Poll Res. 39 (2) : 444-451 (2020)
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ISSN 0257–8050

EFFECT OF PYROLYSIS TEMPERATURE ON BIOCHAR TO REDUCE CADMIUM (CD) CONCENTRATION IN IMPACTED LAPINDO MUD SOIL IN SIDOARJO, EAST JAVA

RUSLAN WIROSOEDARMO[1], AULIA NUR MUSTAQIMAN[1], FAUZANA MAULIDA NURAHMA[1] AND KIKI GUSTINASARI[1]

[1]*Department of Agricultural Engineering, Faculty of Agricultural Technology, Brawijaya University, Jalan Veteran Malang 65145, Indonesia*

(Received 5 November, 2019; accepted 30 January, 2020)

ABSTRACT

This study aims to reduce the content of Cd heavy metals in the soil and to reduce agricultural waste in order to be more useful. The materials for making biochar in this study were corn cobs and rice husks made with temperatures of 500 °C, 600 °C, and 700 °C with pyrolysis using a furnace for 45 minutes which would then be mixed with metal cd contaminated the soil with a ratio of 1:10. The parameters observed were pH, temperature, water content, C-organic content, and Cd content in the soil. The difference in biochar making temperature affects the decrease in cadmium (Cd) heavy metal content of 7.35% - 11.45% for biochar made with raw materials of Corn Cobs and 9.9% - 13.58% for raw materials of husk rice. Biochar made from rice husks and corn cobs can increase soil temperature by 5.82% - 10%, acid soil pH of 7.3% - 12.65%, low soil moisture content of 15.49% - 21.42%, and increase the C-Organic content in the soil by 9.9% - 18.81%. Biochar which is made using rice husks improves soil quality slightly better than corn cobs.

KEY WORDS : Cadmium, Biochar, Lapindo, Pyrolysis

INTRODUCTION

Environmental pollution is the most prominent problem along with the increase in the number of factories that increase the needs of the population which increases the number of needs in a sufficiently large amount which will cause environmental pollution that is properly supported. According to Hidayat (2015) and Yang *et al*. (2016), waste produced by factories contains a variety of non-hazardous. Heavy metals that are on the ground and cannot be degraded, can be placed on soil and water bodies for a long time so that the content will continue to increase over time.

In 2006, Lapindo hot mudflow has sunk several sub-districts in Sidoarjo, East Java. The high temperature of the mud raises the hypothesis of the possibility of a geothermal system that plays a role in the mechanism of discharge of hot mud material that produces hydrothermal solutions which generally contain metal elements such as Cu, PB, Zn, Mn, Fe, Cd, As, Sb, Au, Ag, Hg, and Se. Lapindo mud is an oil sludge (Sludge Oil) which results from the production of petroleum and gas Intermittently which comes from originating from cleaning the pollution control in the Plant, API Separator tank washing activities, oil tanks, separation of oil, solids, emulsions, and water and drilling activity.

Research conducted by Namgay *et al.* (2010) and Yang *et al*. (2016) concluded that the average distribution of metal elements is relatively high and among them is heavy metal Cd. The soil naturally contains heavy metals, some of these heavy metals play a role in the physiological processes of plants such as Fe, Cu, Zn and Ni, but with relatively very a little, if the excess will give the effect of toxicity to plants, but Cd and Pb very mixed and until now it has not known its role for plants, these two elements are the main chemical pollutants in the environment and very toxic to plants, animals and humans

(Hidayat, 2015; Kouping *et al*., 2014; Trakel *et al.,* 2011, *Yang et al*., 2016) The latest development in handling soil contaminated with heavy metals is by using biochar, biochar is organic biomass which undergoes a thermolysis process and can be made on a simple scale which can be developed to overcome polluted environmental problems. Biochar has a large surface area, and high capacity to absorb heavy metals so it can be potentially used to reduce bioavailability and leaching of heavy metals and also organic pollutants in the soil through adsorption and other physicochemical reactions (Namgay *et al*., 2010; Uzoma *et al*., 2011).

Biochar is a co-product of a thermochemical conversion of biomass that is recognized to be a beneficial soil amendment which when incorporated into the soil increases soil water retention, improved the saturated hydraulic conductivity of the topsoil, affected aggregation, infiltration, and water-holding capacity, decreased soil penetration resistance (Baronti *et al*., 2014; Asai *et al*., 2009; Uzoma *et al*., 2011; Busscher *et al*., 2010; Pranagal *et al.*, 2017).

Biochar can play a key role in nutrient cycling, potentially affecting nitrogen retention when applied to soils. Data appeared to suggest that biochar could be used as a potential nutrient-retaining additive in order to increase the utilization efficiency of chemical fertilizers (Ding *et al*., 2010; Vaccari *et al*., 2011) Application of biochar improved available phosphorus, exchangeable cations and cation exchange capacity in biochar treated soils compared to the control soil without biochar (Downie *et al*., 2009; Namgay *et al*., 2010; Ouyang *et al*., 2013).

Evidence suggests that biochar influences soil physical properties, especially soil hydrology, yet relatively little data exists on this topic, especially in relation to soil type or characteristics. With the increasing amount of biochar, changes to bulk density, field capacity, and available water were more pronounced (Lehmann *et al*., 2009, Laird *et al*., 2010; Skjemstad *et al*., 2002; Peake *et al*., 2014). Application of untreated and carbonized rice husks increased total organic carbon, total soil N, the C/N ratio, and available P and K. Not significant or small effects were observed for soil reaction, exchangeable Ca, Mg, Na, and the CEC. (Haefele *et al*., 2010; Uzoma *et al*., 2011). Biochar is stable and could have similar water and nutrient retention impacts as peat moss when mixed in sand-based turfgrass root zones. Saturated hydraulic conductivity (K sat) of the root zones decreased as biochar concentrations increased (Brockhoff *et al.,* 2010; Zhu *et al*., 2014).

As pyrolysis temperature increased, ash content, pH, electrical conductivity, basic functional groups, carbon stability, and total content of C, N, P, K, Ca, and Mg increased while biochar yield, total content of O, H and S, unstable form of organic C and acidic functional groups decreased. The ratios of O/C, H/C, (O + N)/C, and (O + N + S)/C tended to decrease with temperature. Biochar pyrolyzed at high temperature may possess a higher carbon sequestration potential when applied to the soil compared to that obtained at low temperature (Al-Wabel *et al.,*2013; Zhang *et al*., 2017; Khan *et al.*, 2016). The results showed that not all biochar properties changed consistently with increasing pyrolysis temperature during slow pyrolysis. The significant increase in biochar pH with increasing pyrolysis temperature. Additionally, the soil pH increased markedly after the addition of biochar (Steiner *et al*., 2003; Jiang *et al*., 2012).

MATERIALS AND METHODS

Location

The location of the study is in the FMIPA Basic Laboratory in Lambung Mangkurat University in November 2017 - December 2017. Astronomically, it is at 7º57¬'11.9 "S and 112º36'42.7" E.

Stage of Research

Preparation

The preparation stage is by preparing the materials used, including Rice Husk, Corn Cob and Polluted Soil Cadmium (Cd). Polluted Soil Samples Cadmium (Cd) heavy metals were obtained from 100 m soil from the Lapindo Mud embankment in Sidoarjo, East Java. The formula (Biochar dose of Rice Husk and Biochar Corn Cob) uses a ratio of 1: 10, meaning that every 500 grams of Biochar are mixed with 5 kg of Soil.

Implementation phase

The implementation phase starts by mixing Biochar with Cadmium (Cd) heavy metal contaminated Soil. 5 kg of heavy metal contaminated the soil with 500 grams of biochar were made with a temperature of 500 ° C, 600 ° C, 700 ° C and given three replications. Every two weeks for two months a test or analysis of predetermined parameters is carried out. the parameters used in this study include Temperature, pH, C-Organic, Water Content, and Levels of Cadmium (Cd).

Data Analysis

Based On Data obtained from testing the levels of Cadmium (Cd) heavy metals contaminated soil using biochar made from corn cobs, the analysis was carried out in two ways, namely:

A. Analyze data on the effect of differences in the temperature of making biochar using corn cobs to reduce the levels of heavy metal Cadmium (Cd) in polluted soil. The analysis used in this experiment used a Completely Randomized Design (CRD) which was arranged factorially three times. Several reasons were chosen for this complete randomized design arranged in factorial, this experiment was carried out on a laboratory scale. Experiments were carried out on a laboratory scale because the experiments were not large enough and the number of treatments was only three replications. Not only this factorial complete randomized design are, among others, but the statistical analysis of the experimental subjects also is quite simple, flexible in the use of the number of treatments and replications, missing data is relatively smaller .when compared with the other designs.

B. Analysis of data that affects parameters. The parameters observed in this experiment were temperature, pH, water content, cadmium (Cd), and organic C levels. Analysis of the parameters obtained, researchers used descriptive analysis. This experiment was conducted using descriptive analysis which was included in the quantitative analysis to analyze the parameter that had been obtained. Descriptive analysis is an analysis carried out by describing the data that has been collected as it is obtained with the aim of making a conclusion that applies to the public. The following is a descriptive analysis technique that can be used, namely:

i. Presentation of data in visual forms such as histograms, ogives, polygons, pie charts, bar charts, pie charts, and symbol diagrams.
ii. Presentation of data in the form of tables or frequency distributions and cross-tabulations. This analysis is to find out the trends in the findings of the research, whether they are classified as low, medium or high.
iii. Location size calculation (decile, quartile, and percentil).
iv. Calculation of the central dimension (mean, mode and median).
v. Calculation of the size of the distribution of variance, range, standard deviation, quartile deviation, mean deviation, and so on.

RESULTS AND DISCUSSION

Research Location Characteristics

The research location is 100 meters from the Lapindo Mud Embankment in Siring Village, Porong District, Sidaorjo Regency, East Java. Geographically the embankment of the Lapindo Mud is at 7 ° 31 ’37.1 “S and 112 ° 42' 42.1” E. The soil around the embankment is Heavy Metal Polluted Land from Lapindo Waste. Figure 1 below is an area submerged by the mud flow.

(*Source:* Google Earth, 2017)

Fig. 1. Mud Submerged Area

Characteristics of Early Soils

Soil extraction is carried out using a 3 m x 3 m spade with a depth of about 30 cm. The soil that has been taken is then dried and sieved to homogenize the weight and size and has a sandy and dusty texture with pH. Rather acid tends to be neutral, the water content is low, and the neutral pH tends to be acidic. In addition to physical analysis, soil C-Organic chemistry tests were also carried out which were quite high and cadmium (Cd) levels in the soil. Initial analysis of soil physical and chemical properties can be seen in Table 1.

Biochar Characteristics

In this study, the organic material used as soil enhancer to reduce the levels of heavy metal cadmium (Cd) is biochar made from corn cobs as well as rice and rice husk husk with three different pyrolysis temperatures, which are 500 ° C, 600 ° C,

Table 1. Initial analysis of soil physical and chemical properties

Nature of Soil	Value	Criteria
Texture	-	Dusty
Sand (%)	72.4	Sand
Dust (%)	26.9	
clay (%)	0.7	
Water Content (%)	1.79	low
pH	6.5	Neutral
Temperature (°C)	27	Medium
C – Organik (%)	14.65	High
Cadmium (ppm)	3.54	High

Source: Test result by FMIPA Laboratorium Lambung Mangkurat University, 2017

and 700 ° C. Biochar of corn cobs and rice husk is made by drying it first in the sun and then using an oven temperature of 105 ° C to reduce the moisture content of the soil enhancer. The higher the temperature used in making biochar, the less biochar is obtained from the results of pyrolysis. The difference in the mass of making biochar can be seen in Table 2 and Table 3 below.

Analysis of Characteristics of Soil mixed with Biochar

Observation of soil characteristics mixed with Biochar made from corn cobs and rice husks are pH, temperature, moisture content, organic C and cadmium (Cd) levels in the soil. The results of measurements of soil pH after mixing with biochar Corn Cob and rice husk can be seen in Figs. 2 and 3.

Based on Figure 4 above it is known that an increase in soil temperature given corn cob biochar made at a temperature of 500 °C, 600 °C, 700 °C experienced an increase in average. Temperatures of 5.82%, 6.89%, and 6.66 %. Biochar of rice husk made

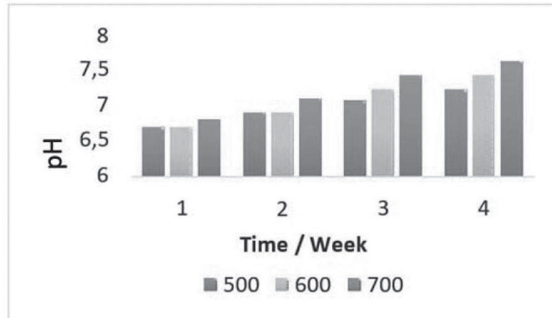

Fig. 2. Bar chart relationship of biochar temperature and time of corn cob to pH

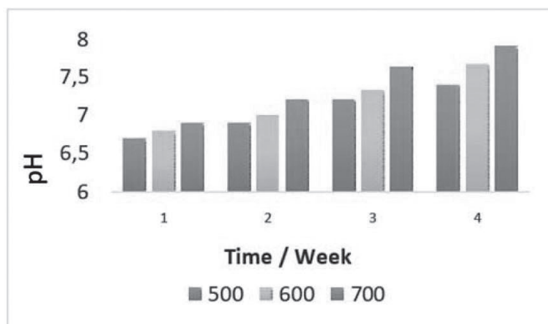

Fig. 3. Bar chart relationship of biochar temperature and time of rice husk to pH

Table 2. The mass produced by Corn Cob Biochar

Biochar Temperature (°C)	Raw Materials (kg)	After Drying (kg)	After become Biochar (kg)	After sifting 60 mesh (kg)
500	24	11.04	7.08	6.45
600	24	11.04	6.95	6.21
700	24	11.04	6.88	6.12

Source: Laboratory Results of FMIPA Laboratory of Lambung Mangkurat University, 2018

Table 3. Mass Results of Making Rice Husk Biochar

Biochar Temperature (°C)	Raw Materials (kg)	After Drying (kg)	After become Biochar (kg)	After sifting 60 mesh (kg)	
500	24	13.44	8.64	7.11	
600	24	13.44	8.42	6.97	
	700		24		13,44
	8.10		6.56		

Source: Laboratory Results of FMIPA Laboratory of Lambung Mangkurat University, 2018 with a temperature of 500 °C, 600 °C, 700 °C experienced an increase in average temperature of 6.89%, 10%, and 10%. It can be seen in Figs. 6 and 7.

Based on Figure 2 above it is known that an increase in soil pH given corn cob biochar made at a temperature of 500 °C, 600 °C, 700 °C has an increase in pH on average 9.54%, 11.34%, and 12.65%. Biochar of rice husk made at a temperature of 500 °C, 600 °C, 700 °C experienced an increase in pH averaging 7.3%, 9.8% and 10.87%. The results of measurements of soil temperature after mixing with biochar Corn cobs and rice husks are seen in Figs. 4 and 5.

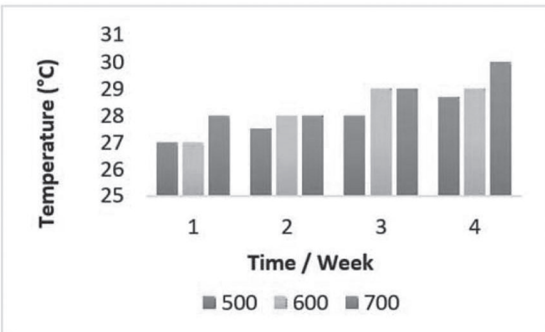

Fig. 4. Bar chart of the relationship of the biochar temperature and time of corncob to temperature

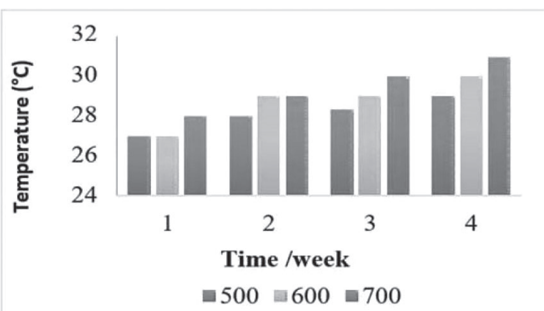

Fig. 5. Bar chart of the relationship between the biochar temperature and time of rice husk to temperature

Based on Figure 6 above, it is known that an increase in soil water content given corn cob biochar made at a temperature of 500 ° C, 600 ° C, 700 ° C has an increase in pH averaging 8.23%, 9.8%, and 10, 87%. Biochar of rice husk made with a temperature of 500 ° C, 600 ° C, 700° C increased the average water content 9.02%, 10.34%, and 11.44%. The results of measurements of soil C-organic after mixing with biochar Corn cobs and rice husks are seen in Figure 8 and Figure 9.

Based on Figure 8 above it is known that an increase in soil C-organic given corn cob biochar

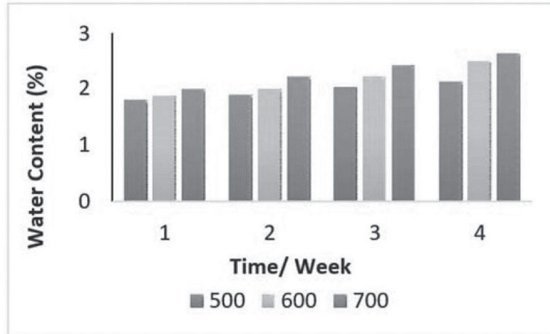

Fig. 6. Bar chart of the relationship between biochar temperature of corn cobs and water content

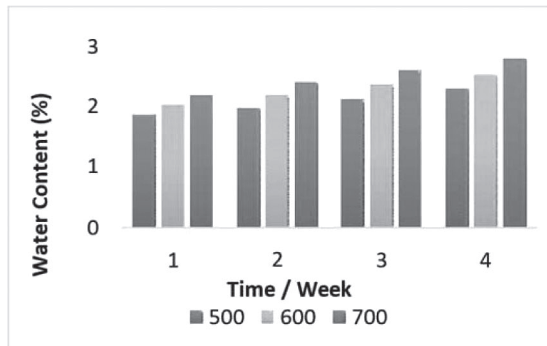

Fig. 7. Bar chart of the relationship between biochar temperature and rice husk time to water content

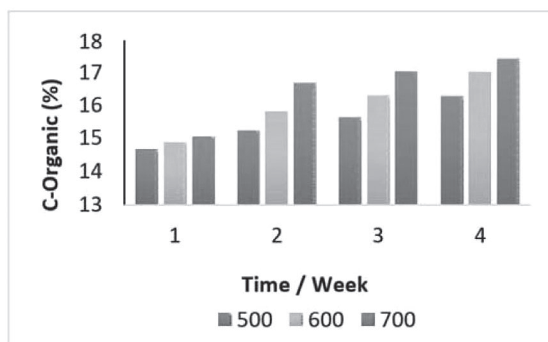

Fig. 8. Bar chart of the relationship between temperature and time of biochar of corn cobs to C-Organic

made at a temperature of 500 ° C, 600 ° C, 700 ° C experienced an increase in C-Organic on average 9.9%, 12.55%, and 13.58%. Biochar of rice husk made at a temperature of 500 ° C, 600° C, 700 ° C experienced an increase in C- Organic averaging 7.35%, 8.18%, and 11.81%. The measurement results of Cadmium (Cd) levels in the soil after mixing with biochar Corn cobs and rice husks are seen in Figures 7 and 8.

Based on Figure 8 above it is known that an increase in the level of Cadmium (Cd) of soil given corn cob biochar made at a temperature of 500 ° C, 600 °C, 700 °C decreased the level of Cadmium (Cd) on average 7.35%, 13, 72%, and 18.43%. Biochar of rice husk made at a temperature of 500 °C, 600 °C, 700 °C decreased the level of Cadmium (Cd) on average 15.88%, 17.60% and 21.34%.

Factors Affecting Soil Improvement using Biochar

The success of Biochar in improving soil properties depends on the type of raw material, pyrolysis temperature and combustion time. According to the Castellini *et al.* (2015), biochar is alkaline, so that when the bases are decomposed or hydrolyzed will release OH- ion so that it can increase the pH of the soil. The increase in pH in acid soils is caused by an increase in the concentration of alkali metal oxides derived from biochar (Steiner *et al*., 2003).

The land used as dried test material is agricultural land classified as dusty sand soil. Coarse-textured soils have a lower water holding capacity than fine-textured soils which can destroy plants which, if planted on the soil, will be more prone to drought than clay or clay textures (Castellini *et al*., 2015). According to Ding *et al.* (2010), in general, biochar has an irregular surface shape with a porous structure so that biochar has high water absorption and is resistant to microorganism decomposition. These properties cause biochar to have high retention power to reduce nutrient leaching and increase water content in the soil (Laird *et al*., 2010).

The presence of C-Organic is increasing in the soil which is an energy source of microorganisms and as the main adhesive agent for microbes that increases soil aggregate stability so that the soil structure becomes good (Ouyang *et al.,* 2013). In addition, Baronti *et al*. (2014) Novak *et al*.(2012) Bruun *et al.(*2014) says that organic materials such as C-Organic have a high capacity to store water because C-organic is an adhesive of loose grains and is the main source of nitrogen, phosphorus, and sulfur so that it can maintain and increase water content in the soil.

This is because Organic Materials that are used as soil enhancers (Biochar) undergo a decomposition process and produce organic substances that act as adhesives in the process of forming soil aggregates. Aggregates can create a good soil physical environment (Ouyang *et al*., 2013; Herath *et al*., 2013). According to (Skjemstad *et al*., 2002**),** Biochar can reduce the mobility of heavy metals in contaminated soils that cannot be absorbed by plants because they are no longer available to plants. Jieng *et al*. (2012) also mentioned that the use of biochar derived from rice husk can reduce Pb and Cd radical mobility by up to 90% in soils that have a low pH. The administration of Biochar can reduce the greatest bioavailability of Cd metal compared to other metals especially through adsorption or co-precipitation (Zhou *et al*., 2008).

Biochar which is made from the same type of material will produce different qualities when made using different temperatures. Biochar which is produced at high temperatures (≥600 °C) generally has a high surface area that good for physical absorption but has fewer functional groups and lower nutrient content, but otherwise biochar is carried at 400 °C-500 °C has a functional group that is diverse and relatively contains more nutrients (Zhang *et al.*, 2013).

CONCLUSIONS

From the research that has been done, it can be concluded as follows:

1. The difference in biochar making temperature affects the decrease in cadmium (Cd) heavy metal content of 7.35% - 11.45% for biochar made with raw materials of Corn Cobs and 9.9% - 13.58% for raw materials of husk rice.
2. Biochar made from rice husks and corn cobs can increase soil temperature by 5.82% - 10%, acid soil pH of 7.3% - 12.65%, low soil moisture content of 15.49% - 21.42%, and increase the C-Organic content in the soil by 9.9% - 18.81%.
3. Biochar which is made using rice husks improves soil quality slightly better than corn cobs because of the comparison of the larger biochar C-Organic rice husks in the soil where C-Organic is an energy source of microorganisms and is the main adhesive agent for microbes which increases aggregate stability soil that improves soil structure.

ACKNOWLEDGMENTS

The authors thank the management of Laboratory of FMIPA Basic Laboratory in Lambung Mangkurat University and management of Environmental Engineering Laboratory Brawijaya University.

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