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Characterization of Micronutrient and Heavy Metal Content in Organic Fertilizers Made from Fly Ash and Organic Waste

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ABSTRACT

The production of electricity from burning of coal produced large amount of fly ash waste. Fly ash is potential to be used as a soil ameliorant material because it has a very fine size. The purpose of the study was to to develop a new alternative organic fertilizer and to find out the contents of micronutrients and heavy metals in organic fertilizer made from fly ash and organic waste. The study was conducted by composting several organic matterials that consisted of fly ash, poultry manure, peanut stover, sawdust and banana stalk in different compositions. The selection of good organic fertilizer was conducted based on the ranking method. The results showed that the selected organic fertilizer was fertilizer that contained 10% of fly ash. The micronutrient (Cu, Mn and Zn) contents of the organic fertilizers were low, but the Fe content was high. The heavy metal (As, Cd, Hg and Pb) contents of the fertilizer were low.

Keywords: Coal, fly ash, Organic fertlilizer, organic waste

ABSTRAK

Produksi energi listrik dari pembakaran batubara menghasilkan limbah *fly ash* dalam jumlah yang besar. *Fly ash* berpotensi untuk dimanfaatkan sebagai bahan amelioran tanah karena mempunyai ukuran yang sangat halus. Penelitian ini bertujuan untuk mengembangkan sebuah alternatif pupuk organik dan mengidentifikasi kandungan unsur hara mikro dan logam berat pada pupuk organik dengan material *fly ash*. Penelitian ini dilaksanakan dengan cara mengomposkan beberapa material organik yang terdiri dari *fly ash,* seresah daun kacang tanah, kotoran ayam petelur, serbuk gergaji dan ares batang pisang dalam beberapa perbandingan. Pemilihan pupuk organik terbaik dengan menggunakan metode perankingan. Hasil penelitian menunjukkan bahwa pupuk organik yang terpilih adalah pupuk organik dengan kandungan *fly ash* sebesar 10%. Kandungan unsur hara mikro seperti Cu, Mn dan Zn pada level rendah tetapi kandungan Fe pada level tinggi. Kandungan logam berat seperti As, Cd, Hg dan Pb pada level yang rendah.

Kata kunci: Batubara, *fly ash,* limbah organik, pupuk organik

INTRODUCTION

Coal fly ash is a byproduct of coal-fired power plants. If the fly ash is not processed well, it can cause environmental pollution. Department of Energy in the United States reported that the coal combustion produces fly ash waste as much as 52% (Brown *et al*. 2015), which means that the waste production is abundance. So far, the research on the utilization of fly ash waste has been conducted in the field of Civil Engineering, such as for making concrete (Maryoto 2008; Haryanto *et al*. 2008) and mortar (Kusdiyono and Rohadi 2012).

The research on the utilization of fly ash in the field of agriculture has been conducted overseas. Fly ash can potentially be used as soil ameliorant and organic fertilizer, in which the application of fly ash is able to improve physical, chemical, and bilogical soil quality (Ram and Masto 2014). In addition, the fly ash can supply macro- and micro-nutrients for plants (Pandey and Singh 2010). At the low level (up to 20% on soil volume basis on Nitrogen (N), Phosporus (P) and Potassium (K) 40:20:20 mg kg^{-1}), the application of fly ash can

increase the availability of micronutrients, soil microbial activities, and the growth of rice plants (Nayak *et al*. 2015).

Fly ash contains essential nutrients, except C and N in which both are low (Ahmad 2017). In addition to contain macronutrients, such as P, K, Mg and S, it also contains micronutrients, *i.e.* Fe, Mn, Zn, Cu, B and Mo (Mishra *et al*. 2017). Trace elements, such as Cu, Mo, Mn, Co, Zn, and B increase activities of some enzymes and enzymatic system in plants and improve the use of macronutrients from soil (Rakhimova *et al.* 2017).

The availability of metallic elements in soil is in general much less than their total concentrations. It has been reported that the available concentrations of metallic elements in soil is an indicator of the available amount that can be taken up by plants. (Mahale *et al*. 2012)

The study about application of fly ash on soils has been conducted (Mahale *et al*. 2012; Ahmad 2017; Mishra *et al*. 2017). However, the potency of fly ash waste utilization as the material of organic fertilizer has not been studied so far. Therefore, the objective of this research is to create a new organic fertilizer made from fly ash waste and to determine the contents of micronutrients and heavy metals in this organic fertilizer.

MATERIALS AND METHODS

Study Site

The study was conducted on the scale of greenhouse and laboratory. The study in the greenhouse was conducted in the State Polytechnic of Cilacap. The analysis of samples was conducted in the Laboratory of Soil science and Laboratory of Geology Universitas Jenderal Soedirman, and Laboratory of Integrated Testing and Research (LPPT) Gadjah Mada University. The study was performed in May until August 2017. The materials used in this study were fly ash taken from steam-electric power plant (Pembangkit Listrik Tenaga Uap/PLTU) Karang Kandri Cilacap, sawdust, poultry manure, peanut stover, and banana stalk.

Research Design

The study about organic fertilizer made from fly ash consisted of two stages. The first stage was to study the chemical characteristics of fly ash using X-Ray Fluorescence (XRF) method, which was conducted in the Laboratory of Geology, Universitas Jenderal Soedirman. The second stage was to make organic fertilizers consisting of different compositions of fly ash and organic wastes as shown in Table 1. All the materials were mixed and incubated for 3 weeks. Then, the fertilizer samples were taken using composite method for analysis. The contents of micronutrients and heavy metals in the fertilizers were analysed in the Laboratory of Soil Science, Universitas Jenderal Soedirman and Laboratory of Integrated Testing and Research (LPPT), Gadjah Mada University. The characteristics of the fly ash were presented in Table 2, and the contents of micronutrients and heavy metals in the fertilizers were presented in Table 3.

The organic fertilizers were classified using the rank method based on the micronutrient and heavy metal contents in the organic fertilizers. The fertilizers were rated based on the soil quality criteria, *i.e*. Soil Measuring Assessment Framework (SMAF) method. The results of analysis were then compared to the standardized organic fertilizer quality according to the Regulation of Agriculture Department of Indonesia (Permentan) Number 70 year 2011.

Table 1. The composition of fly ash and other organic waste for making organic fertilizers.

Composition	Comparison (%)		
	A	B	C
Fly ash	10	20	30
Banana stalk	10	10	10
Peanut stover	20	20	20
Poultry manure	20	20	20
Sawdust	40	30	20

Note : A = 10% fly ash + 10% banana stalk + 20% poultry manure + 20% peanut stover + 40% sawdust, B = 20% fly ash + 10% banana stalk + 20% of poultry manure + 20% peanut stover + 30% sawdust, C = 30% fly ash + 10% banana stalk + 20% poultry manure + 20% peanut stover + 20% sawdust.

Table 2. Chemical characteristics of fly ash from PLTU Karangkandri, Cilacap.

Parameter	Unit	Result
Fe_2O_3	%	71.2
SiO_2	%	16.2
Al_2O_3	%	7.67
CaO	%	2.79
MgO	%	1.05
SO_3	%	0.27
TiO	%	0.22
BaO	%	0.19
K_2O	%	0.17
P_2O_5	%	0.05
ZnO	mg kg^{-1}	48.3
Cl	mg kg^{-1}	31.7
CuO	mg kg^{-1}	ND
MnO	mg kg^{-1}	ND
As_2O_3	mg kg^{-1}	ND
CdO	mg kg^{-1}	ND
HgO	mg kg^{-1}	ND
PbO	mg kg^{-1}	ND

ND : not detected.

Analysis of Organic Fertilizers

The contents of micronutrients (Cu, Fe, Mn, Zn) and heavy metals (As, Cd, Hg) in the organic fertilizers were determined. In addition, C/N ratio and pH of the organic fertilizers were measured. The concentrations of Cu, Fe, Mn, Zn, As, and Cd were measured using Atomic Absorption Spectrophotometer (AAS), while the concentration of Hg was determied using Mercury analysis method. The pH of fertilizer was measured using electrometric method.

RESULTS AND DISCUSSION

Characteristics of Fly Ash

Table 2 presented the characteristics of fly ash taken from PLTU Karangkandri. The results showed that the fly ash contains mainly iron (71.2%), followed by silicate (16.2%) and aluminum (7.67%). Different results were shown by Widyaningsish *et al*. (2011) who reported that the main composition of fly ash from PLTU Karangkandri Cilacap was made of silicate (39.85%), aluminum (12.74%) and iron (18.31%). The different composition of fly ash was caused by the different type of coal used. Shaheen *et al*. (2014) indicated that the chemical characteristics of coal fly ash depend on the geological factors related to the coal deposits and different operating conditions/practices employed at the power plants. Table 2 showed that the content of micronutrients, such as Zn and Cl was low, whereas Cu and Mn were not detected in the fly ash. Therefore, it is safe to use the fly ash as a material of organic fertilizer.

Characteristics of Organic Fertilizers Made from Fly Ash

C/N Ratio and pH

The results showed that the C/N ratio of organic fertilizer made from fly ash in the current study is in the range of the C/N ratio of standradized organic fertilizer quality proposed by the Regulation of Agriculture Department of Indonesia (Permentan) No. 70 Year 2011, *i.e*. 15-25 (Table 3). These C/N ratio indicated that the organic materials used to make the organic fertilizer have been decomposed well or the organic fertilizer has been mature. Then, the mature organic fertilizer can be applied for plants. Komilis and Tziouvaras (2009) showed that the maturity of organic fertilizer indicates that there is no pytotoxin in it.

The pHs of organic fertilizers were alkaline, *i.e*., pH > 7, and they are still in the range of pH of standardized organic fertilizer quality (Table 3). The high pH indicated high buffering capacity of the organic fertilizers. The high pHs of the organic fertilizers were probably due to the increased amount of fly ash in them. This finding corresponds to the

Table 3. The contents of micronutrients and heavy metals in the organic fertilizers made from fly ash.

Parameter	Unit	Fertilizer Treatment						Permentan No 70/2011
		A		B		C		
		Value	Score	Value	Score	Value	Score	
C/N		24.77	1.00	25.02	0.67	19.02	1.00	15 – 25
pH H_2O		8.52	0.67	8.28	0.67	8.52	0.67	4 – 9
Cu	mg kg^{-1}	65.63	0.33	55.60	0.33	55.29	0.33	< 5000
Fe	%	**1.82**	1.00	**2.36**	0.67	**3.39**	0.33	< 0.9
Mn	mg kg^{-1}	595.71	0.33	603.48	0.33	726.05	0.33	< 5000
Zn	mg kg^{-1}	183.45	0.33	166.20	0.33	157.68	0.33	< 5000
As	mg kg^{-1}	3.38	0.67	2.61	1.00	2.09	1.00	< 10
Cd	mg kg^{-1}	0.53	1.00	0.61	1.00	0.55	1.00	< 2
Hg	mg kg^{-1}	0.005	1.00	0.003	1.00	0.023	1.00	< 1
Pb	mg kg^{-1}	8.18	1.00	8.11	1.00	10.38	1.00	< 50
Total score			**7.33**		7.00		6.66	

Note : A = 10% fly ash + 10% banana stalk + 20% poultry manure + 20% peanut stover + 40% sawdust, B = 20% fly ash + 10% banana stalk + 20% poultry manure + 20 % peanut stover + 30% sawdust, C = 30% fly ash + 10% banana stalk + 20% poultry manure + 20% peanut stover + 20% sawdust.

study of Garavaglia and Caramuscio (1994), which showed that the pHs of fly ash are about 8-9. The alkaline pH of the fly ash has a good impact in the decomposition process of the organic fertilizers (Hapsoh *et al.* 2015). Ram and Masto (2010) indicated that the pH of fly ash is one of the important controlling factors in determining the leaching of metals in soils.

Micronutrient Content of Fertilizer

The contents of Cu in the three organic fertilizers were low (Table 3). The highest content of Cu was obtained in the fertilizer A, *i.e.* 65.63 mg kg^{-1}, whereas Cu contents in the fertilizer B and C were 55.6 mg kg^{-1} and 55.29 mg kg^{-1}. The low content of Cu is correlated to the high pH of the fertilizer. This result corresponds to the study of Foth (1998), which showed that the availability of Cu decreased with the increase of soil pH.

The contents of Fe in the fertilizers were high, and they were above the standard Fe content in the organic fertilizer proposed by the Regulation of Agriculture Department of Indonesia (Permentan) No. 70 Year 2011, *i.e.* > 0.9% (Table 3). Among the three types of the organic fertilizers, fertilizer A contained the lowest amount of Fe, *i.e.* 1.82%. The content of Fe in the organic fertilizer is directly proportional to the content of fly ash in it. The high fly ash content as much as 10% increased the content of Fe as much as 0.52%, therefore, the high Fe content in the fertilizer was caused by the high content of Fe in the fly ash used in the current study (Table 2), *i.e.* about 71.2%.

The contents of Mn in the fertilizer A, B and C were low. The lowest content of Mn was measured in the fertilizer A, *i.e.* 595.71 mg kg^{-1}, and the highest one was measured in the fertilizer C, *i.e.* 726.04 mg kg^{-1}. The low Mn content in the fertilizer can be due to no Mn was detected in the fly ash as seen in Table 2.

The contents of Zn in the fertilizer were low. The lowest content of Zn was measured in the fertilizer C, *i.e.* 157.68 mg kg^{-1}, whereas the highest one was measured in the fertilizer A, *i.e.* 183.45 mg kg^{-1}. The presence of Zn in the fertilizer was probably due to the poultry manure and peanut stover used for making the fertilizer. According to Manzeke *et al.* (2014), the manure and leaf litter contributed to the availability of Zn for plants.

The low contents of Cu, Mn and Zn in the fertilizers indicate that the organic fertilizers are safe to be applied for soil and no potential toxicity for plants.

Heavy Metal Content of Fertilizer

The heavy metal (As, Cd, Hg an Pb) contents in the fertilizer was low. The range of heavy metal content of As, Cd, Hg, and Pb were slightly different for fertilizer A, B, or C (Table 3). Based on the standardized organic fertilizer quality proposed by the Regulation of Agriculture Department of Indonesia (Permentan) No. 70 year 2011, the content of heavy metals in the fertilizers were below the maximum threshold allowed by the Indonesian Government. The low content of heavy metals in the fertilizers showed that the fertilizers are safe to

be applied for soil and plants. The low content of heavy metals in the fertilizers was caused by the fly ash used for making the fertilizers probably contained low amount of heavy metals (Table 2).

The Selected Organic Fertilizer

Table 3 showed that the fertilizers made from fly ash in the current study in general meet the standard of organic fertilizer quality proposed by the Regulation of Agriculture Department of Indonesia (Permentan) No. 70 Year 2011. Each parameter was scored based on the level of importance. The rating of score was conducted based on the method of soil quality determination, *i.e*. Soil Measuring Assesment Framework (SMAF) method. The results of scoring showed that the fertilizer A that contained of 10% of fly ash was chosen as a good organic fertilizer based on the chemical caharacteristics. The score for each organic fertilizer was 7.33 for fertilizer A; 7.0 for fertilizer B; 6.66 for fertilizer C, respectively. The maximum total score calculated from all the parameters of fertilizer chemical characteristics was 10.

CONCLUSIONS

The use of fly ash as organic fertilizer material is considered safe. The characteristics of fly ash is determined by the type of coal used. The low contents of Cu, Mn, and Zn in the fertilizers showed that the no potential toxicity for soil and plants is expected from the fertilizers. The high concentrations of Fe in the produced organic fertilizers were caused by the use of fly ash with high Fe content. The low contents of heavy metals in the produced organic fertilizers showed that the fertilizers were safe from potential toxicity of heavy metals.

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