

Research Article

The influence of rice husk and tobacco waste biochars on soil quality

Amir Hamzah¹, Ricky Indri Hapsari¹, Rossyda Priyadarshini^{2*}

¹ Tribhuwana Tunggal University, Jl. Telaga Warna, Tlogomas, Malang 65144, Indonesia

² University of Pembangunan Nasional "Veteran", Jl. Raya Rungkut Madya, Gunung Anyar, Surabaya 60294, Indonesia

*corresponding author: ossy.rsd@gmail.com

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Abstract: Heavy metal pollution in agricultural land threatens soil and food quality. Soil pollution could be remediate using biochar, but the effectiveness of biochar on soil quality improvement is determined by types of feedstock and pyrolysis temperature. This study was aimed to explore the effect of different types of biochar on soil properties. Biochar from rice husk and tobacco waste was applied to soil contaminated with lead and mercury. This study was conducted at Sumber Brantas, Malang East Java, and used a completely randomized design with three replicates. Heavy metals content was measured using AAS. The results of measurements were analyzed using analysis of variance at 5% and 1% significance levels. The initial analysis of the soil properties at the research site showed that the soil nutrient status was low, i.e. N (0.2 %), K (0.50 cmol⁺/kg), and CEC (5.9 me/100g) respectively, but soil pH was neutral (6.8). The research site also has crossed the threshold of heavy metal content for Hg (0.5 ppm), Pb (25.22 ppm), Cd (1.96 ppm), and As (0.78 ppm). Biochar added had a positive influence on soil characteristics improvement. It could increase the content of organic C, i.e. 35.12% and 31.81% and CEC (cation exchange capacity), i.e. 30.56 me/100g and 28.13 me/100 g for rice husk biochar and tobacco waste biochar, respectively. However, N, P, and K contents were low i.e. N (0.33 and 0.30 %); P₂O₅ (148.79 and 152 ppm); K (1.58 and 2.11 mg/100g) for rice husk biochar and tobacco waste biochar, respectively.

Keywords: *biochar, heavy metal, remediation*

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Introduction

Heavy metal contamination in agricultural soils and waters has dramatically increased during the last few decades (Rizwan et al., 2016). Heavy metals are among the major environmental pollutants and the accumulation of these metals in soils is of great concern in agricultural production due to their toxic effects on crop growth and food quality. Soil heavy metal pollution poses a risk to the environment and to human health due to biomagnification (increases in metal concentration as the element passes from lower to higher trophic levels) (Roy and McDonald, 2014). Some of these elements can be essential for living organisms while some others are non-essential. Concentrations of essential elements beyond a

certain threshold will have pernicious health effects, cause they interfere the normal metabolism of living systems. Heavy metals are not degradable and hence accumulate in the environment having the potential to contaminate the food chain. This pollution threatens soil quality, plant survival, and human health. The remediation of heavy metals deserves attention but it is impaired by the cost of these processes. For last several years, there has been growing interest in the use of biochar as an amendment. The potential of biochar in immobilizing toxic substances (Mendez et. al., 2012) and recovering soil fertility is well documented. Biochar is a type of charcoal produced by pyrolysis process through conversion of biomass or biowaste at limited

oxygen supply. Biochar could ameliorate soil productivity and absorb heavy metals (Sukartono and Utomo, 2012; Fellet et al., 2014). Biochar application will improve soil water retention, and soil aggregation thus will decrease soil bulk density. It also increased soil pH and nutrient and reduced nutrient leaching (Berek, 2014), and immobilized heavy metals (Bian et al., 2014). However, to support the application of biochar as a soil amendment, a baseline study and data analysis on biomass resources including types of biochar are needed.

Currently, there is limited information on the effect of rice straw and tobacco stalks biochar on soil properties. Rice husks, wood remains, crop residues such as tobacco stalk are regarded as agricultural waste, but recently such solid wastes have been transformed into biochar. The objective of this study was to find the effect of biochar type on soil characteristics.

Materials and Methods

This study was conducted at Sumber Brantas Village, Batu, Malang Regency. Based on the previous research conducted by Hamzah et al. (2017), this study site has been contaminated with heavy metals, such as lead and mercury. This study consisted of three steps, (1) biochar preparation and characterization, (2) soil sampling and characterization; and (3) field experiment.

Biochar preparation and characterization

Two biochar types, i.e. rice husk and tobacco wastes, were used in this experiment. The Rice husk was collected around the study area (at 07045.78°S and 112032.102° E. The Rice farm in this area was unmanaged properly and had already excessive use of inorganic fertilizers. The collected Rice husk was then oven dried at 70°C for 24 hours and sieved to pass through a 1 mm sieve. The Tobacco waste was obtained from discarded cigarette factory waste.

Biochar was produced at Bioenergy laboratory of Tribhuwana Tunggaladewi University, Malang, East Java, Indonesia. Before burning, the raw material was air dried first. Biochar was produced by a slow-burning (carbonation) method at a temperature of 300-400°C with limited oxygen (pyrolysis) for 4 hours. After burning process, biochar was sieved to pass through a 2 mm sieve. The biochar was analyzed their characteristics, i.e. pH (H₂O), organic C (Walkley-Black), Total-Nitrogen (Kjeldahl), total-P (Olsen), total- K, CEC (ammonium acetate pH 7,0).

Field experiment

The field experiment was set up in 2 x 1 m size, the distance between plots was 0.5 m and between block was 1 m. This experiment was arranged in a completely randomized design with three replicates. A total of nine plots were established for this experiment. The plots were maintained in field capacity condition. The plots were then incubated for two months. At the end of this experiment, soil samples were taken for chemical analyses, i.e. pH, nutrient availability, soil organic content, and CEC. The influence of the treatment on heavy metals sorption and soil properties improvement was tested by t-test at 5% and 1% significance levels.

Soil sampling and characteristics

Soil samples were taken randomly on three plots from three different locations. At each plot, a soil sample was taken compositely at two depths (0-20 cm and 20-40 cm). Then, soil sample was dried and sieved to pass through 2 mm sieve, and subjected to laboratory analyses. Soil physical analyses consisted of texture (pipette), aggregate stability (dry or wet sieve), bulk density (Clod), and water content (%). Soil chemical analyzes included pH (H₂O), organic C (Walkley-Black), N (Kjeldahl), total phosphorus (Olsen), total K, CEC (ammonium acetate pH 7.0). Heavy metals contents [lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), cyanide (Cn), and arsenic (As)] were analyzed using Atomic Absorption Spectrometer. Heavy metals content was analyzed using AOAC method (1990).

Two grams of soil sample were added to the digestive tube with 10 mL of concentrated nitric acid (HNO₃) and 5 mL of perchloric acid (HClO₄) and left overnight. Then the sample was heated at 100°C for 1 hour 30 minutes and after increased to 130°C for 1 hour. The temperature for the digestion of both was increased to 150°C for 2 hours 30 minutes (or until all the yellow steam was exhausted). After all the yellow steam exhausted, the temperature was then raised again to 170°C for 1 hour. The final temperature for the digestion of the sample was 200°C for 1 hour (steam white formed). Sample digestion was completed when a white precipitate was formed and 1 mL of a clear solution.

After digestion, the sample was filled with distilled water up to the 10 mL and then filtered through a Whatman filter paper. Analysis of the total concentration of heavy metals from each extract was done by Atomic Absorption Spectrometer with various heavy metal standard solutions as a comparison.

Results and Discussion

Biochar properties

The characteristics of biochar are determined by their source (the type of feedstocks) and their pyrolysis method. Consequently, they will influence physical and chemical characteristics of biochar that determine their function and uses. Some important characteristics of biochar such as density, elemental or nutrient content, surface charge (pH, CEC), are shown in Table 1. Biochar of rice husk was slightly alkaline and it was almost the same with the one used by Carter et al. (2013). The rice husk biochar had high pH (7.4) and low phosphorus content (0.93 ppm). The cation exchange capacity (CEC = 32.33 me/100g biochar) was high, but rice husk biochar had poor exchangeable K (1.92 mg/100g biochar). Tobacco waste biochar was slightly different; it had neutral pH (6.0). It also had a high cation exchange capacity (CEC=29.02 me/100 g biochar), and low content of phosphorus (0.23 ppm) and exchangeable K (2.12 mg/100 g biochar). Both biochars had high organic matter content (31.92% and 40.24%) and high cation exchange capacity (32.33 me/100g and 29.02 me/100 g) for rice husk and tobacco waste biochar, respectively. These characteristics are important in absorbing soil cations needed by plants. Biochar will exhibit natural oxidation through the formation of functional groups, thus enhances sites that are able to retain nutrients and organic compounds (Lehmann, 2007). The oxidation process will

increase O and H, decrease C content, surface negative charges, and formation of O containing functional groups (Cheng et al., 2008). The oxidized biochar bound to soil mineral will suppress the decomposition process and enhances the ability of soil-biochar complex in absorbing organic compounds due to increasing of surface area (Browdowski et al., 2005). The most critical physical properties of biochar in improving soil properties such as soil adsorption capacity and water retention ability, are porosity and surface area (Kalderis et al., 2014). Application of rice husk biochar has been reported to enhance soil sorption capacity and soil water holding capacity (Lei and Zhang, 2013) if the temperature of pyrolysis method is about 500°-800°C. Above 800°C, the surface area and micro pores will be diminished, because Si content on rice husk which would become ash that will block the micro pores of this kind of biochar, resulting in a relatively low surface area. The porosity of biochar was indicated by their bulk density (0.75 g/cm³ and 0.18 g/cm³ for rice husk and tobacco waste biochar, respectively). Biochar chemical and physical characteristics clearly showed that the two biochar types are potential for improving soil properties. Biochar is formed by pyrolysis process on the temperature of 250-500°C. According to Lehman (2007), biochar has a high capability in absorbing nutrients, and persistent as a soil ameliorant. Adding biochar will increase soil fertility and improve quality of the degraded soil.

Table 1. Chemical properties of rice husk and tobacco waste biochars

Biochar types	Chemical Properties					
	pH (H ₂ O)	Nitrogen (%)	Phosphorus P ₂ O ₅ (ppm)	Potassium (mg/100g)	Organic-C (%)	CEC (me/100g)
Rice husk	7.4	0.14	0.93	1.92	31.92	32.34
Tobacco waste	6.0	0.18	0.23	2.12	40.24	29.02

Biochar will enhance soil structure, texture, porosity, soil particle distribution, and density. The molecular structure of biochar has a porous structure and high specific area that cause the high microbe content and stability of chemical. Besides, it will also a perfect site for a microorganism to grow and influence the cation and anion chelation. Based on the above consideration, it is believed that biochar can support plant growth and suppress the heavy metal content. Ferreira et al. (2013) used biochar for remediating heavy metal. Biochar addition did not result in the decrease of the total content heavy metals of the soil, but biochar reduced the

bioavailability and mobility of Cd, Cr, and Pb. The effectiveness of biochar in reducing heavy metals availability is determined by the type of feedstock, the particle size of the feedstock, and the temperature and the condition of pyrolysis. Their characteristics of biochar make some particular material more suitable than others to remediate different heavy metals. Park et al. (2011) found that biochar from chicken manure was proven effective in lowering cadmium and lead content, but not Cu concentration. While green waste biochar was effective to diminish all of the heavy metals. According to Jiang et al.

(2012), biochar was able to suppress Pb and Cu by 18.8 % and 77%, respectively.

Soil properties

Properties of the soil studied varied widely. Soil pH was neutral (6.8). Nitrogen content, potassium content, and CEC were categorized low to medium (Table 2). On the contrary, phosphorus and organic C contents were high (178.7 ppm and 3.0%, respectively). Nitrogen and potassium contents in this area were in line with the result of the studies conducted by Hamzah et al. (2016), i.e. 0.13% and 0.03 cmol⁺/kg, respectively.

Table 2. Chemical properties of the soil studied

Soil Characteristics	Mean (n=3) ± SD	
pH	6.8	± 0.32
N (%)	0.2	± 0.03
P ₂ O ₅ (ppm)	178.7	± 43.96
K (cmol ⁺ /kg)	0.5	± 0.19
Organic C (%)	3.0	± 0.36
CEC (me/100g)	5.9	± 0.17

Note : SD = Standard Deviation

Nitrogen and potassium are essential plant nutrients. Low levels of nitrogen and potassium were probably caused by high production of food, fiber, and crops at the study site so that the nitrogen and potassium elements were depleted. Most crops absorb as much or more potassium than nitrogen. Low contents of nitrogen and potassium will be a limiting factor for plant production (Senapati and Santra, 2009). According to Tilley (2017), nitrogen deficiency depends on nitrogen supply. Generally, nitrogen deficiency tends to occur on soils with low content of soil organic matter. This was observed on the study site, which had a medium content of organic matter (2.6 %). Low content of soil organic matter causes low soil buffering capability on nitrogen, so the nitrogen content becomes diminished. Besides, most of the research site is located on sloping land (the slope is more than 30%), so most of the nitrogen was lost through leaching. Loss of nitrogen by erosion, runoff, and leaching will cause nitrogen deficiency.

Heavy metal availability

Results of analysis of heavy metal contents as soil health indicators showed that soil heavy metal contents have already passed the heavy metal threshold value of U.S.EPA (1993), i.e. Hg (0.5 ppm), Cd (1.96 ppm), and As (0.78); so that the elements were categorized as toxic. However, Cr

(5.7 ppm) and Cn (not detected) were not categorized as toxic because their values did not pass the threshold. Mercury and cadmium are the most dangerous elements compared to others.

Table 3. Soil heavy metal contents

Heavy Metal (ppm)	Mean (n=3) ± SD	
Pb	25.22	± 0.46
Cd	1.96	± 0.09
Hg	0.50	± 0.51
As	0.78	± 0.10
Cr	5.70	± 2.26
Cn	ND	

Note : ND = not detected

The high contents of mercury and cadmium might come from (1) oxidized silica, and (2) accumulation of pesticide residues. Oxidized silica would form acidic compounds. Silica mineral and ferrous silica will form acidic compounds containing toxic elements that will contaminate the environment, such as As, Hg, Pb, and Cd (Herman, 2006). Naturally, cadmium content is below 1 mg/kg (0.4 mg/kg), but the Cd content on the research site passed through the threshold (1.96 ppm). According to Nopriani (2011), the threshold value for cadmium is < 2 mg/kg. The high content of heavy metal is caused by the accumulation of phosphate which applied for a long time (Tresnawati et al., 2014). Most of the fertilizer only 1-5% is absorbed, the remaining will form a residue and becomes toxic for plants. Mercury content in the soil studied also passed through the threshold limits (0.5 ppm). According to Government Rule No.18, 1999 about management of toxic waste and dangerous, the threshold value is 0.01 mg/kg.

Impacts of biochar on soil quality

Application of rice husk and tobacco waste biochar improved the soil properties, except for P₂O₅ content (Table 4). This is in line with Kamara et al. (2015) who reported that application of rice husk biochar improved soil properties by increasing soil pH, organic carbon, and available nutrients. Biochar application to soils improves soil alkalinity and increases the soil pH, even though not all biochars are alkaline. The pH of biochar has been reported to vary from 4 to 12 depending on the pyrolysis conditions and feedstock used (Bagreev et al., 2001). The biochars used in this study were neutral (tobacco waste) to slightly alkaline (rice husk) (Table 1.).

Table 4. Soil analysis after rice husk and tobacco waste biochar application

	Rice Husk Biochar			Tobacco Waste Biochar		
	Mean (n=3)± SD					
pH	7.40	±	0.40	6.57	±	0.32
N (%)	0.33	±	0.04	0.30	±	0.04
P ₂ O ₅ (mg/kg)	148.79	±	52.33	152.00	±	80.88
K (mg/100g)	1.58	±	0.06	2.11	±	0.13
Organic -C (%)	35.12	±	5.10	31.81	±	9.39
CEC (me/100g)	30.56	±	0.17	28.13	±	0.26

Note : SD = Standard Deviation

The biochar increased the soil pH and soil exchangeable cations. Biochar indirectly influences nutrient availability by changing soil pH. Biochar can increase soil pH by 0.5-1.0 units; and nutrients are directly available through the solubilization of the solid biochar residue (Carter et al., 2013). Biochar application significantly raised soil organic matter content from 3% to 35.12% and 31.81% for rice husk and tobacco waste, respectively. Biochar application also raised cation exchange capacity from 5.9 me/100g to 30.56 me/100g and 28.13 me/100g for rice husk and tobacco waste, respectively. The increase of soil organic matter has an important role in soil fertility and agricultural productivity, as it would affect the nutrient availability. Steiner et al. (2007) stated that application of biochar increases plant nutrient availability and soil productivity. Biochar amendments would increase the soil microbial population and their activity, thus improve bioavailability of nutrients (Lehman et al., 2007)

Effect of rice husk and tobacco waste biochars on soil properties

Different types of biochar affect different types of soil in different ways. Rice husk biochar (RHB) used in this study had slightly alkaline pH with a pH of 7.4; this was relatively higher than that of tobacco waste biochar (TWB) (pH = 6.0) due to the high ash content. Rice husk also has high contents of silicon and potassium, nutrients which potential as soil amendments. Organic materials with relatively high carbon content (e.g. wood) are currently used for the production of activated carbon (Mila et al., 2013). Biochar addition increased pH in the RHB, but not in the TWB. Addition of RHB to soil increased the pH by 0.6 units from 6.8 to 7.4, but the pH increase was not significant (=0.095). This is in line with Lu et al. (2014) who found that soil pH will increase by adding rice straw biochar. The RHB biochar could increase soil pH through the hydrolysis of alkaline metal ion, which produces OH⁻ into the soil from the ash of biochar (Glaser et al., 2002). On the contrary, TWB addition only increased 0.2 units

of pH. This is because of the low dosage of TWB. Jiang et al. (2012) stated that when a higher dose of TWB is added, the pH of amended soil will increase by 1.68 units. But, both of the two types of biochar had no differences influence on soil pH, as shown in Table 2. Biochar application could increase soil organic carbon, and CEC (Table 4). Organic matter content of the soil after RHB application was significantly higher than TWB application (=0.1). The carbon content of RHB and TWB was very high, which did not only improve the soil carbon content directly but also improved soil active carbon and soil microbial activities by creating new habitats and changing the soil microenvironment for soil microorganisms (Lehman et al., 2011). The study also showed that application of biochar could increase soil CEC (Table 4.). This was due to the enhancement of soil organic matter content which in turn increased the soil cation availability. Rice husk biochar had a significantly higher EC value than tobacco waste biochar. This means that greater quantities of dissolved ions were present in rice husk biochar than in tobacco waste. High cation exchange capacity is the capacity to bind cationic plant nutrients on the surface of biochar particles, humus, and clay, thus nutrients are available for uptake by plants. Amendments with high cation exchange capacity translate a high buffering capacity. The increase of soil organic matter and soil CEC would also enhance cation availability as shown in Table 4. Results of the study showed that application of rice husk and tobacco waste biochars had a positive impact on nutrient availability. The cation availability, either nitrogen, potassium, and phosphorus contents increased. Nitrogen content increased about 150%; potassium 288-388 %; and for phosphorus about 84% under biochar treatment (rice husk biochar and tobacco waste biochar). In general, rice husk biochar gave better influence on soil properties characteristics compared with tobacco waste biochar. Some literatures showed that rice straw biochar had high pH and good physicochemical properties. However, for all treatments, there were no significant difference

effects of the two types of biochars on the cation availability, nitrogen, phosphorus, or potassium, as shown in Table 4. Nutrient availability, such as phosphorus is strongly related to the soil pH. Phosphorus is a kind of ion that its availability depends on pH value. Rice husk had better capability in serving nutrient than tobacco waste biochar. Rice husk biochar had significantly higher EC than tobacco waste biochar. This means that rice husk biochar biochar had greater quantities of dissolved ions than tobacco waste biochar. The capability of rice husk biochar in serving cation is determined by the ash and silica contents of their biomass.

Conclusion

The nutrient content of the research area was low categorized, especially for N (0.18-0.23)%, K (0.34-0.72) cmol⁺/kg, and CEC (5.70-6.00) me/100g, and the heavy metal content was pass through the threshold value, (i.e. mercury (0.36 – 1.07) ppm, lead (24.76-25.68) ppm, cadmium (1.90-2.06) ppm, and arsenic (0.71-0.89) ppm). Application of rice husk and tobacco waste biochars had positive effect on soil properties, such as increasing of pH, CEC, soil organic matter content, and cation availability

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