CHARACTERISTICS OF CORN COBS WASTE ACTIVATED CARBON FOR SLOW RELEASE MICRO FERTILIZER CARRIER

Priyadi and Windu Mangiring

Agricultural College of Dharma Wacana Metro, Jl. Kenanga No.3, Mulyojati, Metro Barat, Kota Metro, Lampung 34121, Indonesia

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ABSTRACT

The problem of fertilization, especially micro fertilizers, is toxification due to the excessive application. Using the concept of slow release fertilizer is a very possible solution to overcome the problem. The objectives of this study are 1) to characterize corn cobs activated carbon for slow release micro fertilizer carrier, 2) to produce and to test of slow release micro fertilizer. The research was carried out by converting corn cobs into activated carbon with an activation temperature of 600 °C and water vapor for 90 minutes. Production of slow release fertilizer was carried out by soaking activated carbon in a solution of CuSO₄, FeSO₄ and ZnSO₄ 1N for 24 hours. The results of micro fertilizer were then characterized, then the solubility test was carried out. The results of the characteristic analysis showed that some parameters that could be used as fertilizer carriers include, iodine adsorption 404.21 mg g⁻¹, adsorption of methylene blue 16.88 mg g⁻¹, the pore volume of 0.19 cc mg⁻¹ and surface area of 315.77 m² g⁻¹. While, based on the results of micronutrient solubility test the highest nutrient content that can be absorbed by activated carbon (AA) is found in Cu, followed by Zn and Fe. It relates to the characteristics possessed by activated carbon namely specific surface area, pore volume, and nutrient diameter size.

Keywords: Activated carbon, Adsorption carrier, Corn cobs, Slow release


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INTRODUCTION

Maize is a type of carbohydrate-producing annual crop besides wheat and rice which is widely cultivated in Lampung Province.

According to BPS-Statistics of Lampung Province (2013), the area of harvested corn crops reached 346,315 hectares. The high demand for carbohydrate sources, especially corn, also demanded an increase in corn production. On the other hand, the use of corn as food ingredient also increase corn
production, which is also including corn cobs waste that has not been optimally utilized.

At this time, agricultural waste including stover and corn cobs began to be used as biomass (Graham et al. 2007). One of the uses of waste is as raw material for bioenergy (Zych, 2008); as absorbent of rhodamine b and methanil yellow (Munawaroh, 2012), dye of methylene blue (Al Tufaily & Al Qadi, 2016), substitute for animal feed especially ruminants (Bunyamin et al., 2013), as an animal feedstock preserved in the form of silage (McCUTCHEON & Samples, 2002) and low cost adsorbent from agricultural waste (Tsai et al., 1998). Seeing the potential, it does not rule out the possibility to be used as a basic material of micro fertilizer carrier. The use of micro fertilizer is chosen because it becomes a problem if given excessively. This utilization can be done by turning the corn cobs into activated carbon.

Activated carbon is charcoal which has a configuration of carbon atoms free of other elemental bonds and the pores are free of impurities so that it can increase adsorption ability (Keech et al., 2005). Activated carbon is a highly adsorptive material that has a complex structure composed of atoms carbon (Amin & Alazba, 2017). Adsorption occurs because the molecules will be trapped in the structure of carbon internal pore by Van Der Waals Forces or other bonds of attraction and they will be accumulated into a solid surface (Singh & Ambika, 2018). Utomo et al. (2012) and (Hayashi et al., 2013) revealed that using activated carbon can increase the efficiency of fertilization in rice plants. In addition, Laird et al. (2010) explain that the use of activated carbon can reduce nutrient loss in the soil due to increased cation exchange capacity from the addition of activated carbon. Furthermore, (Clough & Condron, 2010) revealed that activated carbon has the ability to manipulate N cycle levels in soil systems by influencing the rate of nitrification, ammonia adsorption, and increasing NH₄⁺ deposits through soil CECs, thereby reducing N loss in the form of N₂O gas and reducing nitrate leaching. Research by Namgay et al. (2010) shows that activated carbon application can reduce the availability of trace elements (Pb, Cu, Cd, Zn, and As) in plants. Due to this matter, activated carbon is the potential material for slow release micro fertilizer carrier.

At the present time, there is little information about the use of activated carbon as a carrier in slow release. Several studies only focused on the classification for controlling slow release, namely organic compound, water-soluble fertilizer with a physical barrier and inorganic compound (Shaviv, 2001); (Trenkel, 2010). Blaylock et al. (2005) however, classified CRFs as only two major types; those coated with low solubility compounds and those coated with water-soluble materials. Besides, the fertilizer used as slow release material is still limited to macronutrients such as N, P, and K (Du et al., 2006; Adegbidi et al., 2003). With the ability possessed by activated carbon to absorb toxic elements (Rao et al., 2009), heavy metals (Buah et al., 2016) and metal ions in water bodies (Rao et al., 2009), activated carbon can be used as a carrier. Based on the description above, the objectives of this research are to characterize the activated carbon from corn cobs as a carrier of slow release micro fertilizer and to produce as well as to test micro fertilizer slow release.
MATERIALS AND METHODS
The research was carried out in the laboratory of Agricultural college of Dharma Wacana Metro from June 2017 to March 2018. The research began with the prototype of micro fertilizer slow release by utilizing activated carbon from corn cobs. Activated carbon characterization and micro fertilizer test was carried out by the Agricultural Environment Research Institute and the Integrated Laboratory Unit and the Technology Innovation Center of Lampung University.

The materials used in the research consisted of raw materials for the production of activated carbon, materials mixed for producing micro fertilizer slow release and various chemical reagents for analysis. The raw material used in this study is corn cobs for active carbon. The material mixed into activated carbon for the manufacture of slow release fertilizer namely CuSO4·SH2O, FeSO4, and ZnSO4.

The tools used are scales, drum furnace, electric retort and steamer, Wiley mill, oven, furnace, Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) EVO MA 10, Microwave plasma-atomic emission spectrometry (MP-AES) Agilent 4200, and glass tools for chemical analysis.

Procedure
Converting raw materials to charcoal
The corn cobs used in this study were collected from Metro, province of Lampung. Corn cobs are ground and sieved to about 0.015–0.30 mm in size and drying at 110 °C in an oven until a constant weight is reached before carbonization (Buah et al., 2016). Then, the charcoal production process is carried out using a drum furnace with a capacity of 90 kg. The drum furnace is filled with raw materials (known for its weight) placed on small pieces of wood that have been stored first at the base of the drum furnace. The combustion is carried out at a temperature that increases gradually to a temperature of ± 500 °C. After all the raw material in the furnace burns completely, which is characterized by the decreasing of the smoke coming out of the furnace and the changing color of the smoke into bluish color, the combustion is stopped by tightly closing all the paths that the air passes into the furnace. Furthermore, the cooling process is carried out in the furnace for ± 24 hours (National Standardization Agency of Indonesia, 1995).

Activated carbon production and characterization
Activated carbon production is carried out by inserting carbonized charcoal into an electric retort and activated with water vapor at a temperature of 600 °C for 90 minutes. The activated carbon that has been produced is then weighed, finely ground until it passes a 100 mesh sieve screen and analyzed based on SNI 06-3730-1995 which includes: rendemen, water content, levels of flying substances, ash content, activated carbon content, adsorption of iodine, and adsorption of methylene blue (National Standardization Agency of Indonesia, 1995).

Production of slow release fertilizer
Activated carbon that has been obtained is mashed to 100 mesh. Fertilizer preparation is done by soaking the activated carbon in a fertilizer solution for ± 24 hours with the amount
of concentration used is 1000 ppm. Then the immersion results were washed until sulfate free was tested by dripping BaCl₂ 0.5 N and then dried. After obtaining dry powder fertilizer, further analysis was carried out by covering surface topography observations using Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) EVO MA 10. Further testing is carried out to determine the release of nutrients in fertilizer (Yang et al., 2011).

**Nutrient release test**

This experiment aims to determine the release of Cu²⁺, Fe²⁺ and Zn²⁺ elements in fertilizer. The experiment was carried out in two ways, the first method was extracting fertilizer with distilled water extract (fertilizer ratio: extractor = 1: 5) with some extraction time which was 0; 20; 40; 60; and 80 minutes. The second method is by leaching the fertilizer. The leaching process is carried out by flowing 25 ml of distilled water in 5 grams of fertilizer in filter paper which is placed in the funnel 25 times. The results of the leaching process were then dried. After that, a qualitative analysis was performed using SEM-EDX MA 10 and the amount of nutrient release with MP-AES Agilent 4200 (Kamala et al., 2014).

**RESULTS**

**Activated Carbon Characteristics**

The results of charcoal characterization and activated carbon analysis based on SNI 06-3730-1995 are presented in Table 1. Based on Table 1, can be seen some characteristics of activated carbon. The rendemen produced from the activation process was lower compared to the activated carbon rendemen. Activated carbon rendemen was obtained 17.12% while charcoal was obtained at 21.22%. Charcoal flying substance levels decreased after the activation process. The decreasing occurred was around 1% namely 16.33% to 15.32%. Carbon content bound to activated carbon is higher than charcoal. The amount level of bounded carbon produced in activated carbon was higher (63.37%) than in charcoal (57.54%).

Surface area and total pore volume of activated carbon increase with temperature ascension in the activation process. The surface area of corn cob charcoal was 139.23 m² g⁻¹, while for activated carbon with an activation temperature of 600 °C was 315.77 m² g⁻¹.

**Table 1.** Results of carbon characterization analysis at 350 °C and activated carbon 600 °C

<table>
<thead>
<tr>
<th>No</th>
<th>Parameters</th>
<th>Rendemen (%)</th>
<th>Moisture Content (%)</th>
<th>Flying substance levels (%)</th>
<th>Ash content (%)</th>
<th>Fixed carbon (%)</th>
<th>Iodine adsorption (mg g⁻¹)</th>
<th>Methylene blue adsorption (mg g⁻¹)</th>
<th>Total Pore Volume (cc g⁻¹)</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>21.22</td>
<td>5.63</td>
<td>16.33</td>
<td>5.95</td>
<td>57.54</td>
<td>112.30</td>
<td>4.25</td>
<td>0.12</td>
<td>139.23</td>
</tr>
<tr>
<td>2</td>
<td>AA</td>
<td>17.12</td>
<td>3.67</td>
<td>15.32</td>
<td>5.47</td>
<td>63.37</td>
<td>404.21</td>
<td>16.88</td>
<td>0.19</td>
<td>315.77</td>
</tr>
</tbody>
</table>

Description:

A: Corn cobs carbon temperature of 350 °C
AA: Activated carbon of corn cobs activation temperature of 600 °C
Table 2. Nutrient solubility test of micro fertilizers slow release

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>level (ppm) at the time of matching</th>
<th>Total solubility (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>1.</td>
<td>Activated carbon +Cu</td>
<td>100.51</td>
<td>93.22</td>
</tr>
<tr>
<td>2.</td>
<td>Activated carbon +Fe</td>
<td>1.24</td>
<td>0.30</td>
</tr>
<tr>
<td>3.</td>
<td>Activated carbon +Zn</td>
<td>15.76</td>
<td>15.60</td>
</tr>
</tbody>
</table>

The total pore volume of corn cobs charcoal was 0.12 cc g⁻¹ and 0.19 cc g⁻¹ for activated carbon from corn cobs. Other characteristics that play a role in the ability of activated carbon as a carrier are surface morphology. Surface morphology can show both the cavity formed and the presence of nutrients added to activated carbon. The explanation can be seen from the results of SEM analysis (Figure 1) and EDX (Figure 2, Figure 3, Figure 4, and Figure 5).

Figure 1. Morphology of activated carbon surface with 750x magnification (a) Activated carbon; (b) Activated carbon + Cu; (c) Activated carbon + Fe; and (d) Activated carbon + Zn)
Figure 2. EDX observations on activated carbon without fertilizer addition

Figure 3. EDX observations on activated carbon with the addition of Cu fertilizer

Figure 4. EDX observations on activated carbon with the addition of Fe fertilizer.
**Figure 5.** EDX observations on activated carbon with the addition of Zn fertilizer

**Figure 6.** SEM observations on activated carbon + Cu were leaching 25 times

**Figure 7.** EDX observations on activated carbon + Cu were leaching 25 times.
Solubility test of slow release fertilizer

This test aims to determine the release of Cu, Fe, and Zn in a slow release fertilizer. The test was carried out by extracting fertilizer with distilled water at extracting 0, 20, 40, 60, and 80 minutes. The test results are presented in Table 2. Based on Table 2, the Cu element has been able to be aroused in distilled water since the 0 minute matching time. The extracted Cu level was seen to be quite high at the beginning and then decreased and stabilized at the time of subsequent matching. Cu element solubility in 0 minutes was 100.51 ppm, then the decreasing happened in minute 20 (93.22 ppm), minute 40 (87.85 ppm), minute 60 (93.70 ppm) and minute 80 (94.00 ppm). In element solubility test, Fe has the lowest result in which it was 1.24 ppm in minute 0, 0.30 ppm in minute 20, 0.71 ppm in minute 40, 0.40 ppm in minute 60 and 0.46 ppm in minute 80. While, solubility in Zn element was 15.76 ppm in minute 0, 15.60 ppm in minute 20, 12.78 ppm in minute 40, 13.40 ppm in minute 60 and 13.27 ppm in minute 80. From the result of the solubility test, it shows that the total amount of solubility for Cu was 469.28 ± 4.49 ppm, Fe was 3.11 ± 0.38 ppm and Zn was 70.81 ± 1.41 ppm.

DISCUSSION

Activated Carbon Characteristics

At the process of charcoal activation, there is a decreasing in rendemen. Decreasing rendemen at higher temperatures occurs due to the evaporation of water and the thermal decomposition of organic compounds (Yang et al., 2004). Luangkiattikhun et al. (2008) said that the maximum evaporation of H2O organic matter occurs at 220 °C, whereas at higher temperatures of 315–400 °C occurs cellulose decomposition and temperature above 400 °C occurs lignin decomposition. Increasing temperature causes an increasing amount of charcoal reaction to CO2 and H2O. On the contrary, the resulting C was reduced so that the rendemen of the activated carbon produced is low. The decreasing of water content also occurs when the activation temperature was decreased, precisely at 350 °C obtained 5.63% while the temperature of 600 °C obtained 3.67%. Charcoal flying substance levels decreased after the activation process and decreased with increasing activation temperature. This occurs because, at high temperatures, decomposition of non-charcoal compounds such as CO2, CO, CH4, and H2 can be perfect. While the ash content of activated corn cob charcoal did not show significant differences. Ash content in activated carbon can affect the adsorption because the pores in activated carbon will be filled by cations such as K, Na, Ca, and Mg.

Carbon content levels are strongly influenced by the levels of flying substances and ash content. The higher the flying substance and the ash content, the lower the charcoal content is bound. The value of charcoal content bound is directly proportional to the adsorption of the activated carbon, so that the greater the carbon content bound, the greater the ability of activated carbon to adsorb gas or solution (Sudrajat et al., 2005). This can be seen from the adsorption ability of activated carbon to iodine and methylene blue. Activated carbon has a higher adsorption capacity of iodine than charcoal. The adsorption capacity of corn cobs for iodine was...
112.30 mg g\(^{-1}\), while the active adsorption ability of charcoal was 404.21 mg g\(^{-1}\). Increased adsorption ability shows that the charcoal atoms that form hexagonal crystals are increasing so that the pores formed between the crystallite layers also have a larger size. The same thing happened to the adsorption ability of activated carbon to methylene blue. The adsorption ability of methylene blue in corn cobs charcoal was 4.25 mg g\(^{-1}\), while the adsorption ability of activated carbon was 16.88 mg g\(^{-1}\). The high adsorption capacity of activated carbon to methylene blue shows that the hydrocarbon compounds found on the activated carbon surface have become more active and the bond between hydrogen and carbon is completely released so that there is a more active surface area (Pari et al., 2009). The increasing surface of the area and the total pore volume of activated carbon were affected by the activation process. This happened due to the opening of particles found in charcoal biomass so that the surface area becomes larger which is also followed by the total pore volume. The increase in temperature and time in the activation process results in many bonds of esters and polyester from the organic matter being released, so that more new pores are formed in activated carbon.

Based on Figure 2, Figure 3, Figure 4, and Figure 5 it was found that Cu, Fe, and Zn were found in activated carbon derived from corn cobs which had been soaked with CuSO\(_4\), FeSO\(_4\), and ZnSO\(_4\) solutions. Figure 2 shows EDX results from activated carbon without nutrient immersion treatment. This can be seen from the results of the analysis that did not show the typical peaks of nutrients but only contained elements of C, N and O. Figure 3 which is activated carbon + Cu shows the peak of Cu nutrients, as well as in Figure 4 namely activated carbon + Fe and Figure 5 which is the activated carbon + Zn also shows the peak of Fe and Zn. Overall nutrients added to activated carbon can be tied in activated carbon pores. This shows that activated carbon has the ability to bind or absorb added nutrients.

**Solubility test of slow release fertilizer**

Based on Table 2, the Cu element has been able to be aroused in distilled water since the 0 minute matching time. The extracted Cu level was seen to be quite high at the beginning and then decreased and stabilized at the time of subsequent matching. The same thing can also be seen in the solubility of Fe and Zn, where the amount of Fe and Zn elements extracted at the beginning shows a higher amount, then experience stability at the time of matching 20, 40, 60, and 80 minutes. The result of the highest micro-nutrient solubility is found in activated carbon + Cu. While, the solubility of Zn nutrient was lower than Cu solubility, and then followed by the solubility of Fe. The results of the extraction of fertilizers with distilled water showed the number of elements available on the soil with neutral conditions which could be immediately adsorbed by plants. The Cu, Fe and Zn levels extracted by distilled water were much lower compared to the total of these elements in activated carbon after immersion. This data shows that the release of nutrients occurs slowly. Several studies on activated carbon explain that the ability to adsorb is influenced by specific surface area and total pore volume.
Buah et al. (2016) state that activated carbon made from corn cobs with a variety of specific surface area and pore volume can adsorb Pb, Cu, and Cd from wastewater. Furthermore, Aloko & Adebayo (2007) revealed that charcoal from rice husk and corn cobs which were activated by oxidation methods were able to increase specific surface area and pore volume. This increasing can play an effective role in adsorbing the phosphorus elements that pollute the water body.

To find out whether or not the nutrients in the activated carbon are easily lost due to leaching, further testing was carried out by leaching activated carbon 25 times. Then, the fertilizer was dried and observed with SEM and EDX (Figure 6 and Figure 7). Figure 6 and Figure 7 shows that the Cu element was found in the washed activated carbon it has been done 25 times. This illustrates that Cu is strongly adsorbed in activated carbon and is not easily released. Tests were not carried out on other fertilizers because the data of each fertilizer extraction with distilled water showed almost the same results, i.e. very few elements were extracted compared to the total levels of elements in the fertilizer.

CONCLUSIONS

Agricultural waste in the form of corn cobs can be used as a fertilizer carrier by changing into activated carbon. The results of characterization indicated that the parameters for being a fertilizer carrier including the adsorption of iodine were 404.21 mg g⁻¹, the adsorption of methylene blue 16.88 mg g⁻¹, the pore volume was 0.19 cc mg⁻¹ and surface area was 315.77 m² g⁻¹. Solubility test results showed that the activated carbon adsorption ability and the highest micro-nutrient solubility were found in Cu, followed by Zn, and Fe. Adsorption ability and nutrient solubility are influenced by specific surface area and pore volume contained in activated carbon. High levels of solubility occurred at the beginning of shaking. Then, a steady decline occurred indicating that the rate of nutrient release in activated carbon occurs slowly. In addition, the results of the analysis on samples that have been washed as much as 25 times indicate that nutrients are still present in activated carbon both in the appearance of SEM and EDX.

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