

The in situ inactivation of the contaminated intensive paddy field of Pb and Cd using biochar and compost

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ABSTRACT

The increasing of intensive use of the inorganic fertilizer had affected to the high contamination of Pb and Cd in the agricultural land of paddy (*Oryza sativa*L). The extensive use of phosphorous fertilizer as the inorganic fertilizer which unfollowed by adequate use of organic fertilizer potentially contaminated the soil and plants. Finding the sufficient remediation technique of heavy metal contamination was one of most challenges. This study was aimed to investigate the potential of biochar and compost in the treatment of the contaminated paddy field. The procedures were employed to reduce the dissolved of Pb and Cd in soil by improvement the soil chemical properties. The Pb and Cd concentration and its control was measured using Atomic Absorption Spectrophotometry (AAS). The data analysis were addressed by the variance analysis, ANOVA, using Random group. The further analysis had been exercised using Duncan's multiple range test with an error rate of 5%. The optimum dosage of biochar and compost were determined using linear regression analysis. The results showed that the biochar had potential to reduce the contaminated Pb and Cd compared to adding the compost. The optimum dosage of straw compost, husk compost, straw biochar, and husk biochar was 7.90 ton.ha⁻¹, 6.88 ton.ha⁻¹, 7.59 ton.ha⁻¹, and 9.85 ton.ha⁻¹, respectively.

Key words : Pb and Cd contamination, Paddy Field, Biochar, Compost

Introduction

The massive uses of the inorganic fertilizer in the agricultural activities of paddy (*Oryza sativa* L.) had affected to the increasing of Pb and Cd contamination. The use of phosphorous fertilizer as the inorganic fertilizer which unfollowed by adequate uses of the organic fertilizer potentially contaminated the soil and plants (Atafar *et al.*, 2008). The high amount of heavy metal would affect the undesirable changes of soil properties (Mohammed *et al.*, 2011;

Satpathy *et al.*, 2014). Moreover, the heavy metal contamination could migrate to the roots, leaves, and grains of plants as foodstuffs which possessed a risk to public human health (Machiwa, 2010; Ali *et al.*, 2013).

The heavy metal contamination could be reduced using some treatments such as the addition of biomass and manure (*in situ*) as the organic compound which could improve the organic-available of soil. The organic compound could form the complex molecule and form the chelate bonding with Pb and

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Cd. The complex molecule of the organic compound and heavy metal could reduce the contaminated Pb and Cd in the paddy field due to improving the soil properties. Komareket *et al.* (2013) reported that the *in situ* stabilization of heavy metal could be performed by throwing in the soil amendment such as compost and biochar to reduce the metal bioavailability and minimize uptake by plants.

The utilization of biochar had a high correlation to the improvement of soil properties and reported as the potential heavy metal remediation. Felletet *et al.* (2011) reported that the addition of biochar from farming waste at the mining effluent could reduce the heavy metal and showed the high remediation by increasing the dosage of biochar. Moreover, the increasing of biochar dosage would also increase the pH of effluent, cation exchange capacity, water holding capacity, and reduce the metal bioavailability of Cd, Pb, and Zn (Felletet *et al.*, 2011). Uchimiya *et al.* (2010) also reported that the utilization of biochar immobilized the heavy metal to reduce the contamination in soil. The research conducted by Chan *et al.* (2007) switched that the biochar could enhance C-organic, pH, soil structure, Cation Exchange Capacity (CEC), and soil water storage capacity. In the other hand, Ahmad *et al.* (2012) had successfully remediated the toxicity of Pb up to 92.5 % using the biochar from clamshell and also implying the bioavailability of Pb to 75.8% using the biochar from cow bone of the contaminated soil of military firing range in Korea. The remediation was caused by the lime contained the biochar which intimately absorbed the contaminated Pb.

Materials and Methods

The materials used in this study were the contaminated soil from paddy field, and the chemicals received without any purification. They were hydrogen peroxide 30%, ether, hydrochloric acid, sodium hydroxide, and the other material which supported the laboratory analysis. The equipment used in this study were soil drill, hoe, bucket, tape meter, sieve, label, Atomic Adsorption Spectroscopy (AAS), kjeldahl flask, electronic analytical balance, analytical dropper, volumetric flask, volumetric glassware, erlenmeyer flask, volumetric dropper, mortar and pestle, filter paper, oven, and the other equipment to support the laboratory analysis

The soil sample was collected from the contami-

nated surface approximately located at 0-20 cm from the highest contaminated soil (the determination was carried out using the exploration research). The as-prepared sample was dried using an oven, meshed using mortar, and filtered using filter paper (d=2mm) for greenhouse material experiment. The research design was customized using the completely randomized design with two factorial factor. The first factor was the kinds of material of biochar and compost in which the second factor were the dosage of biochar and compost. The compost and biochar were obtained from straw compost (J1), husk compost (J2), straw biochar (J3), and husk biochar (J4). The dosage of compost and biochar were set at 4 level as control (D0), 2.5 ton.ha⁻¹ (D1), 5 ton.ha⁻¹ (D2), 7.5 ton. ha⁻¹ (D3), and 10 ton.ha⁻¹ (D4).

All the treatment was prepared in triplicate, and sixty samples were collected with the distances between the treatment of 0.5 m and 1.0 m between replication. The incubation process was obtained by adding 5 kg of the contaminated soil which have been prepared before to the pot. Furthermore, the biochar and compost were mixed with the as-prepared sample and distilled water. The incubation process was run for sixty days. After the incubation process, the as-prepared sample was analyzed to investigate the influences of compost and biochar treatment in the remediation of contaminated Pb and Cd in soil.

To investigate the Pb and Cd concentration, 1 g of soil sample was mixed with 1 ml of perchloride acid and 5 ml of high purity nitric acid in the digest tube and storage for one night. The as-prepared sample was heated at 100°C for 1.5 hours until the yellow gas had been fully run out. Furthermore, the sample was heated at 170°C for one hour and then heated again at 200°C for one hour until the white gas formed. The destruction of the sample was finished when the white precipitate formed, and the solution was approximately 1 ml. The solution was cooled to room temperature, diluted and mixed using distilled water to 10 ml. The sample solution was measured by AAS using the Pb and Cd concentration standard as the references standard.

Results

The characteristic of Biochar and Compost

The results in table 1 confirmed that the highest pH of the as-prepared biochar and compost were at

9.36, 7.53, 7.11, and 6.60 for straw biochar, straw compost, husk compost, and husk biochar, respectively. The CEC of the as-prepared samples were 93.14 cmol.kg^{-1} , 88.34 cmol.kg^{-1} , 70.35 cmol.kg^{-1} , and 55.96 cmol.kg^{-1} for straw biochar, straw compost, husk compost, straw compost, and husk biochar, respectively. The values of C-organic of the as-prepared sample were 28.23%, 27.78%, 23.28%, and 21.59% for husk biochar, husk compost, straw biochar, and straw compost, respectively. The value of humic and fulvic acid of the as-prepared sample were 465.12 and 411.45 ppm for husk biochar, 395.67 and 327.63 ppm for straw biochar, 283.45 and 200.84 ppm for huskcompost, and 211.73 ppm and 175.99 ppm for straw compost.

The Scanning electron microscopy analysis was carried out to investigate the morphology of the as-prepared biochar and compost. The sample analysis was exercised using the high magnification (2,500 times) (Fig. 1-4). Fig. 1 and 2 confirmed that the mor-

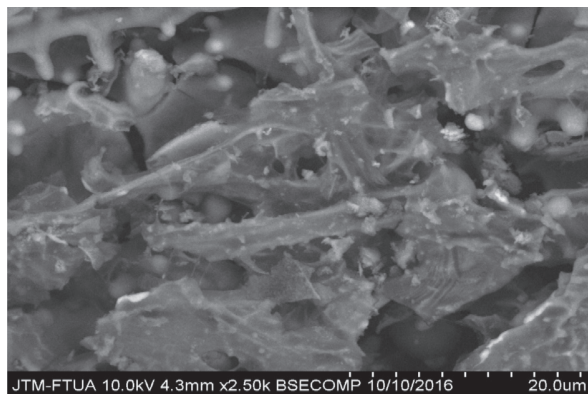


Fig. 1. The SEM Image of the straw biochar.

phology of both biochar sample had the large surface area and Fig. 3 and 4 showed an orderly arrangement of pores compared to the morphology of both composts. The smoother surface of samples indicated the small specific surface area due to small pored. The diameter size of biochar showed the greater pored (20-30 μm) compared to compost (~20 μm).

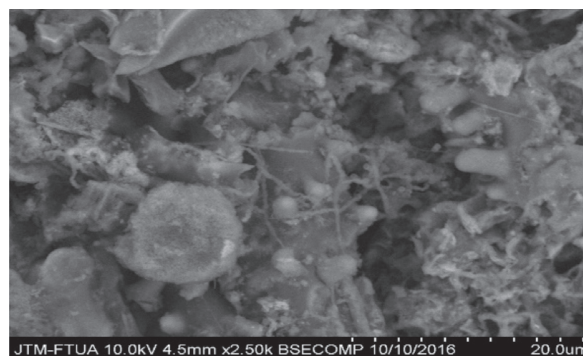


Fig. 2. The SEM image of husk Biochar.

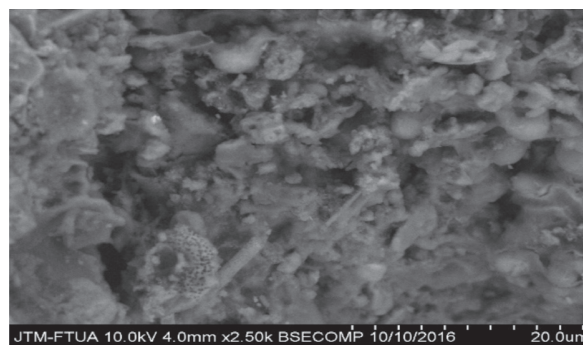


Fig. 3. The SEM image of straw compost

Table 1. The characteristics of compost and biochar.

Characteristics	Compost		Biochar	
	Rice Straw	Rice Husk	Rice Straw	Rice Husk
C-Organic (%)	21.59	27.78	23.28	28.23
Cation Exchange:-				
K ⁺	11.98	5.44	0.39	4.56
Na ⁺	0.06	0.07	0.05	0.02
Ca ⁺⁺	1.01	1.03	0.67	0.40
Mg ⁺⁺	0.44	0.57	0.35	0.26
Cation Exchange Capacity (CEC)	70.35	88.34	93.14	55.96
pH (H ₂ O)	7.53	7.11	9.36	8.60
pH (KCl)	7.20	6.80	8.60	5.72
Humic acid (ppm)	211.73	283.45	395.67	465.12
Fulvic acid (ppm)	175.99	200.84	327.63	411.45
Total Acidity (ppm)	387.72	484.29	723.29	876.57

The influences of dosages and types of the organic material to the remediation of contaminated Pb and Cd

Table 2 showed that variance analysis of the dosage of the organic material (D) provided a significant effect on the availability of contaminated Pb and Cd. For the types of organic material, the variance analysis also provided the significant effects on the availability of Pb but showed no significant effect on the availability of Cd. The interaction between the dosage of the organic material and the types of organic material exhibited the significant impact on the availability of Pb in soil.

Table 2. Variance analysis results of the dosage effect on the availability of Pb and Cd in soil.

No	Observation	D	J	DJ
1	Pb-available	519.232*	69.846*	5.843*
2	Cd-available	39.650*	2.154	1.037

D = Organic Dosage; J= Type of organic material; DJ= The interaction of dosage and type of the organic matter
* = Significant effect; KK = Coefficients diversity

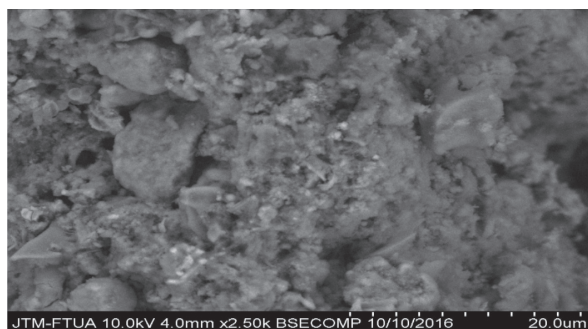


Fig. 4. The SEM image of husk compost.

The result also reported that the dosage of the organic matter (D), type of organic material (J), and the interaction of dosage interaction of type or or-

ganic raw material provided the significant effects on the availability of Pb in soil. The DNMRT test and tabulation data of the availability of Pb could be shown in Table 3.

Table 4 confirmed that the organic matter dosage showed the significant effect on the availability of Cd in soil. While the types of organic material (J) and the interaction provided the insignificant effect on the availability of Cd. The results of DNMRT test and tabulation data of the availability of Cd could be indicated in Table 5.

Discussion

The concentration of the Available Pb and Cd in soil

The results showed that all the organic material could decrease the concentration of the dissolved Pb and Cd in soil. The highest reducing of Pb was exhibited in the straw biochar treatment at the 10 ton.ha⁻¹ of dosage i.e. 3 ppm. In the other hand, the husk biochar was also showed the high reducing of Pb i.e. 3.06 ppm by using 10 ton.ha⁻¹ of the dosage. Furthermore, the highest reducing of Cd was showed in the straw biochar at 7.5 ton.ha⁻¹ of dosage i.e. 0.27 ppm and the combination of husk biochar at 10 ton.ha⁻¹ of dosage showed 0.30 ppm as the reducing of Cd. The results showed that the biochar had the better ability in the remediation of contaminated Pb and Cd compared to compost. The optimum dosage of straw compost, husk compost, straw biochar, and husk biochar was 7.90 ton.ha⁻¹, 6.88 ton.ha⁻¹, 7.59 ton.ha⁻¹, and 9.85 ton.ha⁻¹, respectively.

The alkalinity of biochar had the important role in the mechanism of the dissolved Pb and Cd remediation (Debela *et al.*, 2012). The pH value of straw biochar and husk biochar were calculated as

Table 3. The results of DNMRT test, the tabulation data of the dosage effects, the types of organic material, and interaction on the availability of Pb.

Dosage (D) (ton.ha ⁻¹)	Types of organic material (J)				Average (D)
	Straw Compost	Husk Compost	Straw Biochar	Husk Biochar	
0	13.60 i	13.60 i	13.60 i	13.60 i	13.60 d
2.5	5.04 ef	8.86 h	4.08 bcd	4.47 de	5.61 c
5	3.83 abc	7.36 g	3.64 abc	4.42 cd	4.81 b
7.5	3.31 ab	6.04 f	3.35 abc	3.29 abc	3.99 a
10	3.17 ab	5.98 f	3.00 a	3.06 ab	3.80 a
Average (J)	5.68	8.37	5.53	5.77	

Table 4. The variance analysis of the availability of Cd in soil.

Sources	Deg. of Freedom	Squares	Central squares	F-count	Sig.
Treatment_D	4	0.897	0.224	39.650	0.000
Treatment_J	3	0.037	0.012	2.154	0.109
Treatment_DJ	12	0.070	0.006	1.037	0.436
Error	40	0.226	0.006		
Total	59	1.230			

Table 5. The results of the DNMRT test and the tabulation data of the dosage effects, the types of organic material, and interaction on the availability of dissolved Cd in soil.

Dosage (D) (ton.ha ⁻¹)	Types of organic material (J)				Average (D)
	Straw Compost	Husk Compost	Straw Biochar	Husk Biochar	
0	0.64	0.64	0.64	0.64	0.64 d
2.5	0.55	0.62	0.51	0.55	0.56 c
5	0.50	0.38	0.41	0.45	0.44 b
7.5	0.33	0.41	0.27	0.33	0.34 a
10	0.32	0.42	0.29	0.30	0.34 a
Average(J)	0.47	0.49	0.42	0.45	

9.36 and 8.60. Both biochar showed that the high alkalinity which had the calcification effects to reduce the mobility of heavy metal in soil. Table 6 showed that the *in situ* treatment could effectively increase the pH of soil in which the straw biochar, husk biochar, straw compost, and husk compost could subsequently improve the pH to 6.42, 6.37, 6.28, and 6.24, respectively. Some research also documented that the increasing of pH could be greatly influenced by the dosage and types of the raw material supplied biochar (Uchimiya *et al.*, 2010; Cui *et al.*, 2011; Jiang *et al.*, 2012).

Table 6. The influence of the type of organic matter to the soil pH.

Treatment	Average
Control	5.52
Straw Compost	6.24
Husk Compost	6.28
Straw Biochar	6.42
Husk Biochar	6.37

The increasing of soil pH would influence the chemical reaction in soil including the organo-metal complexation reaction. In general, the organo-metal complexation increased as the increasing of soil pH which means that the existences of Pb and Cd in soil would decrease as the increasing of pH (Komarek *et al.*, 2013). The correlation between pH and the availability of Pb and Cd shown in table 7.

Table 7. Calculation summary of simple linear regression model between the pH and CEC to the concentration of Pb and Cd available.

Independent Variables	Dependent Variables	
	Pb available	Cd available
pH (Soil)	Y=59.08 – 8.37X R square = 0.80	Y=2,07 – 0.26X R square = 0.69
CEC (Soil)	Y=16,80 – 0.35X R square = 0.59	Y=0,87 – 0.01X R square = 0.82

In addition, the cation exchange capacity (CEC) also become the factor which affected to the availability of Pb and Cd in soil. The study showed that the highest CEC were in the addition of straw biochar followed by husk biochar, straw compost, and husk compost as 30.74; 29.57; and 28.84 cmol (+)kg⁻¹, respectively.

Lu *et al.* (2012) explained that the increasing of CEC in soil by adding the biochar caused by the increasing of the negative charge derived by a carbonyl group (C=O). Furthermore, the biochar also had the high aromatic series which could form the organo-complex with Pb and Cd (Ippolito *et al.*, 2012). As the increasing of pH, the functional group of biochar might dissociate to increase the ligand ion affinity reacted with the metal cation (Komarek *et al.*, 2013). The Soil which had the high CEC value would have the strong performances to maintain the cation included Pb and Cd cation. The higher CEC would decrease the availability of Pb and Cd. Fur-

thermore, the adding of biochar to improve the soil CFC could increase the soil tolerances to the contaminated heavy metal (Ahmad *et al.*, 2012). The correlation between CEC and the availability of Pb and CD were shown in Table 7.

The study had provided that the treatment which could increase the pH and CEC of soil could extensively reduce the contaminated heavy metal such as Pb and Cd. The treatment which used straw biochar to improve the soil characteristics showed the highest reducing of the availability of Pb and Cd due to increasing the soil pH. The increasing of pH was caused by the high contain of humic acid contained the straw biochar compared to the other treatment.

CONCLUSION

The treatment which used to reduce the contaminated Pb and Cd could be carried by utilizing the Biochar. The biochar showed the better ability compared to the compost. the study showed that the optimum dosage of the treatment was 7.90 ton.ha⁻¹, 6.88 ton.ha⁻¹, 7.59 ton.ha⁻¹, and 9.85 ton.ha⁻¹ for straw compost, husk compost, straw biochar, and husk biochar, respectively.

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