International Journal of Applied Engineering Research ISSN 0973-4562 Volume 12, Number 6 (2017) pp. 1035-1042

Biochar as a Carrier for Nitrogen Plant Nutrition: The Release of Nitrogen from Biochar Enriched with Ammonium Sulfate and Nitrate Acid

E. I. Wisnubroto[1)], W.H. Utomo[2)] and H.T. Soelistyari[1)]

[1)] University Tribhuwana Tunggadewi, Malang, Indonesia.

[2)] International Research Centre for Management of Degraded and Mining Lands, University of Brawijaya, Malang, Indonesia.
**Corresponding author*

Abstract

An experiment was conducted to study the characteristics and stability of biochar enriched with ammonium sulfate and nitrate acid. Two feedstuffs of biochar (namely poultry litter and corn-cobs) were enriched with ammonium sulfate and nitrate acid. To investigate the release of nitrogen from the enriched biochar, a lysimeter study was carried out.. The results showed that either ammonium sulfate or nitratr acid was good enough to be used as the materials for enriching biochar. However, ammonium sulfate yielded a relative better enriched biochar compared to the nitrate acid enriched biochar. Nitrogen in ammonium enriched biochar was relatively more stable compared to that of nitrogen in nitrate enriched biochar. Until 120 days of incubation, nitrogen content in a soil applied with ammonium enriched biochar made from corn-cobs was 0,13 %, 0.15 %, and 0.14 % for acid, neutral and calcareous soil respectively. These were higher compared to nitrogen content applied with the same biochar feedstuffs enriched with nitrate, i.e.: 0.012 %; 0.11%; and 0.11 % in acid, neutral and calcareous soil. Biochar with diameter size of less than 0.5 mm was good enough used for enrichment.

Keywords: Soil amendments, organic fertilizers, slow release fertilizer.

INTRODUCTION

The discovery of high soil fertility due to the occurrence of high black carbon (biochar) content is actually not a new phenomenon. In 1870, James Orton has found that the black soil in Amazon River basin was very fertile. These soils was believed has been used for crop production for thousands of years[1]. The black fertile soil has been known as the "terra preta soil". However, until the end of the 20th century, the scientific progress on studying the terra preta soil has been very limited. Very few scientific literatures tried to explain these fertile black soil mystery, some of them are Herbert H. Smith in 1879, and William Katzer in the early of 20th century [1].

The first scientific explanation of these fertile black soils was given by Sombroek in 1960 [2]. Unfortunately, since then very view attention has been given to the potential of black soil (biochar) as a soil amendment to increase the soil fertility. Johannes Lehmann and his colleagues in Cornell University doing extensive research in the early of 2000, and after these works, together with the establishment of International Biochar Initiative (IBI), biochar has attracted attention to the soil scientists as one of the approach to increase soil carbon and improving soil function.

Science now has proven that biochar is one of the best and promising soil amendments [3]. Regardless of its controversy [4,5] a numerous studies have proven that biochar application to the soil, especially when applied to a degraded soil, can improve the soil fertility and plant productivity. A lot of study has shown that biochar application improved crop growth and increased crop yield; these includes: rice[6,7], maize[8,9], cassava[10], soybean[11], and even horticultural crops such as red chili[12]. However, it should be noticed that the increase in plant growth and production was not directly attributed to biochar application. The increase in plant growth and production was more influenced by the the improvement of soil quality resulted from the application of biochar. The improvement of soil chemical fertility, such as soil organic matter, soil pH, Cation Exchange Capacity have been shown by many workers[7,13]. A similar improvement has been observed for soil physical[9, 14] and biological quality[15].

The application of biochar to a poor fertility soil can increase the soil cation exchange capacity. The increased of soil cation exchange capacity would reduce nutrient loss caused by leaching[16], and hence increases fertilizer application efficiency[17,18]. These phenomena lead to the hypothesis that biochar can be used as the carrier of some elements of plant nutrition, especially nitrogen.

The study discussed here was aimed to study the possibility for developing nitrogen enriched biochar as organic fertilizer. The study was done by enriching biochar with various nitrogen sources, and then investigating the release of nitrogen from the enriched biochar. It was expected that the N-rich biochar fertilizers would increase the efficiency of nitrogen fertilization, and at the same time improve soil quality.

MATERIALS AND METHODS

Biochar production

Biochar was made at the bioenergy Laboratory University Tribhuwana Tunggadewi, Malang, Indonesia, with the technique as described by Masulili *et al*.[7] at a final temperature of 300°C. There were 2 type of feedstock used in this experiment, namely: (i) poultry litter, and (ii) corn-cobs. Poultry litter was chosen with the consideration of nitrogen rich material, and corn-cobs as the low nitrogen content material. Biochar was produced with diameter of 2.0 – 3.36 mm, 1.0 - 2.0 mm; 0.5 – 1.0 mm; 0.25 – 0.50 mm; and less than 0.25 mm, and was enriched with nitrogen originated from: (i) ammonium sulfate, and (ii) nitrate acid. These treatment combinations were arranged in fully randomized design with 4 replications.

The enrichment of biochar with ammonium sulfate was done by modification of the method described by Taghizadeh-Tossi *et al.*[19]. Biochar was diluted in a sodium hydroxide solution in airtight bottle, and then the ammonium sulfate was injected and stored in a room temperature for one week. The enriched biochar was then air dried in room temperature. The enrichment of biochar with nitrate nitrogen was done by the modification of the method proposed by Jassal *et al.*[20]. Biochar was diluted in nitrate acid solution in an erlenmeyer. Sodium hidroxide solution was added to avoid acidification, after which it was shacked for 4 hours. The nitrate enriched biochar was then stored at a room temperature for one week, and after that it was air dried at room temperatur.

The air dry enriched biochar was stored in a plastic polypropylene bag (0.012 mm thick) for stability determination of nitrogen absorbed in the biochar. Total nitrogen in enriched biochar was measured starting at 1 (one) day, 30 days and 120 days after enrichment.

Lysimeter experiment.

The experiment was aimed to investigate the release of nitrogen in the soil applied with enriched biochar. The enriched biochar was applied to a simulated rice field in a lysimeter made from PVC pipe with diameter of about 21 cm and height of 60 cm. The soils used in this study were: (1) Acid soil from Pontianak, West Kalimantan; (2) Neutral soil from Malang, East Jawa, and; (3) Calcareous soil from Kupang, East Nusa Tenggara.

The air dried soils was passed through 2.0 mm diameter sieve and remolded into a lysimeter. Then enriched biochar of ≤ 0.05 mm (equal to 5 $t.ha^{-1}$) was apllied to a depth of 10 cm from soil surface. The experiment was conducted for 120 days and during the experiment the soil in the column was submerged with deionized water at about 5 cm height.

Soil sample to a depth of 10 cm was taken at 1, 7, 15, 30, 60 and 120 days after biochar application for nitrogen analysis. Soil pH, organic-carbon content and soil Cation Exchange Capacity (CEC) was determined at 120 days after enriched biochar application.

Laboratory analysis.

Biochar and soil were analyzed for its pH, organic carbon content, total nitrogen content and Cation Exchange Capacity. Biochar characterization was done by the method of Ahmedna[21]. The Biochar was ground and passed through a 0.50 mm diameter sieve prior to the pH measurement. The Biochar was then dried at 80°C for 24 hours for characterization. The suspensions of biochar was prepared by adding 1 g of biochar into 100 ml of de-ionized water. The biochar suspensions then was heated to about 90°C and then stirred for 20 minutes to allow the dissolution of the soluble biochar components. The suspensions were then cooled to room temperature, and then pH was measured with a pH-meter (Jenway 3305). The total organic-carbon content determination of biochar samples was done using the method described in ASTM D 3176 [22].

Soil pH was measured in H_2O (1:2.5 ratio) and read with a pH meter (Jenway 3305). To determine soil organic matter content, the Walkley and Black (wet oxidation) method was used in all samples[23]. The total soil Nitrogen content was determined using the Kjeldhal method[24]. Some characteristics of soil and biochar used in this study is presented in Table 1.

Table 1. Chemical characteristics of soil and biochar used in the experiment.

Chemical Properties	Acid soil (Pontianak)	Neutral soil (Malang)	Calcareous soil (Kupang)	Poultry litter biochar	Corn-cobs biochar
Water content (% w/w)	-	-	-	8.65	5.86
pH-H_2O	4.32	6.46	7.52	7.95	8.14
C (%)	1.02	1.30	1.32	28.45	47.06
N ((%)	0.11	0.13	0.12	0.02	0.00
CEC ($cmol\ kg^{-1}$)	6.47	14.96	12.28	15.50	14.75

RESULTS AND DISCUSSION

The experiment results presented in Table 2 shows that the capacity of biochar to absorb nitrogen was influenced by biochar diameter and the nitrogen enriched materials. The influence of biochar diameter to nitrogen fixing capacity is related to the surface area of the biochar. The devrease in the biochar diameter would increase its surface area, and hence it would adsorbed more nitrogen from the solution. However, decreasing biochar diameter from 0.50 mm to less than 0.25 mm did not significantly increase the biochar capacity for absorbing nitrogen. Based on this result, it can be concluded that biochar diameter of less than 0.50 mm was appropriate for nitrogen enrichment biochar.

Table 2. Nitrogen content of poultry litter and corn-cobs biochar enriched with Ammonium Sulfate and Nitrate Acid Solution.

Biochar Feedstock	Biochar diameter (mm)	Total N content of enriched biochar (%)	
		Ammonium sulphate	Nitrate acid
Poultry litter	2.00 – 3.36	2.54 ab	2.26 a
	1.00 – 2.00	2.52 ab	2.351a
	0.50 – 1.00	3.69 d	3.45 cd
	0.25 - 0.500	3.82 d	3.38 cd
	< 0.25	3.30 cd	3.56 cd
Corn-cobs	2.00 – 3.36	2.15 a	2.05 a
	1.00 – 2.00	2.27 a	2.33 a
	0.50 – 1.00	3.48 cd	2.97b
	0.25 - 0.500	3.58 cd	3.16 bc
	< 0.25	3,46 cd	3.45 cd

*) means followed by the same letters is not significantly different ($p = 0.05$)

The results from this experiment suggested that the properties of biochar did not significantly influenced the ability of biochar to fix nitrogen. Jassal *et al*.[20] suggested that H:C ratio of biochar was unrelated to the nitrogen fixing capacity. The ability to fix nitrogen was more influenced by the active surface of biochar. These authors found that poultry litter and spruce-pine-fir biochar which has the similar H:C ratio possessed a similar N sorption capacity.

Looking from the materials for nitrogen enrichment point of view, although there was no significant different ($p = 0.05$), there was a tendency that ammonium sulfate yielded a higher fixed nitrogen than that of nitrate acid. Except for poultry litter biochar with diameter of less than 0.25 mm and corn-cobs biochar with diameter of 1.00 – 2.00 mm diameter, all biochar enriched with ammonium sulfate had a higher fixed nitrogen compared to that of enriched with nitrate acid.

Nitrogen absorbed in enriched biochar was relatively stable. The result presented in Table 3 shows that the nitrogen content in enriched biochar stored until 120 days did not decreased significantly. This result implied that biochar has a good prospective to be develop as the carrier for nitrogen nutrient, or in other term as a “slow nitrogen release fertilizer”

Table 3. Nitrogen content of enriched biochar at different days after storage

Treatment		Nitrogen content at………… days of storage		
Biochar feedstuffs	Enriched materials	0	30	120
Poultry litter	Ammonium sulfate	3.82 b	3.78 b	3.67 ab
	Nitrate acid	3.38 ab	3.42 ab	3.35 ab
Corn-cobs	Ammonium sulfate	3.58 ab	3.68 ab	3.59 ab
	Nitrate acid	3.16 a	3.22 a	3.25 ab

*) means followed by the same letters is not significantly different ($p = 0.05$)

The application of nitrogen enriched biochar increased the organic-carbon content either in acid, neutral or cacareous soil as expected (Table 4). The high organic carbon content, even at 120 days after application is a consequence of the high stable organic compound in the biochar [11, 12].

The result presented in Table 4 also show that the Cation Exchange Capacity of a soil applied with enriched biochar was higher compared to that of non treated soil. The increase of Cation Exchange Capacity of the soil applied with biochar is reasonable, because the organic carbon compound in the applied enriched biochar would contribute to the nett negative charge in the soil. If the increase in cation exchange capacity was presented as the percentage to the initial cation exchange capacity, it can be seen that the cation exchange capacity increase in acid soil (22 %) which is higher compared to the neutral (9%) or calcareous soil (13 %). However, this difference was not attributed to the acidity, probably due to the clay content. The acid soil possess a very low clay content (about 8%).

Table 4. Effect of N-enrichment biochar application on Organic carbon content and cation exchange capacity (CEC) of soils with different acidity at 120 days after application.

Treatments	C (%)			CEC (cmol kg^{-1})		
	Acid soil	Neutral soil	Calcareous soil	Acid soil	Neutral soil	Calcareous soil
No biochar	0.90 a	1.30 a	1.37 a	6.27 a	15.40 a	13.42 a
Poultry litter biochar-NH_4	1.46 b	1.85 b	1.94 b	7.42 b	16.88 b	14.58 b
Poultry litter biochar-NO_3	1.28 ab	1.66 ab	1.96 b	7.68 b	16.90 b	14.65 b
Corncobs biochar-NH_4	1.68 b	1.91 b	1.98 b	7.45 b	17.14 b	15.27 b
Corncobs biochar-NO_3	1.66 b	1.84 b	1.87 b	7.02 b	16.35 b	15.20 b

*) means followed by the same letters for the same characteristics is not significantly different (p = 0.05)

The results discussed above indicated that enrihment of biochar with ammonium sulfate and nitric acid did not influence the ability of biochar to increase soil organic matter and its cation exchange capacity.

Enriched biochar application increased pH of acid and neutral soil, but did not significantly influence the pH of alkaline soil (Table 5). It seems that enrichment of biochar with both ammonium sulfate and nitric acid did not influence its capability for increasing pH of acid soil as shown by Masulili *et al*.[7]. Nur *et al.*[25] also reported that application of either biochar or fortified biochar did not significantly influenced the pH of calcareous Kupang soil.

Table 5. Effect of N-enrichment biochar application on soil pH with different acidity

Treatment	Soil pH (120 days after application)		
	Acid soil	Neutral soil	calcareous soil
No biocchar	4.36 a	6.48 a	7.46 a
Poultry litter biochar-NH_4	5.90 c	6.98 bc	8.05 a
Poultry litter biochar-NO_3	4.56 ab	6.66 ab	7.55 a
Corn-cobs biochar-NH_4	5.85 c	7.44 c	7.95 a
Corn-cobs biochar-NO_3	4.96 b	6.86 ab	7.48 a

*)means followed by the same letters in the same column is not significantly different (p=0.05)

The result presented in Table 6 show that at one day after application, nitrogen content in the soil applied with enriched biochar significantly higher compared to the nitrogen content of the soil with no biochar application. However, after 120 days application, only the soil applied with ammonium sulfate enriched biochar had a significant higher nitrogen content than the no biocahr soil. Nitrogen content of the soil applied with nitrate acid enriched biochar was not significantly different compared to that of the no biochar soil. This data indicated that nitrogen in biochar enriched with nitrate acid was less stable compared to that of enriched with ammonium sulfate.

Those phenomena can be explained from the nutrient adsorption and cation exchange reaction mechanism. The soil applied with biochar would has a high negative charge, which is shown by its high cation exchange capacity (Table 4). This negative charge would adsorb ammonia-N (NH_4^+), but not nitrate-N (NO_3^-). Therefore nitrogen resulted from nitric acid enriched biochar leach easily. As a result, after 120 days of application, nitrogen content in soil applied with Nitrate-enriched biochar did not much different with the control (no biochar treatment).

Table 6. Effect of N-enrichment biochar application on total nitrogen content of soils with different acidity

Treatment	Total nitrogen content (%) at .... days					
	1 day			120 days		
	Acid soil	Neutral soil	Calcareous soil	Acid soil	Neutral soil	Calcareous soil
No biochar	0,11 a	0,12 a	0,11 a	0,09 a	0,11 a	0,09 a
Poultry litter biochar-NH_4	0,18 b	0,21 b	0,17 b	0,14 b	0,14 b	0,14 b
Poultry litter biochar-NO_3	0,17 b	0,20 b	0,16 b	0,12 b	0,12 ab	0,12 ab
Corn-cobs biochar-NH_4	0,17 b	0,19 b	0,18 b	0,14 b	0,15 b	0,14 b
Corn-cobs biochar-NO_3	0,17 b	0,17 b	0,17 b	0,12 b	0,11 a	0,11 a

*)means followed by the same letters in the same column is not significantly different (p=0.05)

The results presented in Figure 1, 2 and 3 show the nitrogen release pattern of enriched biochar in Acid (Figure 1); Neutral (Figure 2) and Calcareous soil (Figure 3).

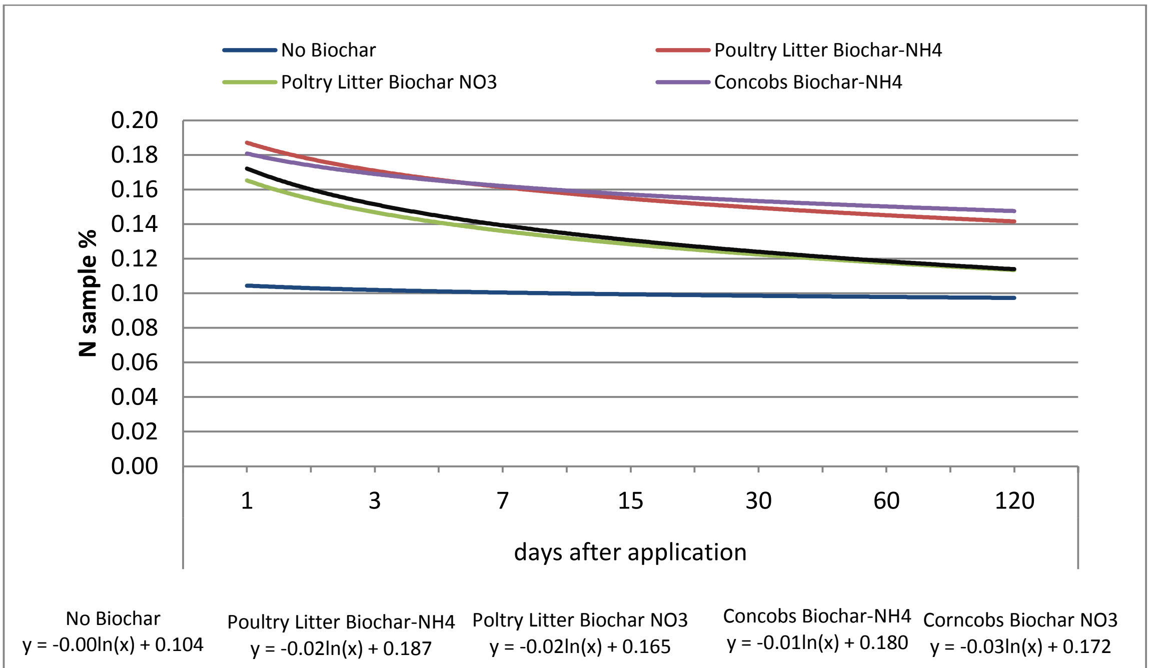

Figure 1. Effect of N-enrichment biochar application on total nitrogen content of acid soil at different days after application

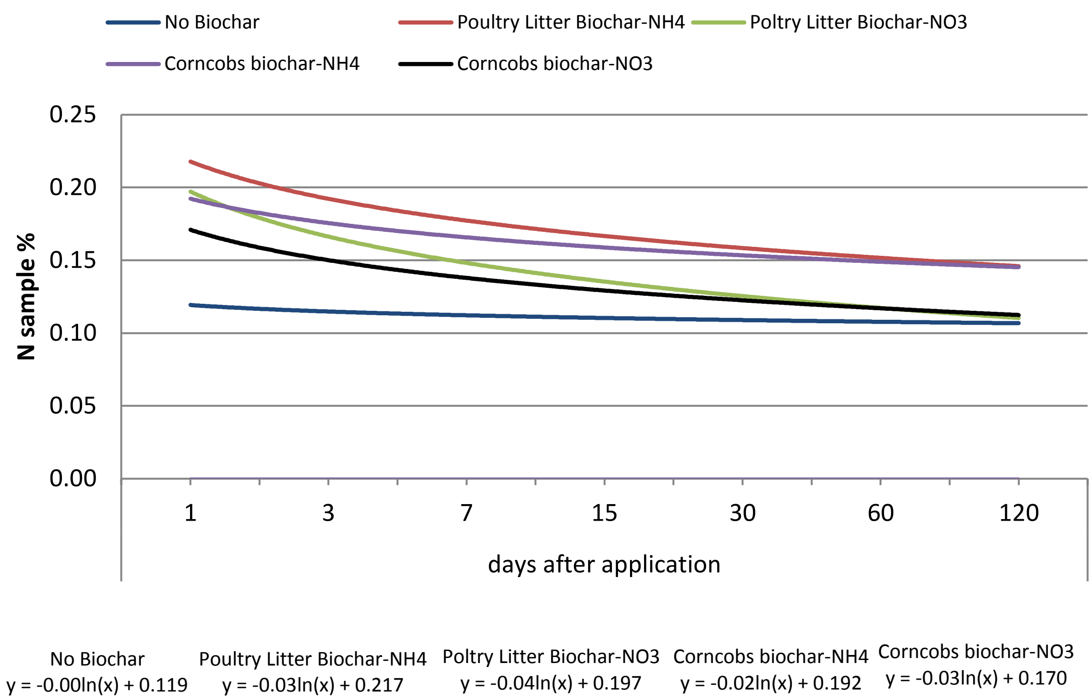

Figure 2. Effect of N-enrichment biochar application on total nitrogen content of netrual soil at different days after application

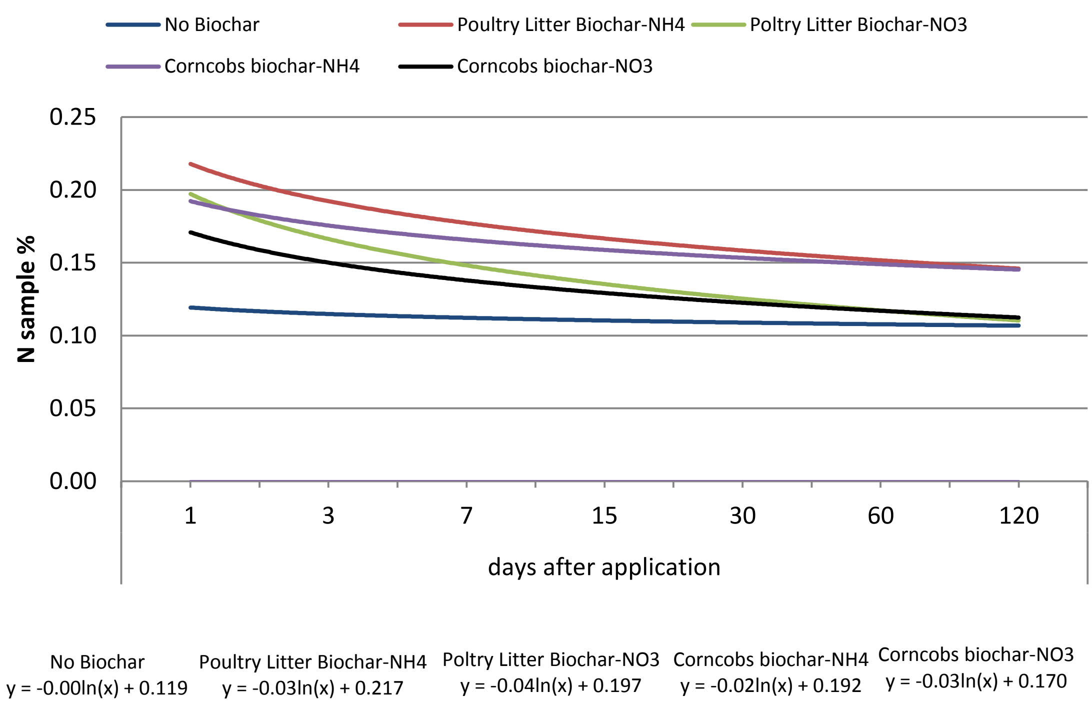

Figure 3. Effect of N-enrichment biochar application on total nitrogen content of netrual soil at different days after application

The results presented in Figure 1; 2 and 3 shown that nitrogent content of either acid, neutral or calcareous soil, applied with biochar enriched with ammonium consistenly higher compared to the that of applied with biochar enriched with nitrate. The release of nitrogen from enriched biochar follows an exponential model of:

$$Y = - a \ln x + b$$

In which:

Y is the nitrogen content in the soil

X is time (days after application)

a and b are the constant parameters obtained from the experiment

ACKNOWLEDGEMENT

This research was funded by Directorate General for Research and Development Strengthening, Indonesian Ministry of Technology, Research and Higer Education, under Strategic National Research Scheme with Contract No. 137/SP2H/DPRM/2016, 10 March 2016

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