from BEFBs contain functional groups of C-H, C≡C, C-C, C-OH, and CH\(_2\) at wavenumber 2887 cm\(^{-1}\), 2360.97 cm\(^{-1}\), 2339.5 cm\(^{-1}\), 1573 cm\(^{-1}\), 1393.63 cm\(^{-1}\), and 998.21 cm\(^{-1}\), respectively. As the best sample, AC-2M shows higher heavy metal adsorption as much as 87.41\% for Pb and 62.35\% for Cu.

1. Introduction

The use of biomass waste for activated carbon production is massively studied by broad-wide scientists in order to achieve sustainable and green technology in industrial waste treatments [1–4]. One of the highlighted wastes is heavy metal in industrial liquid wastes [5,6]. The presence of heavy metal is dangerous for living organisms as well as both indirectly and directly impacts on human health. Adsorption technique by activated carbon can be utilized for removing the concentration of metal ions in liquid wastes [7–9]. The raw materials for biomass activated carbon can be easily obtained from agricultural waste that contains lignocellulose and lignin [10,11].

Banana empty fruit bunches (BEFBs) are abundant biomass sources from banana plantation waste. The fabrication of activated carbon from BEFBs is carried out through two stages, namely, carbonization and activation process. Carbonization is designed to reduce non-carbon contents of the raw materials which carried out by closed-burn systems. The carbonization process can be boosted by microwave irradiation-assisted for rapid process and obtaining high yield outcome [12].

The main objective of this research is to investigate the effect of activating agent KOH on the activated carbon yield, physical properties, and its absorption capacity for removing heavy metals. The activated carbon is activated by varying KOH concentrations from 2M, 3M, and 4M. The activation process is also assisted by microwave irradiation with an output power of 630 W for 15 minutes.
Furthermore, the activated carbon will be tested for its absorption efficiency to eliminate heavy metals of industrial liquid waste, namely, lead (Pb) and copper (Cu).

2. Experimental method

2.1 Preparation of BEFBs activated carbon

The initial process of activated carbon production from BEFBs is cleaning the banana bunch from the dehydration process result which following cutting the banana bunch into small-sized, about 5 mm. Pre-carbonization was carried out using an electric oven at a temperature of 180°C for an hour. After this process, the sample was mashed up using a mortar and sieving with a size of 100 mesh to obtain a uniform size of the pre-carbonized grains. The chemical activation with assisted microwave irradiation was used to produce the activated carbon. Potassium hydroxide was used as an activating agent with a variation in concentration of 2 M, 3 M, and 4 M. This process was carried out using a hot plate stirrer for 2 hours at a temperature of 60°C. The microwave irradiation was used a microwave oven with an output power of 630 watts for 15 minutes under N₂ gas treatment. The next process was to clean the activated carbon using distilled water until the pH neutral (pH=7), and this sample dried out on temperature 105°C for at least 9 hours. For each sample was labeled as AC-xM, where x is the concentration of KOH.

2.2 Characterization of activated carbon

The activated carbon was characterized to get the physical properties for each sample. The characterization was using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX), Fourier’s transform infrared (FTIR), and atomic adsorption spectroscopy (AAS). The X-ray diffraction was used to obtain the microcrystalline profile. The interlayer spacing was calculated using the Bragg equation:

\[ n\lambda = 2d \sin \theta \]  

(1)

The microcrystalline dimension consisting of stack height \( (L_c) \) and stack width \( (L_a) \) were calculated using Scherer’s equation [13]:

\[ L_c = \frac{0.89 \lambda}{\beta \cos \theta_{002}} \]  

(2)

\[ L_a = \frac{1.94 \lambda}{\beta \cos \theta_{100}} \]  

(3)

where’s \( \beta \) is full width at half maximum (FWHM) and \( \theta \) is diffraction angle. SEM and EDX were used to show surface area morphology elemental compositions of the activated carbon. FTIR was used to find functional groups from activated carbon with a certain range of wavenumber. Atomic adsorption spectroscopy was used to find adsorption of activated carbon. The adsorption capacity of the AC-xM can be calculated from the following equation:

\[ \text{Adsorption} = \frac{C_0 - C_1}{C_1} \times 100\% \]  

(4)

where \( C_0 \) is the initial concentration and \( C_1 \) concentration after activation.

3. Result and Discussion

3.1 Microcrystalline structure

The comparison between the diffractogram pattern of each activated carbon is presented in Figure 1. The diffraction pattern formed two peaks at scattering angle (2θ) 22°-24° and 42°-44°, this peak associated with diffraction plane of (002) and (100), respectively.
Table 1 shows microcrystalline dimensions (stack height and stack width) and the number of the microcrystalline layer from activated carbon. The value of $L_c$ is increasing and $L_a$ is decreased against increasing concentration of KOH. This result indicates that the surface area increases proportionally with the increasing concentration of KOH. This result indicates that the surface area increases proportionally to the increasing concentration of KOH. The value of $L_c$ was inversely proportional to the surface area.

### Table 1. Interlayer spacing and microcrystalline dimension of activated carbon BEFBs

| Sample  | $2\theta_{002}$ | $2\theta_{100}$ | $d_{002}$ | $d_{100}$ | $L_c$ | $L_a$ | $L_c/d_{002}$ |
|---------|-----------------|-----------------|-----------|-----------|-------|-------|----------------|
| AC-2M   | 21.393          | 43.367          | 4.150     | 2.085     | 10.966| 9.051 | 2.642          |
| AC-3M   | 21.406          | 43.259          | 4.148     | 2.090     | 19.370| 9.776 | 4.669          |
| AC-4M   | 20.224          | 43.772          | 4.387     | 2.066     | 47.431| 5.956 | 10.11          |

### 3.2 Surface morphology

Surface morphological from the AC-xM was characterized by using SEM with magnification 10,000x for each sample. The result of each sample was showed in Figure 2. The surface morphology from the AC-xM shown not uniform pores. The forming and enlargement of pores were caused by the evaporation of the cellulose component and disappeared of substances. The purpose of the activation process was to increase pore size with the breaking hydrocarbon binding and oxidation of molecules on the surface of activated carbon. This process involved activated carbon to increase surface area and adsorption. Figure 2 showed pores of activated carbon have the size of macropore. Mesopore and micropore cannot be detected because the magnification of SEM not sufficient to reach that size.
Figure 2. The SEM micrograph of the banana empty fruit bunches activated carbon (a) AC-2M, (b) AC-3M, and (c) AC-4M

3.3 Chemical compositions
Elemental composition of activated carbon BEFBs was characterization using EDX. The ACxM sample content consists of carbon (C), oxygen (O), potassium (K), scandium (Sc), zirconium (Zr), and silica (Si). Table 2 show the elemental atomic percentage composition in the activated carbon.

Table 2. Percentage of chemical contents of activated carbon BEFBs

| Elemental compositions | AC-2M  | AC-3M  | AC-4M  |
|------------------------|--------|--------|--------|
| C                      | 87.20  | 84.62  | 74.36  |
| O                      | 9.52   | 10.55  | 20.06  |
| K                      | 3.28   | -      | -      |
| Sc                     | -      | 4.24   | 5.24   |
| Zr                     | -      | 0.59   | -      |
| Si                     | -      | -      | 0.34   |
| Total                  | 100    | 100    | 100    |

Based on Table 2, the KOH concentration affects the carbon content in the ACxM sample. The lower KOH concentrations, indicating a low carbon content indicated by the AC-2M sample with an atomic percentage of 87.20%. This is due to the elemental content of the AC-2M is purer than the AC-3M and AC-4M samples.
3.4 Functional group analysis
The functional group was obtained from characterization using FTIR analysis. FTIR results on BEFBs activated carbon are shown in Figure 3. The adsorption area at the number 3500-3200 cm\(^{-1}\) indicates the O-H functional group. From the results obtained a decrease in the adsorption peak, occurs due to the breakdown of hydroxyl groups and adsorbed water. The C-H function group has been detected by strain vibrations at wave number 2887 cm\(^{-1}\). This indicates that the activation process can break up and eliminate a number of elements of hydrogen [14]. The absorption peaks of 2360.97 cm\(^{-1}\) indicate the presence of C=C functional groups in the alkyne group. The peak of activated carbon at wave number 1573 cm\(^{-1}\) indicates the presence of C-C strain due to aromatic rings being formed. This reinforces that activated carbon has formed due to the formation of new pores [15]. At the absorption peak of 1393.63 cm\(^{-1}\), the presence of the C-H functional group symmetry was seen to decrease after the activation process because the activation process can break and remove a number of hydrogen elements. Furthermore, the absorption peak of 998.21 cm\(^{-1}\) indicates the presence of OH, CH, C-OH, and CH\(_2\) functional groups in the glycosyl unit in activated carbon.

![Figure 3. FTIR spectrum of BEFBs for AC-xM samples](image)

3.5 Adsorption performance

The adsorption of the AC-xM to heavy metals can be determined by using atomic adsorption spectroscopy (AAS) analysis. The object of adsorption measurement in the activated carbon BEFBs is
industrial wastewater. The heavy metals measured in this study were copper (Cu) and lead (Pb). The efficiency of activated carbon adsorption from banana bunches for each sample can be seen in Figure 5.

The maximum adsorption of metal ions from AC-xM was obtained in AC-2M samples, namely Cu at 62.35% and Pb at 87.41%. The AC-3M sample had Cu and Pb adsorption capacity of 61.54% and 78.71%, while the AC-4M sample had adsorption capacity of 60.32% and 68.88%, respectively. The higher concentration of KOH was used, the adsorption efficiency produced is lower. This is due to the activation using 3M and 4M have a higher concentration and the number of ions in the solution is not proportional to the number of pre-carbonize powder from banana empty fruit bunches so that the surface of the AC-xM reaches the saturation point and the adsorption efficiency decreases.

4. Conclusion
The results of this study indicate that different KOH concentrations produce different physical properties. The surface morphology analysis of the AC-xM based on the SEM micrograph showed that the pores formed are not uniform. X-ray diffraction data shows that the highest value of the lowest Lc is obtained at AC-2M with a value of 10.966 nm. The results of the identification with FTIR spectroscopy showed that the activated carbon in this study contained O-H, C≡C, C-H, C-OH, and CH2 functional groups. The adsorption of the AC-xM to heavy metals shows that the AC-2M sample has the highest adsorption with a percentage of 62.35% for Cu and Pb of 87.41%.

Acknowledgements
The author would like to acknowledge LPPM Universitas Riau for financial support through Penelitian Bidang Ilmu grand with the contract no. 841/UN.19.5.1.3/PT.01.03/2019.

References
[1] Schrder E, Thomauske K, Oechsler B and Herberger S 2011 Activated Carbon from Waste Biomass (InTech)
[2] Maneerung T, Liew J, Dai Y, Kawi S, Chong C and Wang C H 2016 Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies Bioresour. Technol 200 350–359
[3] Kosheleva R I, Mitropoulos A C and Kyzas G Z 2019 Synthesis of activated carbon from food waste Environ. Chem. Lett 17 429–438
[4] Ani J U, Akpomie K G, Okoro U C, Aneke L E, Onukwuli O D and Ujam O T 2020 Potentials of activated carbon produced from biomass materials for sequestration of dyes, heavy metals, and crude oil components from aqueous environment Appl. Water Sci 10 1–11
[5] Kanamarlapudi S L R K, Chintalpudi V K and Muddada S 2018 Application of Biosorption for Removal of Heavy Metals from Wastewater (InTech)
[6] Wong S, Ngadi N, Inuwa I M and Hassan O 2018 Recent advances in applications of activated carbon from biowaste for wastewater treatment: A short review J. Clean. Prod 175 361–375
[7] Zubrik A, Matik M, Hredzák S, Lovás M, Danková Z, Kováčová M and Briančin J 2017 Preparation of chemically activated carbon from waste biomass by single-stage and two-stage pyrolysis J. Clean. Prod 143 643–653
[8] Van Tran T, Bui Q T P, Nguyen T D, Le N T H and Bach L G 2017 A comparative study on the removal efficiency of metal ions (Cu2+, Ni2+, and Pb2+) using sugarcane bagasse-derived ZnCl2-activated carbon by the response surface methodology Adsorpt. Sci. Technol 35 72–85
[9] Kane S N, Mishra A and Dutta A K 2016 Characterization of sodium carbonate (Na2CO3) treated rice husk activated carbon and adsorption of lead from car battery wastewater Journal of Physics: Conference Series 180 012149-1-012149–12
[10] Sarkar N, Ghosh S K, Bannerjee S and Aikat K 2012 Bioethanol production from agricultural wastes: An overview Renew. Energy 37 19–27
[11] Saini J K, Saini R and Tewari L 2015 Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments 3 Biotech 5
337–353

[12] Ahmed M J and Theydan S K 2014 Optimization of microwave preparation conditions for activated carbon from Albizia lebbeck seed pods for methylene blue dye adsorption J. Anal. Appl. Pyrolysis 105 199–208

[13] Carrott P J M, Nabais J M V, Ribeiro Carrott M M L and Pajares J A 2001 Preparation of activated carbon fibres from acrylic textile fibres Carbon N. Y 39 1543–55

[14] Hesas R. H, Niya A, Daud W, and Sahu J N 2013 Preparation and characterization of carbon from apple waste by microwave-assisted phosphoric acid activation: application in methylene blue BioResources 8(1) 2950-2966

[15] Thuan T V, Thinh P V, Quynh B T, Cong H T, Tam D T, and Bach L G 2016 Production of activated carbon from sugarcane bagasse by chemical activation with ZnCl₂: preparation and characterization study Iciet 39 32–44