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Methods of Reducing the Presence of Heavy Metals and Rehabilitating Soil Polluted by Screen Printing Liquid Waste

I Putu Sujana[a*], **Ni Gst. Ag. Eka Martiningsih**[b], [a,b]Faculty of Agriculture, University of Mahasarawati Denpasar, Bali, Email: [a*]sujana.umd.jp@gmail.com

The solution to rehabilitating land/rice fields that have been contaminated with garment liquid waste is by utilising organic matter such as biochar. This study was conducted in laboratories, in greenhouses and in the fields. Prior to this research, field observations were carried out to assess the distribution of garment sites; to take garment liquid waste which was found to be polluting agricultural land; to undertake secondary data collection (rainfall and subak data); to make a site map; and to collect raw materials for biochar manufacturing. The chemical properties of soil contaminated with screen printing liquid waste contain heavy metals which consists of Pb, Cu, Cd, and Cr. Rice husk biochar shows better potential compared to chicken manure biochar and other organic matters in terms of improving soil properties and thus decreasing the availability of heavy metals. The application of rice husk biochar with a dosage of 12 tons ha-1 can reduce most of the availability of heavy metals in soil. Research which looks at the characteristics of biochar and organic matter and its effect on soil properties and the growth of maize on land degraded by garment liquid waste has never been done before. Therefore, this research has significant originality and its findings can importantly be implemented as the basis for the improvement of soil that has been contaminated with garment liquid waste.

Key words: *Heavy Metal, Incubation Process, Soil Contaminated, Screen Printing Liquid.*

Background

The textile industry is still the backbone of national exports although the value of textile exports declined after the monetary crisis. In early 2015, there was a gradual increase in textile exports, both in the form of cloth and apparel such as garments. The Indonesian Textile Association projected that the export value of apparel products would reach US$13 billion by the end of 2015 or grow by as much as 20% compared to what was realised in 2014, which was US$10.83 billion. The textile industry is expected to add positively to national economic growth. The development of dyeing, screen printing and convection industries have been able to meet the demand for tourist textiles in Bali, and in Denpasar, in particular. This development has been rapid and has been responsible for the creation of many job opportunities. It has also helped increase the exportation of products from Bali. In 2016, textile exports from Bali, in the form of apparel, were worth US$82,026,850. There was an increase over the same period in 2015, which was worth US$74,195,573 (Industry and Trade Office of Bali, 2016).

Purbawangsa et al (2019) state that in Indonesia, corporate governance and corporate profitability have a significant and positive effect on CSR disclosure. According to Hutahayan et al (2019), there are a set of connections between organisational power mechanisms and organisational learning. In particular, we consider that many institutional changes in governmental organisations are quasi-institutionalisations, and are thus fragile, unless efforts are put in place to achieve full institutionalisation, involving, among other things, the use of strategies which reinforce learning. If the textile industry sector is not equipped with wastewater treatment plants it has the potential to cause environmental pollution, especially in the water and land in surrounding agricultural areas. In the Rancaekek Sub-district of Bandung Regency, agricultural land is contaminated with textile wastewater which contains heavy metals with the following concentrations: Pb 15.04 ppm, Cd 0.13 ppm, Cr 19.30 ppm, and Cu 58.0 ppm (Kurnia et al., 2005). These conditions are similar to land in Denpasar which was also found to be contaminated with garment liquid waste. The garment industry's waste generally contains heavy metal compounds which include lead (Pb), cadmium (Cd), copper (Cu), and chrome (Cr). The impacts of the accumulation of heavy metals in the water and the soil are land degradation which result in a decline in the quality (and quantity) of agricultural products. When absorbed by plants, the heavy metals that are contained in garment liquid waste can interfere with their physiological processes.

Hazardous waste that is often created by the textile industry includes a heavy metal called chrome. If textile industrial waste containing chrome is disposed of directly into the environment without prior processing, it results in an increase in the number of metal ions in the water. Drinking water which contains chromium can cause serious health issues due to the accumulation of chromium in the kidneys. In addition, high COD levels in the water indicates that it has been polluted by non-biodegradable organic materials. This has something to do with the high content of surfactants in these wastes while the value of Suspended Solids (TSS) reflects solids that cause turbidity of water, is not dissolved and does not settle, and can inhibit the production of organic substances in water.

Based on the Global Assessment of Soil Degradation (GLASOD) approach, land degradation is shown to be caused by five factors, namely: (1) deforestation, (2) overgrazing, (3) agricultural activities, (4) excessive vegetation exploitation, and (5) bio-industrial and industrial activities. Soil degradation can cause soil damage. In general, soil damage can be classified into three main groups, namely: the deterioration of chemical, physical and biological properties of the soil. Soil chemical damage can occur due to soil contamination processes, accumulation of salts (salinisation), in pollution by heavy metals from garment waste, that are contaminated with organic compounds and xenobiotics, such as pesticides or oil spills (Djajakirana, 2001).

Soil management is one of the most important factors for achieving optimal and sustainable results. Soil management should be therefore be pursued without causing damage to the environment or degrading the soil quality, and should be directed towards the optimum improvement of the physical, chemical, and biological properties of the soil. The interaction between the biotic and abiotic components of the soil on the land provides an optimal balance for the availability of nutrients in the soil, which ensures the sustainability of land productivity, and the success of farming. By way of this system, a stable agroecosystem can form, with minimum input, which can increase the growth and yield of plants without degrading the quality of the environment.

Based on data from the BPS (Central Bureau of Statistics) of Denpasar (2013), there was 2,597 ha of agricultural land , with 41 *subak* water management (irrigation) systems for the paddy fields on the island of Bali. Subak areas whose land was contaminated with garment liquid waste from dyeing, screen printing and convection industries were mostly found in South Denpasar Sub-districts, which included *Subak Kerdung* (215 ha), *Subak Kepaon* (119 ha) and *Subak Cuculan* (99 ha). The result of preliminary research showed that garment liquid waste polluting agricultural land in Denpasar contains heavy metals such as Cu, Pb, Cd and Cr, with a Cr concentration value that is above the pollution threshold, and organic C and Total N values that are low (Attachment 1). When the soil is planted, plants accumulate these hazardous substances and compounds, which can then have a negative impact on those who consume the end product.

The cultivation of maize crops in the rice fields of South Denpasar is not in accordance with its potential and suitability. The water used to irrigate the crops is also contaminated by garment liquid waste. In 2011, the maize harvest covered an area of 309 ha, which produced 5,935 tons ha of maize [1]. In 2012, the area of harvest and its production remained at 5,935 ton ha^{-1}. The maize plants in South Denpasar are mostly grown on land contaminated with garment liquid waste (Agriculture Office of Denpasar City, 2013).

One solution for overcoming this problem and rehabilitating land/rice fields that have been contaminated with garment liquid waste is by utilising the potential of organic matters such as biochar. The addition of biochar (derived from the combustion of agricultural waste with limited oxygen) has good potential as a soil enhancer, since organic C still persists in black carbon and has long-term effects in chelating metallic elements (Ferizal & Basri, 2011). This statement is supported by the results of research conducted by Chan et al., 2007, which showed that biochar applications can increase organic C, pH, structure, CEC (Cation exchange capacity), and the groundwater storage capacity of soil. Several other research results also showed that biochar applications on soil can improve the yields of maize, cowpea, and peanuts (Yamato et al., 2006), soybean crops (Tagoe et al., 2008), rice yields in the highlands (Asai et al., 2009) and rice yields from acid sulphate soil (Masulili, 2010). Fernandes, et al (2019) state that good governance will affect agricultural policy. Fernandes & Taba (2018) also state that government policy will affect workforce competitiveness positively.

The addition of organic ingredients and recycling actions provides great advantages. Typical compounds capable of contributing to the formation of complex compounds and ion exchange in organic matter are those which belong to functional groups such as carboxyl (-COOH), hydroxyl (-OH), carbonyl (=C=O), methoxyl ((-OCH_3), and amino (-NH_2). One type of organic matter that can be utilised for biochar materials is the waste from rice husk and chicken manure, both of which are readily available locally.Rice husk biochar and chicken manure biochar have different physical and chemical characteristics that allow for the improvement of soil properties that have been degraded by garment liquid waste. Research into the characteristics of biochar and organic matter and its effect on soil properties and the growth of maize on land that has been degraded by garment liquid waste has never been done before. This research is therefore of great importance and can be implemented as the basis for the improvement of soil that has been contaminated by garment liquid waste.

Land that has been contaminated by screen printing waste contains heavy metals such as Cu, Pb, Cd and Cr withconcentrations in the range of pollution values as well as organic C and N total values which are low. The soil's ability to supply nutrients, store water, modify pollutants and resist degradation is strongly influenced by the content of organic matter present in the soil. The heavy metal uptake by plants can be moderated by adding organic matter, since organic matter has functional groups capable of chelating metal (Brown et al., 2004; Zhang et al., 2013). The impact of heavy metal pollution can be suppressed when the metal is in an unavailable form.

Previous studies have reported that the impact of biochar applications on soil productivity depends on the nutritional content of biochar (Chan et al., 2007, 2008) and the pyrolysis temperatures (Chan et al., 2008). This is due, in part, to changes in the composition of chemical elements that make the elements less available. In addition, there is a decrease in nutrient availability due to the high pH of soil as a result of biochar applications (Chan & Xu, 2009). Applications of poultry biochar produced at 450 °C in soil resulted in higher radish production than biochar produced at 550 °C. This is due to a decrease in the availability of P on biochar produced at higher temperatures (Chan et al., 2008). According to Fernandes & Solimun (2017) uncertainty has an indirect effect on the environment on business performance and has insignificant value.

The addition of biochar as a soil enhancer derived from the combustion of agricultural waste with limited oxygen shows good potential as a soil amendment material, since organic C still persists in black carbon and has long-term effects in chelating the metallic elements (Zhang et al. , 2013; Wang et al., 2010; Liu et al., 2011; Xu et al., 2013). This is supported by the results of research conducted by Chan et al. (2007), which showed that biochar applications can increase organic C, pH, structure, CEC, and the groundwater storage capacity of soil. Increased crop yields through biochar use also occurred in maize, cowpea, and peanuts (Yamato et al., 2006), Soybeans (Tagoe et al., 2008), rice yields in the highlands (Asai et al., 2009) and rice yields from acid sulphate soil (Masulili, 2010).

Typical compounds capable of contributing to the formation of complex compounds and ion exchange in organic matter are the presence of functional groups such as carboxyl (-COOH), hydroxyl (-OH), carbonyl (=C=O), methoxyl ((-OCH_3), and amino (-NH_2). One type of organic matter that can be utilised for biochar materials is the waste of rice husk and chicken manure which is readily available locally. Rice husk biochar and chicken manure biochar have different physical and chemical characteristics that allow for the improvement of soil properties that have been degraded by screen printing liquid waste.

Material and Methods

This study was conducted in laboratories, in greenhouses and in the fields. Prior to this research, field observations were carried out to assess the distribution of garment sites; to take garment liquid waste that was found to be polluting agricultural land; to undertake secondary data collection (rainfall and subak data); to make a site map; and to collect raw materials for biochar manufacturing. Laboratory studies concerning soil analysis, quantitative analysis of the characteristics of rice husk biochar, chicken manure biochar, rice husk and chicken manure, were conducted at the Soil Science Laboratory of the Faculty of Agriculture of Udayana University. On the other hand, qualitative analysis was carried out at the Joint Mathematics and Science Laboratory. Total microbial analysis was conducted at the Microbiology

Laboratory of Mathematics and Science. SEM (Scanning Electron Microscope) analysis was conducted at the Civil Engineering Laboratory and heavy metal analysis was carried out at the Technical Implementation Unit of Analytical Laboratory of Udayana University. The pot experiment was conducted in the greenhouse of the Faculty of Agriculture of Udayana University from April 2 to July 7, 2017.

Table 1: Organic Matter Properties

Organic Matter	**Properties**
Chicken Manure	Chicken manure is organic matter that affects the physical and chemical properties of soil so as to stimulate plant growth. This manure has high levels of nutrients and organic matter and low water content. Each chicken can produce excreta which amounts to approx. 6.6% of the body weight per day (Taiganides, 1977). Chicken manure contains nutrient contents of 1% N, 0.80% P, and 0,40% K, as well as 55% water content. (Lingga, 1986)
Rice Husk	Rice husk contains SiO2 (52%), C (31%), K (0.3%), N (0,18%), F (0,08%), and calcium (0,14%). It also contains other elements such as Fe2O3, K2O, MgO, CaO, MnO and Cu in small quantities and several types of organic matter. High silicate content can be beneficial for plants because it makes plants more resistant to pests and diseases due to tissue hardening.
Chicken Manure Biochar	Chicken Manure Biochar is solid matter resulting from biomass carbonisation processes. Biochar is a porous charcoal substance, often called charcoal from chicken manure. This substance can improve the physical properties of soil, including an increase in soil aggregation, water binding capacity, and the strength of soil along with its chemical properties, for example, increased pH, C, Na, K, Ca, Mg, CEC and P, and decreased Al (Chan et al., 2007).
Rice Husk Biochar	Rice Husk Biochar is solid matter resulting from a biomass carbonisation processes. Biochar is a porous charcoal substance, often called charcoal from Rice Husk. This substance can improve the physical properties of soil, including the increase in soil aggregation, water binding capacity, and the strength of soil along with its chemical properties, for example, increased pH, C, Na, K, Ca, Mg, CEC and P, and decreased Al (Chan et al., 2007).

This study was conducted in a greenhouse, using a split-plot design with 3 replications. The main plot contained a type of organic matter consisting of four types, namely:
P = Chicken Manure
Q = Rice Husk
R = Chicken Manure Biochar
S = Rice Husk Biochar

While the sub-plot contained a dose of organic matter consisting of five levels, namely,
D0 = Control
D1 = 18 g pot^{-1}
D2 = 36 g pot^{-1}
D3 = 54 g pot^{-1}
D4 = 72 g pot^{-1}

The implementation of field trial activity was conducted between August 2017 and November 2017 on a paddy field which was degraded by garment liquid waste, located in Subak Cuculan of Pemogan Village, Denpasar Sub-District. The types of variables set out in this study, to test the proposed hypothesis included: soil, plant, biochar characteristics, and organic matters (quantitative and qualitative). Soil variables included the physical, chemical, and biological parameters of the soil. Qualitative variables included FT-IR and SEM. Plant variables included plant height parameters, number of leaves, total wet weight of plants, total oven dryed weight of plants, yield of wet maize seed per pot, yield of wet maize seed per tile and yield of wet maize seed per hectare.

The parameters of the physical properties of the soil included: Soil Texture, Soil Water Level, Soil Volume, Porosity or Soil Pore Space, and Soil Specific Gravity. The parameters of the chemical properties of the soil included: Electrical Conductivity, pH value, Phospor, Potassium, Available Nitrate, Transferable Cations, and Availability of heavy metal such as Pb, Cd, Cu, and Cr. The parameters of the biological properties of the soil included: Organic C of soil (%), and the total number of soil microbes (CFU g^{-1}).

Plant variables included: 1) Plant height (cm): Observation of plant height was done by measuring the height of the plant from the ground to the end of the growing point starting from the age of two weeks after planting with a two-week interval until the maximum plant height. 2) Number of leaves: Observation of the number of leaves was done by counting the number of leaves that were fully open and green with a two-week interval from planting until the harvest period, 3) Total wet weight of the plants (g): Observation was done once at harvest period by weighing all parts of the plant consisting of roots, stems, leaves, and cobs. 4) Total oven dry weight of the plants (g): Observation was done once after the harvest period, by weighing 100 g of the total wet weight of the plants, then the value of the total oven dry weight was converted to the total wet weight of the plants. 5) Wet weight of seeds per pot (g): Observation was done once after the harvest period, by weighing all the seeds of the harvest from the plants in the pot. 6) Wet weight of seeds per tile (kg): The calculation was done once at harvest time, by weighing all the wet weight of seeds on the existing plant in the tile. 7) Wet weight of seed per hectare (ton): This was calculated by converting the wet weight of the seeds per tile to hectare. 8) The content of total heavy metal which consisted of Pb, Cu, Cd, and Cr on seeds and on corn stover by using the wet ashing method, using HNO_3 and H_2SO_4. The extract was analysed by the AAS tool. The AAS (Atomic Absorption Spectrophotometer) tool used in this research is the Shimadzu AA 700 brand. The analysis of heavy metals was carried out using an Atomic Absorption Spectrophotometer (AAS) based on the Lambert-Beer law which stated that the amount of light absorbed is directly proportional to the substance content. What absorbs light is an atom, and heavy metal ions or compounds must be converted into atomic forms.

The characteristic variables of biochar and organic materials are quantitative and qualitative. The quantitative parameters of biochar and organic matter which were observed were almost the same as the soil parameters. They were qualitatively characterised by spectrum analysis by FT-IR (Fourier Transform Infrared) Spectrometry to obtain a qualitative description of the functional groups and their group names, by smoothing the material to be analysed into polders, then KBr compounds were added with a ratio of 1:3, and the mixture was stirred until homogeneous. This was then pressed into a thin solid pellet, and the spectrum of the aromatic compound was analysed by inserting it into the Infrared Spectrometer. The differences in morphology and the surface microstructure of rice husk biochar and chicken manure biochar were analysed using a SEM (Scanning Electron Microscope).

Field observation activities were carried out to obtain secondary data relating to subsequent research activities. The secondary data which was sought included data about rainfall, subak number, agricultural land area in Denpasar City, land use, maize production per year and a map of the research location. Besides this, samples of soil contaminated with garment liquid waste, uncontaminated soil, and garment liquid waste that entered into the irrigation channel were also taken. In addition, preparation of organic matters for biochar and rice husk biochar as well as chicken manure biochar was also conducted in this study.

Samples of soil, garment liquid waste, organic matters and biochar were taken from the field to conduct an initial quantitative analysis to establish the initial characteristics of each sample. Samples of soil and garment liquid waste were analysed in the Soil Laboratory of the Faculty of Agriculture of Udayana University and in the Analytical Laboratory of Udayana University. The type of parameters in the analysis was in both types of samples. As for the sample of biochar and organic matters, quantitative and qualitative analysis was done in the Joint Mathematics and Science Laboratory of Udayana University. On the other hand, SEM

(Scanning Electron Microscope) analysis of biochar was conducted at the Civil Engineering Laboratory of Udayana University.

Data analysis on the variables tested was analysed by Analysis of Variance (ANOVA) according to the design used. If there was a significant interaction effect on the observed variables, then researchers would proceed with Duncan's multiple-range test with a 5% error rate, so if only a single factor effect is real, then researchers would proceed with Duncan's multiple-range test with a 5% real level. To determine the optimum dosage of biochar and organic matters, regression analysis was performed.

Results and Discussion

Physical, Chemical and Biological Properties of Soil Prior to Treatment

Samples of soil which was analysed for physical, chemical and biological properties was taken from a depth of 15-20 cm from two different places. Uncontaminated soil was taken from an upstream area in Second Subak of North Denpasar. On the other hand, contaminated soil was taken from Subak Cuculan of South Denpasar. The results of the analysis are presented in Table 2. The results of the analysis in Table 2 showed that the chemical properties (total concentrations of heavy metals such as Cu, Pb, Cd and Cr) were higher in the contaminated soil compared to the uncontaminated soil. The P value was available, K was available, and the pH was higher in contaminated soil than in uncontaminated soil. While the value of CEC and BS (Base Saturation) in the uncontaminated soil was higher than the contaminated soil, the N total value was equally low. Similarly, from the physical properties, it was visible that the uncontaminated soil had faster permeability, had a large capacity of water content and had a higher content weight value than the contaminated soil. When viewing the texture, the contaminated soil had a texture of clay, while the uncontaminated soil had a texture of dusty clay. The results of the soil biological properties analysis showed that the value of organic C was equally low.

Table 2: Physical, Chemical and Biological Characteristics between Land Polluted by Liquid Waste Garments with Non-Polluted

	Soil	
Chemical Properties	**Polluted**	**Not polluted**
pH H_2O	6.800	5.700
P Bray-1 (available ppm)	101.020	26.600
K Bray-1 (available ppm)	325.350	212.550
KTK (me/100g)	25.830	33.540
KB (%)	93.690	97.300
Cu (ppm)	36.588	20.286
Pb (ppm)	33.358	25.827
Cd (ppm)	0.732	0.698
Cr (ppm)	3.919	2.010
N total (%)	0.140	0.100
DHL (mmhos/cm)	3.970	5.780
Physical Properties		
Soil Water Level KU (%)	16.340	13.310
Soil Water Level KL (%)	30.680	32.330
Permeability	5.301	18.028
Content Weight (g/cm^3)	1.187	1.181
Texture	Clay	dusty clay
Sand (%)	48.800	24.460
Dust (%)	39.770	50.360
Clay (%)	11.440	25.180
Biological properties		
C- Organic (%)	0.450	0.440

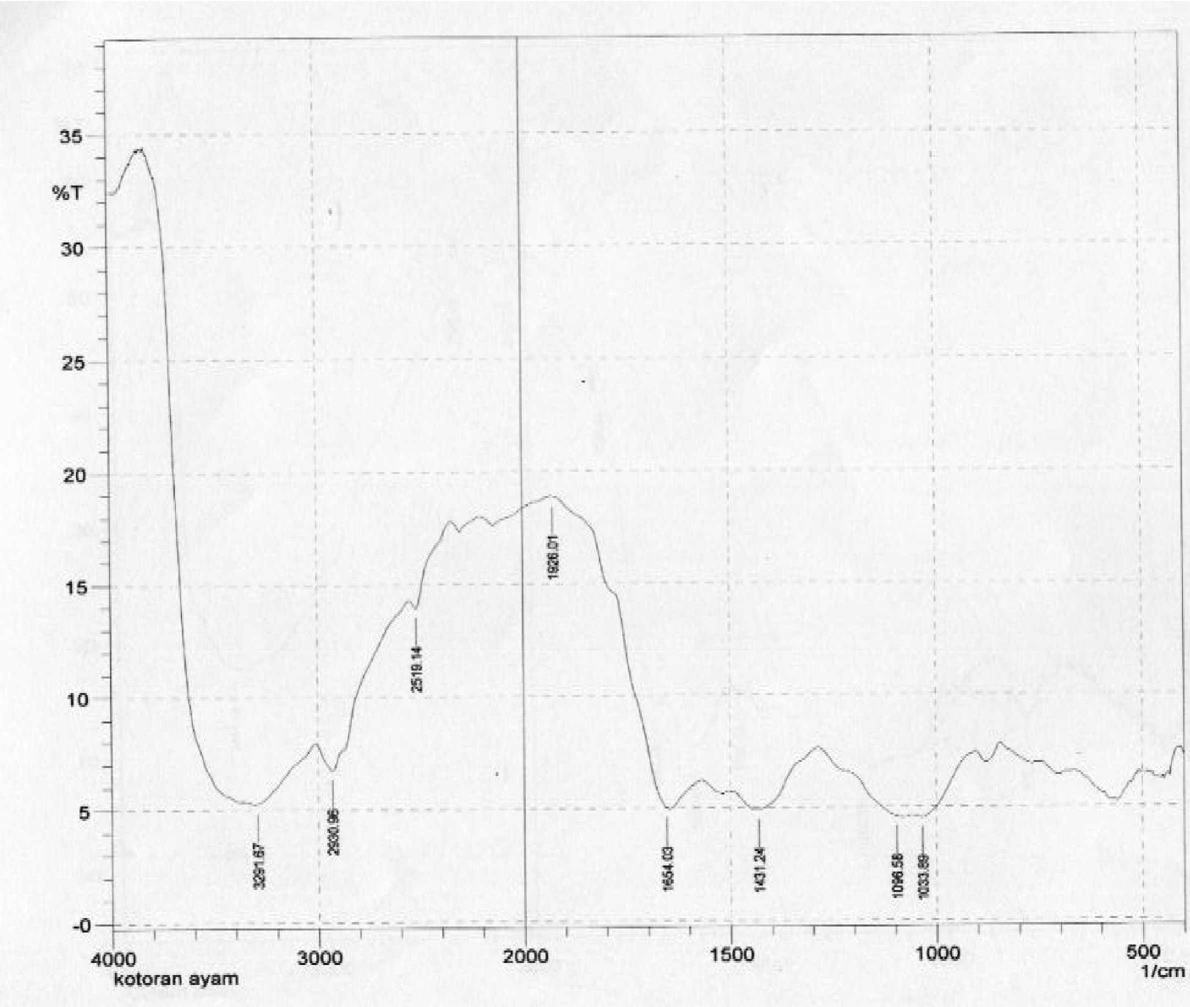
Characteristics of Biochar and Organic Matters (Quantitative and Qualitative)

The results of the laboratory analysis of the initial characteristics of biochar and organic matters (quantitative) as listed in Table 2 showed that the value of Cation Exchange Capacity (CEC) on chicken manure biochar was higher than the rice husk biochar. The rice husk biochar had a pH of 8.110, a total K content of 37.220%, and the K was available on 900.700 ppm which was relatively higher than chicken manure biochar, except in the organic matter of chicken manure. A content of Ca was 63.830%, which was also relatively higher, was found in rice husk. The total N content in chicken manure was 0.260%, and after it was converted to chicken manure biochar, the N content decreased to 0.170%. Similarly, the total N of rice husk after it was converted as biochar decreased from 0.350% to 0.230%. The Ca content of rice husk of 63.830% decreased to 61.150% after it was converted into biochar. The content of the Mg element was only found in the chicken-based biochar, which was 3.080%. The Si content in rice husk and biochar could not be detected by this method of analysis, whereas rice husk was classified as a high silicon-containing plant, as well as its biochar, as reported by Karyasa (2012) that biochar (black ash) rice husk contained 31.200% of Si.

Characteristics of Biochar and Organic Matters (Qualitative)

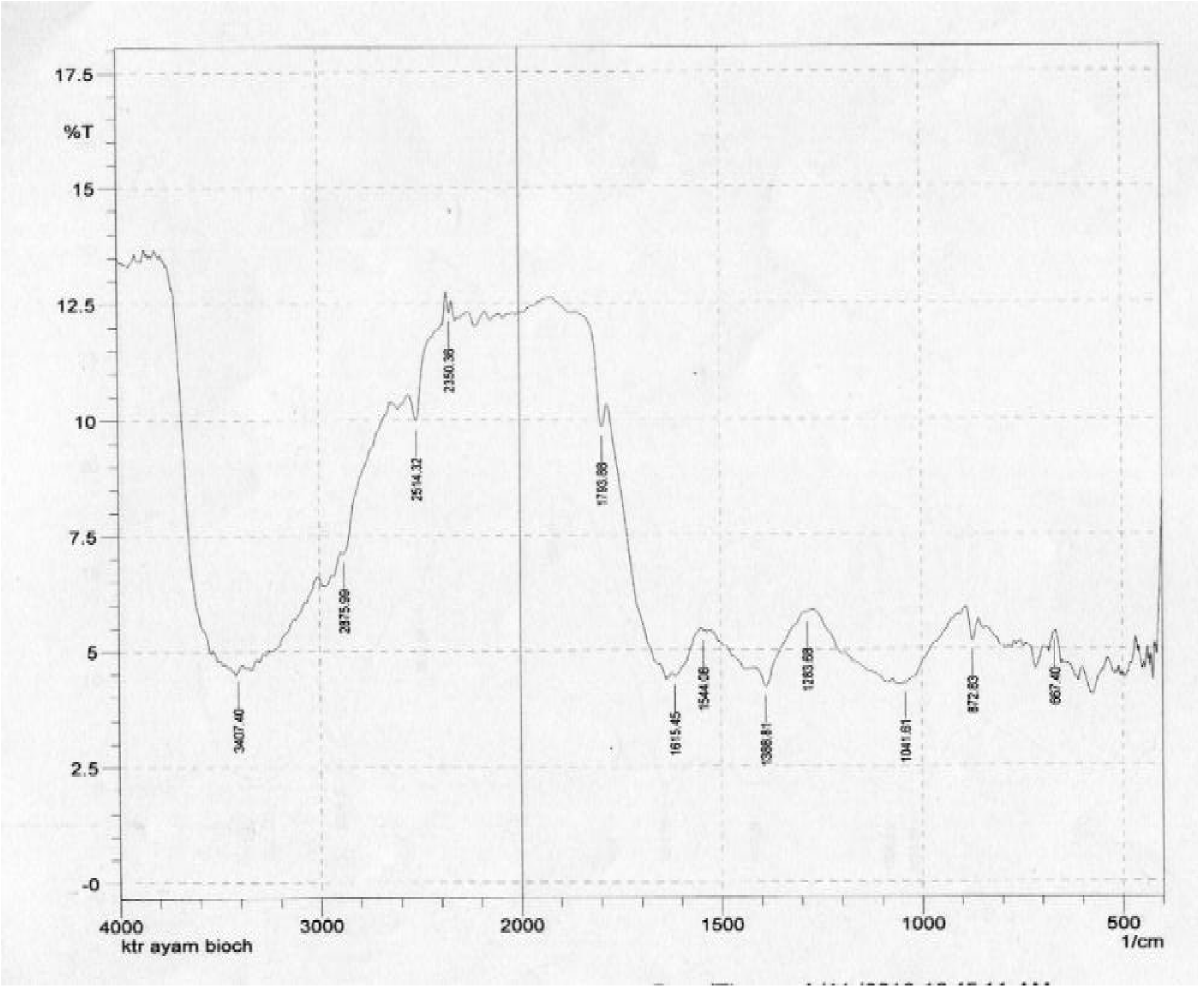
FT-IR spectrum analysis was performed to obtain a qualitative picture of the aromatic degree and functional group name contained in chicken manure, rice husk, chicken manure biochar and rice husk biochar. Infrared spectra analysis of chicken manure and chicken manure biochar showed some functional groups. The spectra of FT-IR analysis on chicken manure and chicken manure bichar showed significant differences (Figure 1 and 2). Qualitatively, regarding the analysis of spectra (FT-IR) for organic matter of chicken manure and chicken manure biochar as shown in Figure 1 and 2, it was identified that there were some functional groups in chicken manure, i.e. in the absorption of the stretching band of 3291.670 cm^{-1} with a functional group of (O-H) that may be possessed by an alcohol compound, hydrogen bond, or phenol; in the absorption of the stretching band of 2930.600 cm^{-1} with a functional group of (C-H) that was commonly possessed by alkane compounds; in the absorption of the stretching band of 2519.140 cm^{-1} with a functional group of (O-H) that was possibly owned by compounds with hydrogen bonds, and/or carboxylic acids; in the absorption of the stretching band of 1654.030 cm^{-1} with the functional group of (C=C) that was commonly possessed by alkene compounds; in the absorption of the stretching bands of 1431.240 cm^{-1} with the functional group of (C-H) that was commonly owned by alkanes.

Figure 1. (FT-IR) Spectrum of Chicken Manure Organic Matters



In chicken manure biochar, the results of FT-IR spectra analysis identified the presence of N-H bonds in the absorption of the stretching band of 3407.400 cm^{-1} that was likely to be possessed by amine or amide compounds; in the absorption of the stretching band of 2875.990 cm^{-1} with a functional group of (C-H) with a type of alkane compound; in the absorption of the stretching band of 2514.320 cm^{-1} with a functional group of (O-H) with a type of carboxylic acid hydrogen bonding compound; in the absorption of the stretching band of 1544.080 cm^{-1} with a functional group of (C=C) that was commonly held by compounds containing aromatic rings, i.e -C=C- alternating rings resulting in electron delocalisation; in the absorption of the stretching band of 1615.450 cm^{-1} with a group of (C=C) that was possessed by alkene compounds; in the absorption of the stretching band of 1388.810 cm^{-1} with a functional group of (C-H) that was commonly possessed by alkane compounds; in the absorption of the stretching band of 1283.680 cm^{-1} with a functional group of (C-N) that was generally owned by amine or amide compounds.

Figure 2. (FT-IR) Spectrum of Chicken Manure Biochar



Based on a FT-IR spectra analysis of chicken manure and chicken manure biochar, the occurrence of pyrolysis or burning resulted in the oxidation of -C-H, -N-H and –O-H groups into -C=O, -C-N-, and -C=C- aromatics (delocalisation). The presence of a ring-containing bond within the -C=C- aromatic group indicated the occurrence of a carbonation or graphitisation process (the release of water molecules in carbohydrate compounds into carbon chains containing C-C and alternate C=C), thus affecting the related chemical properties with its ability to bind heavy metal ions.

Infrared spectrum analysis on rice husk organic matters and rice husk biochar showed an indication of changes in some functional groups due to pyrolysis of the rice husk into rice husk biochar (Figure 3 and 4). The absorption of the stretching band of 3441.160 cm^{-1} was identified as a functional group of (-N-H) that was possessed by amine and/or amide compounds; absorption of the stretching band of 1707.080 cm^{-1} was identified as a functional group of (-C=O) which may be possessed by aldehydes, ketones, carboxylic acids, or esters; absorption of the stretching band of 1503.580 cm^{-1} was identified as a functional group of (-C=C-) that was possibly possessed by a carbon compound with an aromatic ring (a ring with C-C and C=C alternating bonds); absorption of the stretching band of 1206.530 cm^{-1} with a functional group of (-C-N-) which possibly belonged to amine and/or amide compounds; absorption of the stretching band of 808.210 cm^{-1} with a functional group of (-C-H) was generally owned by alkane compounds. In rice husk biochar, the following was identfiied: absorption of the stretching band of 3554.810 cm^{-1} identified as a functional group of (-O-H) of the hydrogen bonding compound of phenol; absorption of the stretching band of 3392.790 cm^{-1} with the functional group of (-N-H) of amine, amide compound; absorption of the stretching band of 2223.920 cm^{-1} with a functional group of (-C≡N) of nitrite compound; absorption of the stretching band of 1699.290 cm^{-1} with a functional group of (-C=O) a type of aldehyde, ketone, carboxylic acid, and esther compounds; absorption of the stretching band of 1550.770 cm^{-1} with a functional group of (-C=C-) identified the presence of carbon compounds with aromatic rings (i.e. rings having C-C and C=C alternating bonds); absorption of the stretching band of 964.410 cm^{-1}, and 804.320 cm^{-1} with a functional group of (-C-H) of the alkene compound.

When using other references, the absorption in the range of 900 - 1000 cm which $^{-1}$ appeared in the FT-IR biochar spectra showed the presence of Si-O-Si bonds (Simanjuntak, et al., 2012). Similarly, the absorption in the range of 800 - 900 cm^{-1} that appeared in the FT-IR rice husk spectra and rice husk biochar identified the presence of Si-O-C bonds (Simanjuntak et al., 2012) in both organic matters. Thus, rice husk and rice husk biochar contain silicon in the form of Si-O-C or Si-O-C.

Figure 3. (FT-IR) Spectrum of Rice Husk Organic Matters

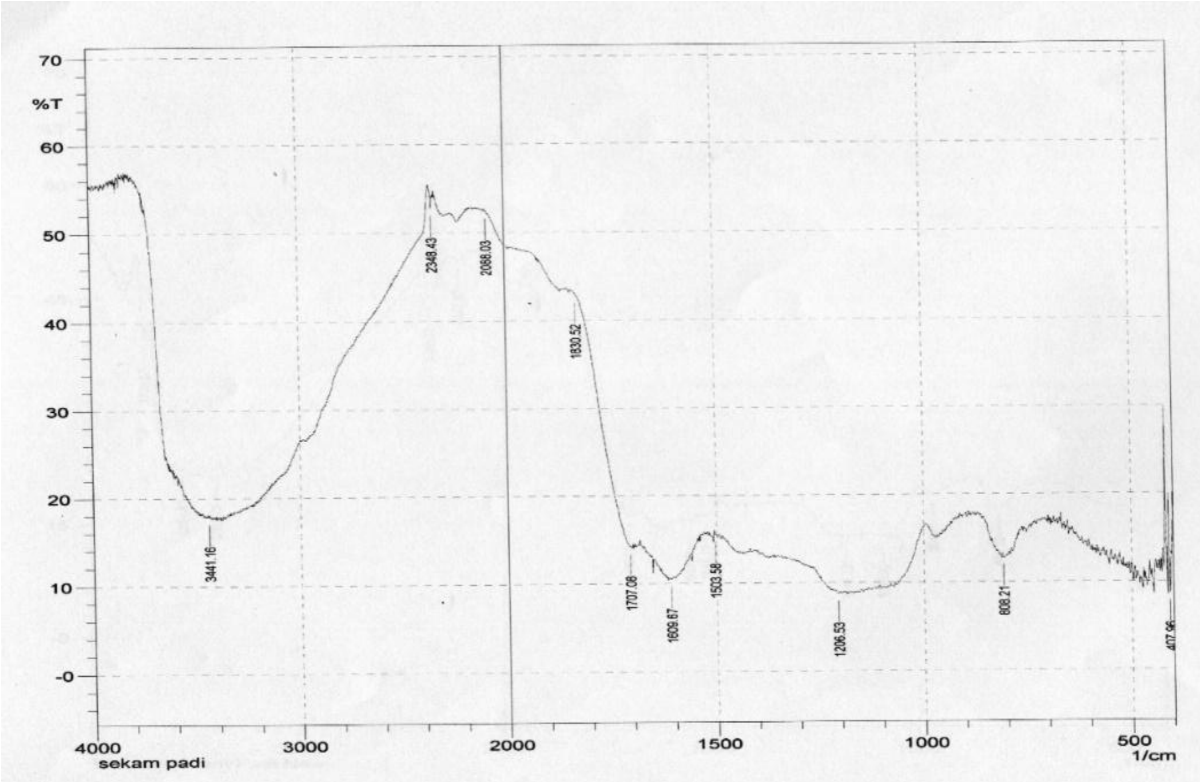
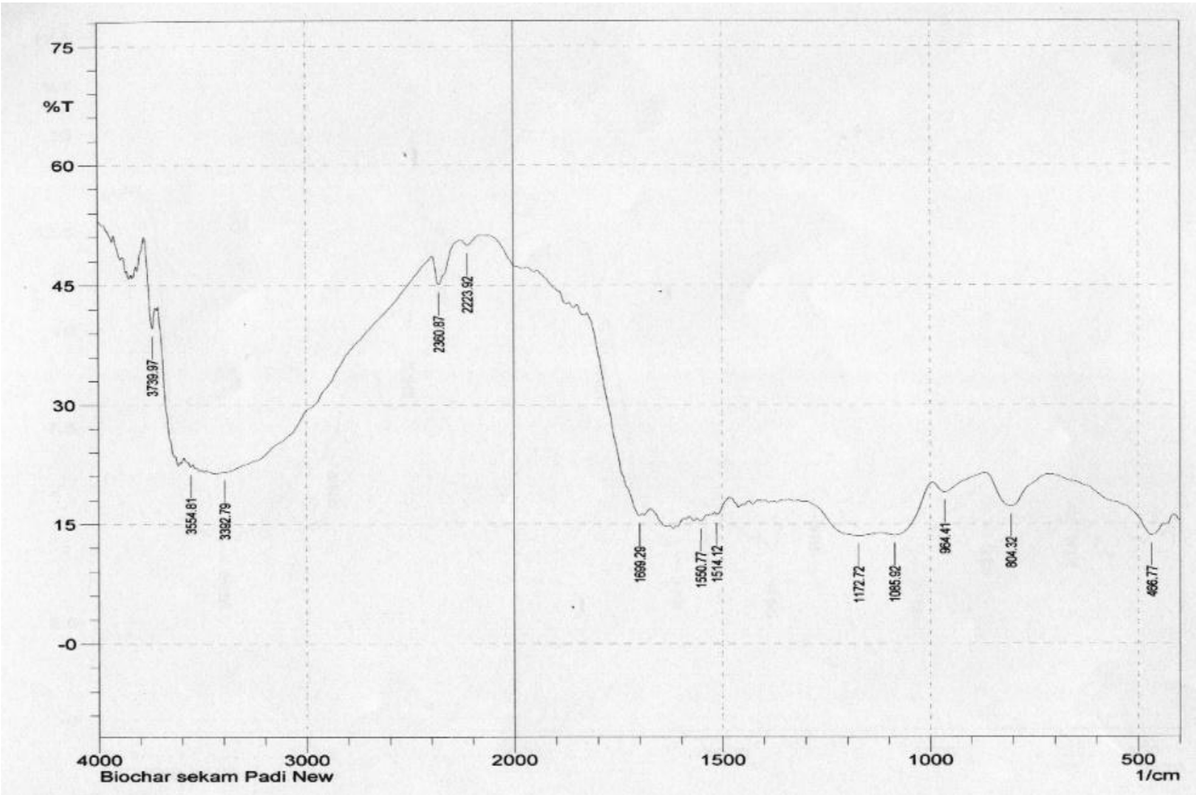
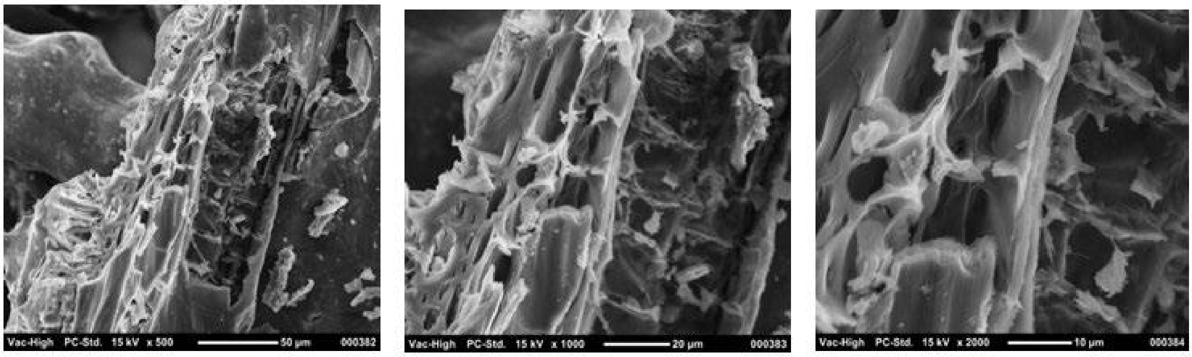


Figure 4. (FT-IR) Spectrum of Rice Husk Biochar



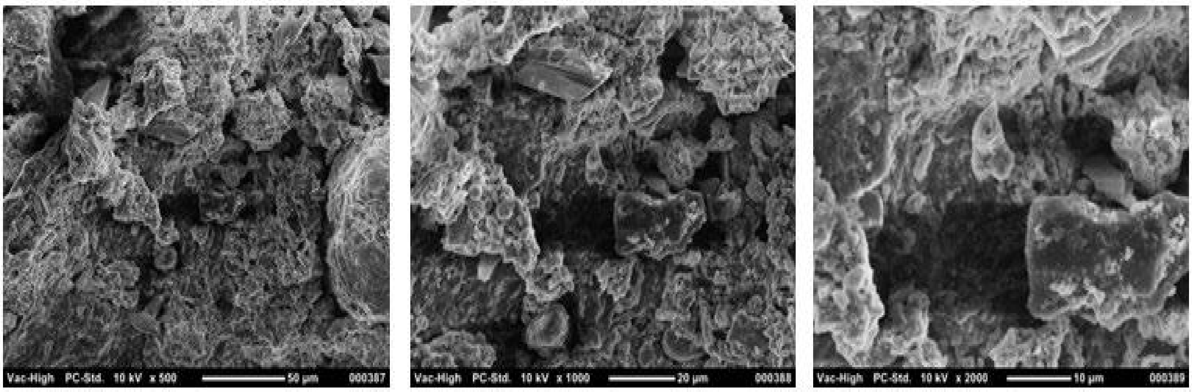
The result of the characterisation analysis of chicken manure biochar with rice husk biochar through photos of SEM with various magnification obtained differences in morphology and microstructure. The results of the characterisation of chicken manure biochar through SEM photographs with a magnification of 2000 times obtained results from a morphological view, namely: there were many visible open pores with granules of irregular shapes and sizes but the pores were smaller than the rice husk biochar in the same area size of 10 µm. The microstructure of rice husk biochar appeared to be neatly arranged and homogeneous with a stable framework, while the microstructure of chicken manure biochar was more irregular and fragile. Based on the shape and size of the pores, chicken manure biochar had a smaller absorption power compared to the rice husk biochar.

Figure 5. SEM Biochar Photo of Rice Husk with 500 to 2000x Enlargement



(a) 500x (b) 1000x (c) 2000x

Figure 6. SEM Biochar Photo of Chicken Manure with 500 to 2000x Enlargement

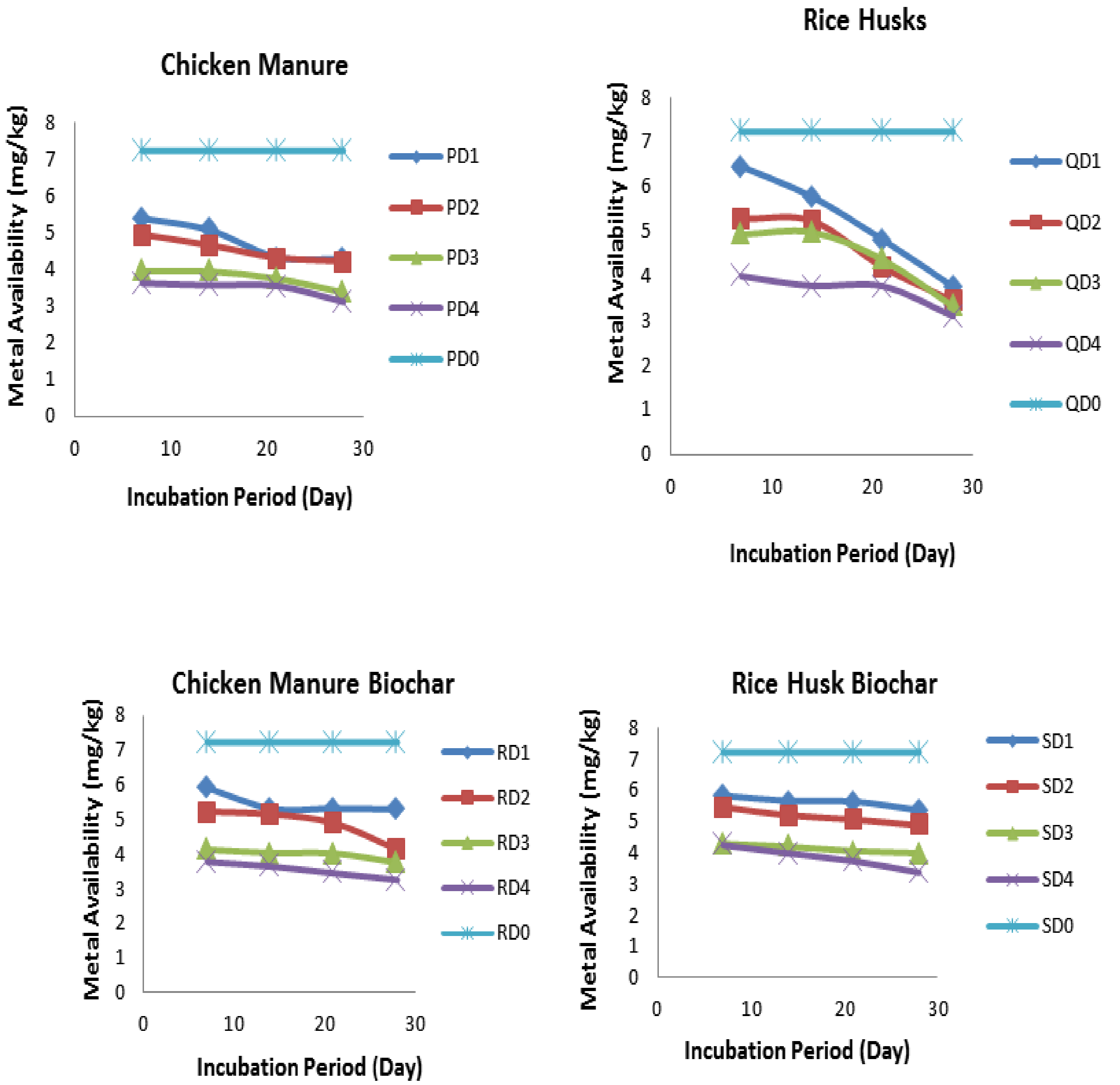


(a) 500x (b) 1000x (c) 2000x

The Effect of the Dosage and the Organic Material Types on the Heavy Metal Availability during Incubation

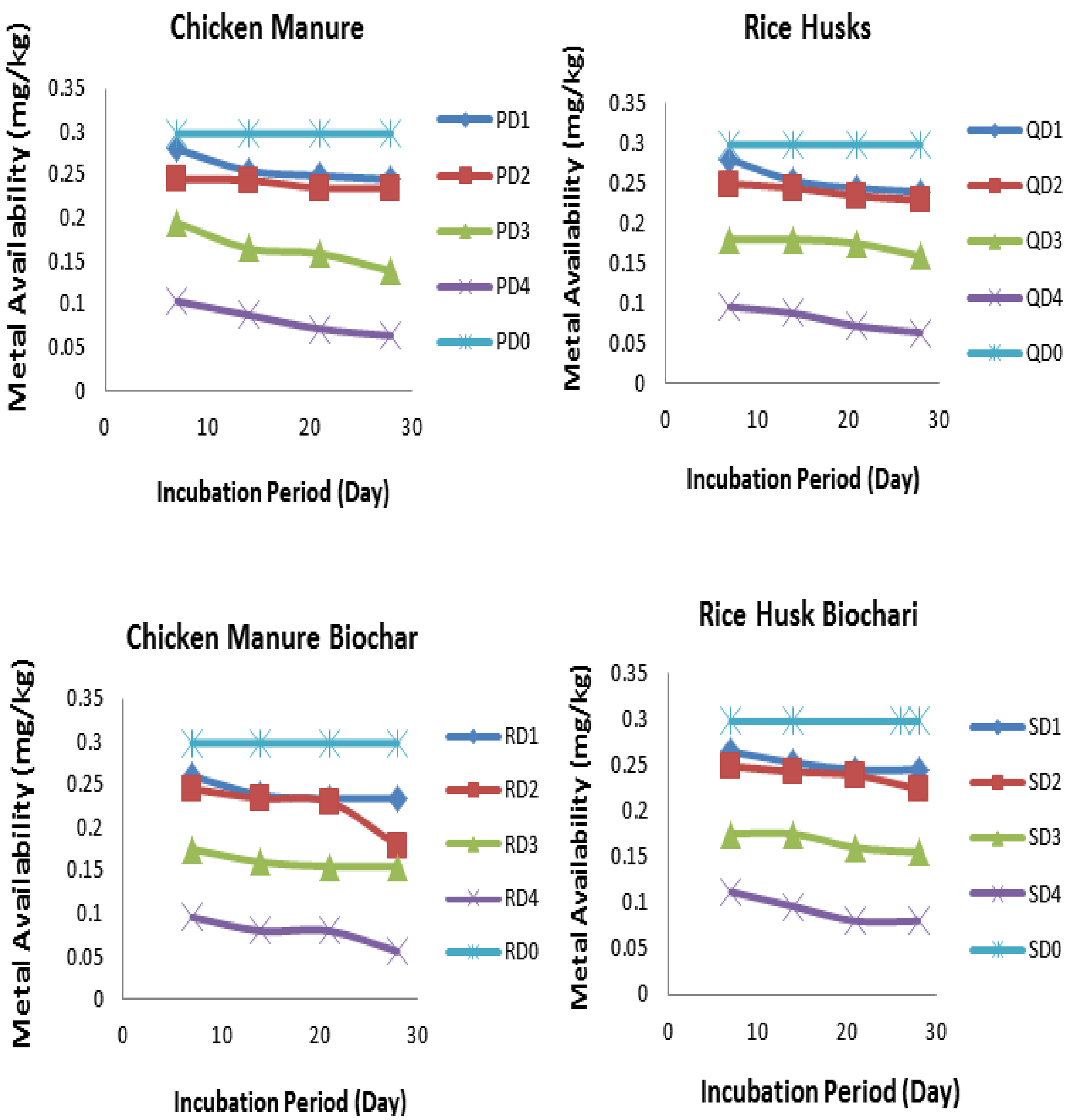
The effect of dosage and the chicken manure organic material (P), rice husks (Q), chicken manure biochar (R), and rice husks biochar (S) on the availability of Pb in the soil during incubation showed that the higher dosage of organic material was followed by a longer incubation period of Pb availability in the soil to decrease. The 72 g pot^{-1} dosage gave the lowest value of metal availability and the highest was 18 g pot^{-1} dosage (Figure 7).

Figure 7. The Development of Pb Availability Caused by the Organic Material Dosage



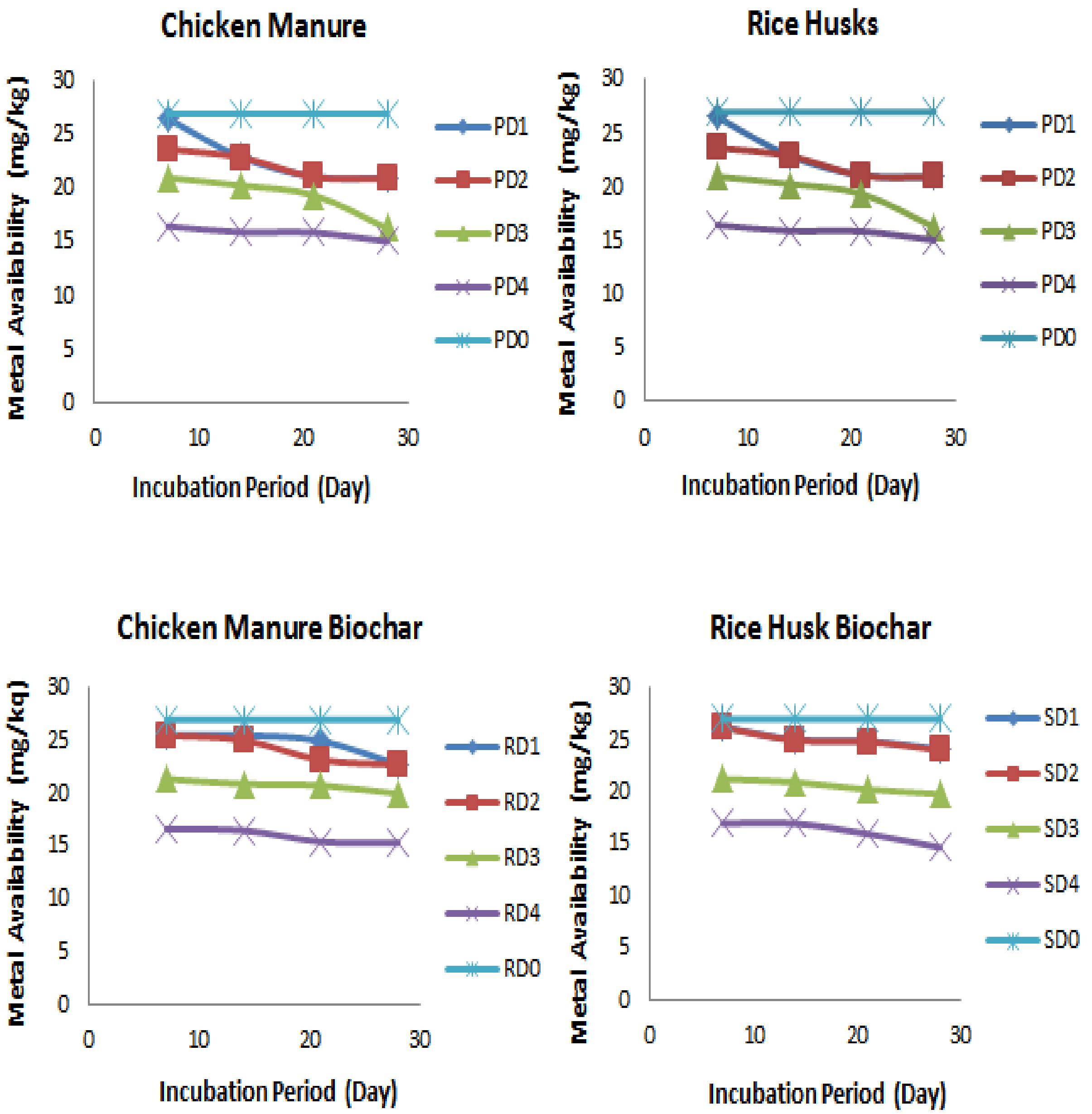
The effect of dosage and the chicken manure organic material (P), rice husks (Q), chicken manure biochar (R), and rice husks biochar (S) on the availability of Cd in the soil during incubation showed that the higher dosage of organic material was followed by a longer incubation period of Cd availability in the soil to decrease. The 72 g pot^{-1} dosage gave the lowest value of metal availability and the highest was 18 g pot^{-1} dosage (Figure 8).

Figure 8. The Development of Cd Availability caused by Organic Material Dosage



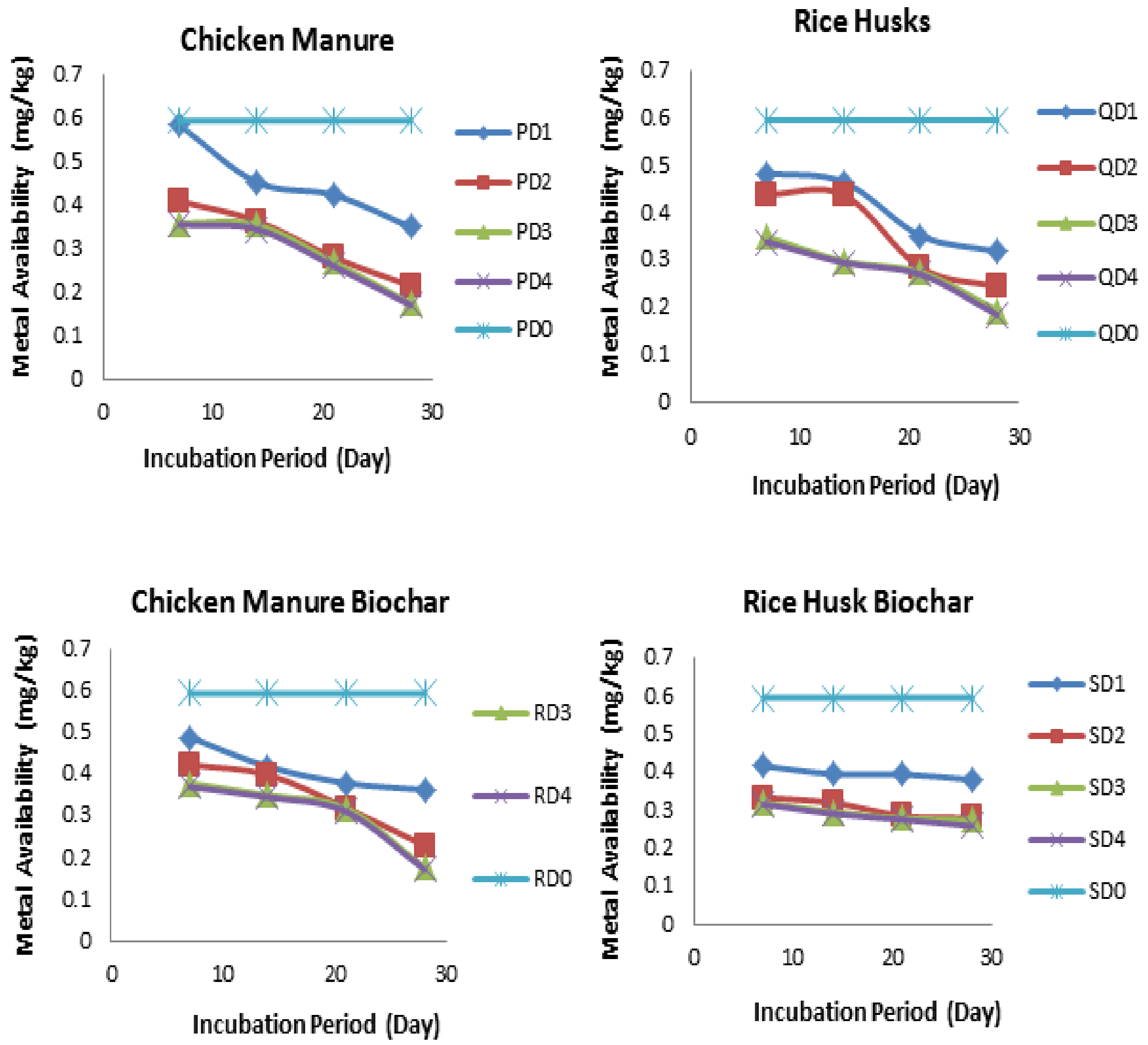
The effect of dosage and the chicken manure organic material (P), rice husks (Q), chicken manure biochar (R), and rice husks biochar (S) on the availability of Cu in the soil during incubation showed that the higher dosage of organic material was followed by a longer incubation period of Cu availability in the soil to decrease. The 72 g pot^{-1} dosage gave the lowest value of metal availability and the highest was 18 g pot^{-1} dosage (Figure 9).

Figure 9. The Development of Cu Availability caused by Organic Material Dosage



The effect of dosage and the chicken manure organic material (P), rice husks (Q), chicken manure biochar (R), and rice husks biochar (S) on the availability of Cr in the soil during incubation showed that the higher dosage of organic material was followed by a longer incubation period of Cr availability in the soil to decrease. The 72 g pot^{-1} dosage gave the lowest value of metal availability and the highest was 18 g pot^{-1} dosage (Figure 10).

Figure 10. The Development of Cr Availability caused by Organic Material Dosage



The treatment effect of organic material types with the dosages provided evident interactions on the availability or Cd, Cr, and Cu metals, whereas the interaction in Pb metal was not evident. The higher dosage of each organic material was able to decrease the heavy metal availability of Cd, Cr, and Cu evidently. If this is compared to the metal availability threshold according to Soepardi (1983), the concentrations of Cd, Cr, and Cu had been below the threshold. If this is compared to the concentration of the control treatment, the concentrations had decreased accompanied by the increase of organic material dosage. The lowest Cd availability value (0,139 mg kg^{-1}) was shown in the chicken manure treatment with 72 g pot^{-1}dosage which was evidently different from the other treatment. The lowest Cr availability value (0,013 mg kg^{-1}) was shown in the rice husk biochar treatment with 12-ton ha^{-1} dosage. However, this was not evidently different from the chicken manure biochar treatment with 72 g pot^{-1} dosage which was valued at 0,018 mg kg^{-1}. Then, the lowest Cu availability value

(12,120 mg kg^{-1}) was shown in the chicken manure biochar treatment with 72 g pot^{-1} dosage (Table 3).

Table 3. The effect of dosage interaction with the organic material type on the concentration of heavy metal availability in the 30-day incubated soil

Cd (mg kg^{-1})

Dosage	Organic Material Type			
	Chicken manure (P)	**Rice husks (Q)**	**Chicken manure biochar (R)**	**Rice husks biochar (S)**
0	0,298 ^{a}	0,298 ^{a}	0,298 ^{a}	0,298 ^{a}
1	0,149 ^{ij}	0,164 ^{fg}	0,182 ^{cd}	0,190 ^{ab}
2	0,148 ^{ij}	0,160 ^{gh}	0,175 ^{de}	0,186 ^{bc}
3	0,142 ^{ij}	0,154 ^{hi}	0,17 0 ^{ef}	0,176 ^{de}
4	0,139 ^{k}	0,146 ^{ijk}	0,164 ^{fg}	0,169 ^{ef}

Cr (mg kg^{-1})

Dosage	Organic Material Type			
	Chicken manure (P)	**Rice husks (Q)**	**Chicken manure biochar (R)**	**Rice husks biochar (S)**
0	0.595 ^{a}	0.595 ^{a}	0.595 ^{a}	0.595 ^{a}
1	0.060 ^{b}	0.060 ^{b}	0.037 ^{de}	0.02 7 ^{fghi}
2	0.057 ^{b}	0.057 ^{b}	0.029 ^{efgh}	0.018 ^{ijk}
3	0.048 ^{c}	0.048 ^{c}	0.022 ^{hijk}	0.016 ^{jk}
4	0.038 ^{d}	0.038 ^{d}	0.018 ^{ijk}	0.013 ^{k}

Cu (mg kg^{-1})

Dosage	Organic Material Type			
	Chicken manure (P)	**Rice husks (Q)**	**Chicken manure biochar (R)**	**Rice husks biochar (S)**
0	26.925 ^{a}	26.925 ^{a}	26.925 ^{a}	26.925 ^{a}
1	15.466 ^{bc}	14.173 ^{ef}	13.666 ^{f}	13.493 ^{f}
2	15.36 6 ^{bcd}	13.89 3 ^{ef}	13.400 ^{f}	14.686 ^{cde}
3	14.636 ^{cde}	13.640 ^{f}	12.593 ^{g}	14.566 ^{de}
4	14.286 ^{ef}	13.553 ^{f}	12.120 ^{g}	13.493 ^{f}

	Cd	**Cr**	**Cu**
Critical limit*	0.1-7	2.5	2-100

Note: Superscript letters indicate advanced test results (Duncan's). Value followed by the same letter was not evidently different from the 5% test level of Duncan’s
* According to Soepardi (1983)

The characteristic differences in the organic materials and their biochars were caused by the pyrolysis reaction of the organic materials in becoming biochars. The study of Sujana et al. (2014) showed the pyrolysis reaction of the chicken manure organic material in becoming chicken manure biochar. After the FT-IR analysis, a new functional group was identified. It was a –C=C– group from the aromatic carbon ring, a –C=O group from the alkehid, ketone and/or carboxylate compounds, and –C–N– and –N–H groups from amine and/or amide compounds. The same condition occurred when rice husks were made into biochar. –C=C– functional groups were formed from the aromatic carbon rings, nitro group (–N_2), nitride (–C≡N), and carboxylate or ether (–C=O). This condition described the oxidation and carbonisation processes.

Based on the results of the above research, it can be concluded that: (1) agricultural lands contaminated with garment waste contain more heavy metals and other hazardous chemicals compared to uncontaminated soil/land; (2) contaminated agricultural soil that has organic matter and/or biochar added shows improvement in its physical, chemical and biological properties; (3) contaminated agricultural soil that has been improved in characteristics by the addition of organic matter and/or biochar from the organic matters, when cultivated with maize seeds, have better maize yields than soil that has not been improved by the addition of organic matter and/or biochar; (4) the addition of organic matter and/or biochar at optimum dosages leads to a maximum yield of plants; (5) Each type of organic matter (in this case, chicken manure and rice husk) and its respective biochar (chicken manure and rice husk biochar) have different soil-fixing properties, thus, their ability to repair contaminated rice fields will also be different, and the provision of the types of organic matters and/or biochar will also produce different maize crops; (6) rice husk biochar mixture at optimum dosages with chicken manure organic matter at optimum dosages is capable of repairing agricultural land contaminated with garment waste containing heavy metals and other harmful contaminants until they fall below critical pollution thresholds, which will result in good soil quality and maize yields.

Conclusion, Recommendation, and Findings

Some of the conclusions obtained in this study are as follows: (1) The chemical properties of soil contaminated with screen printing liquid waste contain heavy metals which consist of Pb, Cu, Cd, and Cr; (2) Rice husk biochar shows better potential compared to chicken manure biochar and other organic matters in terms of improving soil properties and decreasing the availability of heavy metals; (3) The application of rice husk biochar with a dosage of 12 tons ha^{-1} can reduce the availability of most of the heavy metals in soil.

Several recommendations from this study are outlined as follows: (1) Rice husk biochar with a dosage of 12 tons ha^{-1} can be used as a soil enhancer that can overcome the constraints of heavy metal pollution of Pb, Cd, Cu and Cr on land that has been contaminated by garment liquid waste; (2) The government is expected to provide guidance and knowledge to garment entrepreneurs not to dispose of their liquid waste into irrigation channels. In addition, the government also needs to take remediation action on agricultural lands that are contaminated by heavy metals; (3) It is necessary to conduct further research by increasing the sampling locations so that the distributions of heavy metals in land contaminated by screen printing liquid waste can be obtained.

Some of the new findings obtained in this study are: (1) Rice husk biochar with optimum dosages of 9.28 tons ha^{-1} can improve the physical, chemical, and biological properties of soil contaminated by heavy metals such as Cu, Pb, Cd, and Cr from garment liquid waste; (2) Formulation of the dosage of rice husk biochar with a dosage of 9.28 tons ha^{-1} combined with chicken manure organic matters with a dosage of 8.544 tons ha^{-1} can improve soil quality and the yields of maize crop on land contaminated by heavy metals such as Pb, Cd, Cu, and Cr until it drops below the contamination threshold.

The above findings have implications for the addition of science in the field of agriculture, especially with respect to the role of adding organic matters and/or biochar to improve the physical, chemical and biological characteristics of agricultural land that has been exposed to contamination by garment waste containing heavy metals. However, remediation needs to be supported by more comprehensive empirical evidence. In addition, the findings of this research have implications for the development of more efficient, safer and cheaper agricultural farm remediation technology so that the application of this technology provides better and affordable assurances of results for all parties. The findings of this study also have implications for policymakers to produce policies that protect agricultural lands against pollution exposure and policies for undertaking measures to address these rice fields by providing more appropriate and affordable agricultural technology to farmers.

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