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Research Article

Improvement of post-nickel mining soil fertility with biochar and calcite

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Abstract

Reclamation of post-nickel mining soil requires a long process and renewable innovations to improve soil properties. One of the alternative technologies for post-mining soil reclamation is utilizing oil palm empty fruit bunches (OEFB) as biochar and applying calcite ($CaCO_3$). The objective of this research was to determine the effect of OEFB and the application of $CaCO_3$ on the properties of post- nickel mining soil and the growth of *Mucuna* sp. This research was a pot experiment using a factorial randomized block design method. Treatments tested were combinations of three OEFB biochar (B) levels, i.e., B1 = 2.5%, B2 = 5%, and B3 = 7.5% of soil weight, and three calcite (K) dosages, i.e., K1 = 1.5, K2 = 3, K3 = 4.5 t ha^{-1}. The soil parameters measured included soil pH, available P, organic C, cation exchange capacity, and exchangeable Al, Ca, Mg, K, and Na. The parameters of *Mucuna* sp. measured were plant height and plant dry weight. The results showed that applying biochar and calcite to post nickel mining soil significantly increased soil pH, available P, organic C, cation exchange capacity, growth of *Mucuna* sp. and decreased exchangeable Al content. Treatment of biochar 7.5% by weight of soil and 4.5 t calcite ha^{-1} gave the best effect on improving soil fertility and growth of *Mucuna* sp. compared to other treatments.

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Introduction

The open-pit mining can cause damage to the ecology (Thomas et al., 2015), mainly to soil physical damage and fertility, due to loss of topsoil along with the organic matter, compaction and the unavailability of plant nutrients. The soil organic matter content is very low, soil pH varies, and there may be symptoms of toxicity of certain elements (Bato, 2016; Neswati et al., 2020; Neswati et al., 2022). Mining activities can increase soil acidity, which directly affects the availability of macronutrients P and K needed by plants, as well as high Fe and Al contents so that they can be toxic to plants (Allo, 2016). Management of post-mining soil requires serious attention and goes through a long process of rehabilitating it so that environmentally friendly innovations are needed. One of them is by utilizing oil palm empty fruit bunches (OEFB) to overcome the problem of post-mining soil. The reason for using OEFB as the source of biochar, in addition to the nutrient content possessed by OEFB, is that this material is abundantly available around the nickel mining area in Sorowako, Indonesia, namely oil palm plantations that are scattered in several districts adjacent to the mining area. According to Erwinsyah et al. (2015), OEFB is the largest solid waste generated from the processing of the palm oil industry. OEFB contains chemical constituents of fat, cellulose, lignin and hemicellulose. In the process of producing crude palm oil in palm oil mills, the amount of OEFB produced reaches 21-23% of the total weight of fresh fruit bunches (Kresnawati et al., 2017).

Biochar is a porous substance of wood charcoal which provide a good environment for microbes and keep the carbon-nitrogen balance. It is even able to hold and provide water and nutrients for plants (Sihotang et al., 2018). OEFB biochar produced by the pyrolysis process has been proven to be effective in increasing soil fertility because it can hold water and maintain the availability of nutrients that are important for plants by reducing soil acidity (Kresnawati et al., 2017). Adding other substances is necessary to increase the effectiveness of the use of biochar in post-mining soil. According to Allo (2016), the soil in Sorowako is classified as Oxisol, which developed from ultrabasic rock. These rocks are characterized by low silica content (<45%) and dominated by dark ferromagnesian crystallized minerals, such as olivine, pyroxene, and amphibole, which are generally dark grey to black or greenish in color (Fox and Tan, 1971). These rocks are rapidly weathered (Lee et al., 2004; Alam et al., 2012), releasing very high amounts of Mg due to the dominance of ferromagnesian as a rock constituent. These conditions lead to an imbalance of cations in the soil, consequent Mg toxicity and other cation deficiencies (Anda, 2012). The problem can be solved by means of calcium carbonate ($CaCO_3$) to reduce the imbalance of cations and increase the soil pH to keep the availability of P and Mo, and reduce the toxicity of Fe, Mn and Al (Irwan dan Nurmala, 2018).

This study aimed to explore the effect of oil palm empty fruit bunches (OEFB) biochar and calcium carbonate and the growth of *Mucuna* sp. in post-nickel mining soil.

Methods

A pot experiment was carried out at the Faculty of Agriculture, Hasanuddin University, Indonesia. The materials used included samples of soil, biochar of OEFB, and *Mucuna* sp. seeds. The tools used in this study were a set of assembled biochar-making tools to burn OEFB by pyrolysis method, planting pots, and a set of soil sampling equipment. The biochar was prepared by the 'drum klin" method using a heat-resistant metal drum to carbonize charcoal. The oil palm empty fruit bunches (OEFB was) chopped and then dried with direct sunlight, then the dried OEFB was put into a drum that was assembled and heated with a temperature of 250-300 ^{o}C for 1 hour. Soil samples were collected at a depth of 0-40 cm from the post-nickel mine reclamation site in East Luwu Regency, Indonesia (Figure 1). Treatments tested were the combinations of three biochar (B) levels (% of the weight of the soil), i.e., B1 (2.5%), B2 (5.0%), and B3 (7.5%), and three calcite (K) dosages, i.e., K1 (1.5 t ha^{-1}), K2 (3 t ha^{-1}), and K3 (4.5 t ha^{-1}). The nine treatment combinations were arranged in a factorial randomized block design with three replications. Each treatment combination was mixed with 5 kg post-nickel soil in a 10 kg pot. Three *Mucuna* sp. seeds were then planted on each pot for 48 days. The soil chemical properties measured in this study were pH, organic C, cation exchange capacity (CEC), available P, and exchangeable Al, Ca, Mg, K, and Na. Soil pH (H_2O and KCl) was measured using a pH meter. Organic C was determined using the Walkley and Black method (Walkley and Black, 1934). Cation exchange capacity and exchangeable Ca, Mg, K, and Na were determined using the ammonium-saturation method (Chapman, 1965). Available P was measured using the technique developed by Olsen (1954). Exchangeable-Al was determined using the extraction method of KCl 1 N. The growth parameters of *Mucuna* sp. cover crops measured were plant height, number of leaves, and plant dry weight. The results of the observations were analyzed by means of variance followed by Tukey's HSD (honestly significant difference) test at a 95% confidence level.

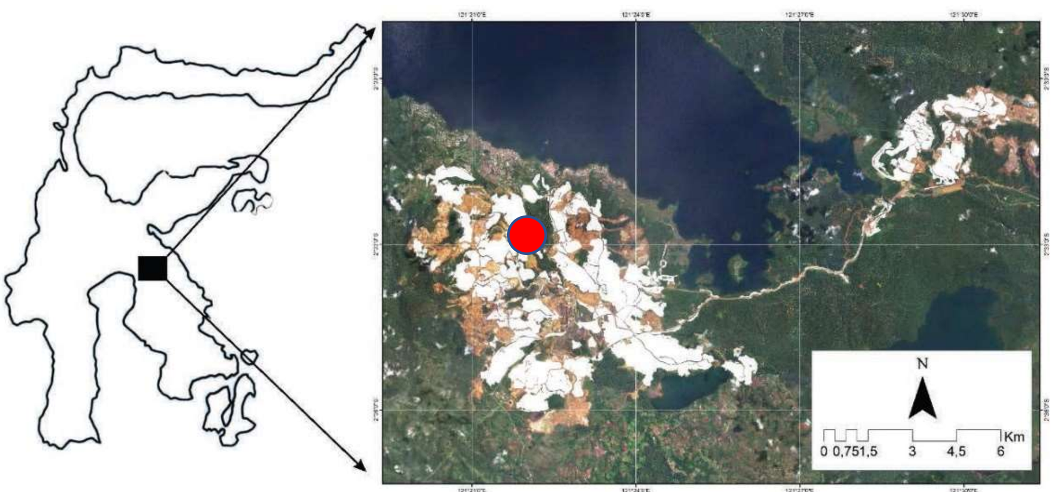

Figure 1. Location of soil sampling (red dot).

Results and Discussion

Soil properties

The results showed that the effect of biochar and calcite treatment on chemical properties and soil fertility, and plant growth of *Mucuna* sp. was statistically significant at the 95% confidence level, as shown in Table 1. The results of soil chemical analysis showed improvement in soil fertility after biochar and calcite combinations treatments which were indicated by an increase in soil pH, organic C, CEC, base saturation, available P, and Ca/Mg ratio and a decrease in exchangeable Al. Soil reaction (pH), organic C, and CEC with B3K3 treatment have higher values and were significantly different from other treatments. A similar result was also found in the available-P parameter, which the highest was found in the B3K3 treatment (14.80 ppm) and was significantly different from other treatments. The lowest exchangeable Al value was found in the B3K3 treatment (0.88 cmol kg^{-1}) and significantly different from other treatments with exchangeable Al values >1 cmol kg^{-1} and some even reached a value of 3.76 cmol kg^{-1}. The value of exchangeable bases, which included Ca, Mg, K and Na cations, was significantly affected by the increase due to the treatment tested. The highest values of Ca, Mg and Na, were found in the B3K3 treatment, namely 4.16, 5.32 and 0.42 cmol kg^{-1}, respectively, and significantly different from other treatments. As for the K parameter, the highest value was found in the treatment that gave the best effect, indicated by the B3K2 treatment, which was 0.51 cmol kg^{-1} and significantly different from the B3K1, B1K1, and B1K2 treatments. The highest Ca and Mg ratio values were found in the B3K3 treatment, which was 0.78 and significantly different from the B3K1 and B1K1 treatments.

Table 1. Effects of biochar and calcite on chemical properties of post-nickel mining soil.

Treatments	pH		Organic C (%)	Available P (ppm)	CEC	Exchangeable					Ca/Mg
	H_2O	KCl				Al*	Ca (cmol kg^{-1})	Mg	K	Na	
B1K1	5.71^{ab} ++	5.89^{a} ++	1.47^{g} **	7.99^{h} **	15.50^{e} **	3.76^{f} *****	1.41^{g} *	1.91^{e} ***	0.28^{cd} **	0.20^{e} **	0.46^{c}
B1K2	5.66^{bc} ++	5.92^{a} ++	1.56^{f} **	9.29^{fgh} **	15.97^{e} **	3.28^{ef} *****	1.84^{f} *	2.83^{d} ****	0.27^{d} **	0.30^{cd} **	0.66^{ab}
B1K3	5.70^{ab} ++	5.95^{a} ++	2.21^{de} ***	8.51^{gh} **	16.41^{de} **	2.96^{de} *****	2.30^{e} **	3.53^{c} ****	0.42^{ab} ***	0.31^{cd} **	0.66^{ab}
B2K1	5.75^{a} ++	5.89^{a} ++	2.21^{e} ***	9.79^{ef} **	15.87^{e} **	2.24^{cd} ****	2.70^{d} **	3.67^{c} ****	0.40^{ab} ***	0.33^{c} **	0.73^{a}
B2K2	5.71^{ab} ++	5.93^{a} ++	2.44^{c} ***	10.54^{de} **	19.40^{bc} ***	2.16^{bcd} ****	2.85^{d} **	3.64^{c} ****	0.47^{ab} ***	0.31^{cd} **	0.74^{a}
B2K3	5.73^{a} ++	5.94^{a} ++	2.49^{bc} ***	13.08^{c} ***	20.28^{ab} ***	2.08^{bc} ****	2.92^{cd} **	3.90^{bc} ****	0.45^{ab} ***	0.34^{bc} **	0.74^{a}
B3K1	5.62^{c} ++	5.85^{a} ++	2.21^{e} ***	8.99^{fgh} **	18.42^{c} ***	1.68^{ab} ****	2.96^{c} **	5.06^{a} ****	0.39^{b} **	0.25^{de} **	0.59^{b}
B3K2	5.70^{ab} ++	5.88^{a} ++	2.53^{ab} ***	13.31^{bc} ***	19.31^{bc} ***	1.04^{a} ***	3.65^{b} **	4.90^{a} ****	0.51^{a} ***	0.34^{c} **	0.74^{a}
B3K3	5.76^{ab} ++	5.95^{a} ++	2.60^{a} ***	14.80^{a} ***	21.28^{a} ***	0.88^{a} ***	4.16^{a} **	5.32^{a} ****	0.43^{ab} ***	0.42^{a} ***	0.78^{a}

Notes: Numbers followed by the same letters (a, b, c, d) mean no significant difference in the treatment of biochar and $CaCO_3$ in the HSD test of 0.05. ++ Slightly acid, * Very Low, *** Medium, ****High, ** Low, ***** Very High. B1 = biochar 2.5% soil weight, B2 = biochar 5.0% soil weight, B3 = biochar 7.5% soil weight. K1 = 1.5 t calcium carbonate ha^{-1}, K2 =3 t ha^{-1}, K3 = 4.5 t calcium carbonate ha^{-1}.

The results of soil analysis after treatment showed an increase in the pH value along with an increase in the dose of biochar and calcite applied. This indicates that the provision of biochar and $CaCO_3$ can enhance soil pH. This is similar to that reported by Setiawan et al. (2018) that an increase in pH due to the addition of biochar occurs because of the process of mineralization of organic anions into CO_2 and H_2O.

According to Steiner (2007), an increase in pH associated with the addition of biochar to acid soils is caused by an increase in the concentration of basic cations (Ca^{2+}, Mg^{2+} and K^{+}) and a decrease in the concentration of soluble Al^{3+} in the soil. The pH (KCl) value of all treatments was higher than the pH (H_2O), which indicates that the soil is advanced developed. The soil has been associated with intensive leaching and strongly oxidizing conditions, dominated by the Fe and Al oxides, so that the concentration of H^{+} increases, resulting in the pH of H_2O being lower. In addition to soil pH, organic C and CEC parameters also experienced a significant increase. The increase in organic C and CEC was influenced by the addition of biochar and $CaCO_3$. This is similar to the opinion of Cheng et al. (2006) that the increase in soil CEC after biochar application was caused by the formation of carboxylate groups resulting from abiotic oxidation that occurred on the outer surface of the biochar particles. In addition, according to Lehman and Stephan (2009), biochar in the soil is in the form of particles which can cause stable organic C form mineralization and create a negatively charged particle surface which makes CEC larger and nutrient retention increase. Biochar contains high C atoms, which form aromatic compounds linked by six C atoms together without oxygen or hydrogen (Lehman and Stephan, 2009). In addition, the increase in CEC and organic C is influenced by the function of $CaCO_3$. This is in accordance with Rowley et al. (2020) that calcium carbonate contributes to the important C fraction in the soil that links the long-term geological C cycle with the long-term biogeochemical cycle of soil organic carbon. This underlies the increase in CEC and organic C values after applying biochar and $CaCO_3$.

The results of the available P analysis showed that the B3K3 treatment gave the highest effect compared to other treatments, which was indicated by an increase in available P from 6.60 ppm to 14.80 ppm. This increase in available P was influenced by the P nutrient content in biochar and an increase in pH by $CaCO_3$. This is in line with Mosharrof et al. (2021), who used biochar and manure on acid soils which showed that the combination of biochar and manure treatment could improve soil properties, in particular, an increase in the available P. Deluca et al. (2009) states that the biochar is a direct source of dissolved P, complexing P metal chelators (Al^{3+}, Fe^{3+}, Ca^{2+}), modifiers soil pH, promoter of microbial activity and P mineralization. In addition, the increase in P availability was influenced by an increase in soil pH. This was correlated with the increase in soil pH value with increasing doses of biochar and calcite. Krisnhakumar et al. (2014) stated that P is most widely available in the pH range between 5.5 and 6.5.

Based on the results of the exchangeable Al analysis, it was found that the B3K3 treatment gave the best effect compared to other treatments, as indicated by the decrease in exchangeable Al from 3.80 cmol kg^{-1} to 0.88 cmol kg^{-1}. This indicates that biochar and $CaCO_3$ can reduce the content of Al in the soil. The provision of biochar can improve soil pH, lowering the concentration of aluminium can exchange and reduce the ability of iron and aluminium oxide in a bind P (Ratmini et al., 2018). In addition, the provision of $CaCO_3$ raised the pH of the soil as well as liberated the N and P from Al and Fe bonds. Rais et al. (2017) stated that the administration of $CaCO_3$, where calcium replaces hydrogen and aluminium ions in the adsorption complex.

The resulting hydrogen ions react with carbonates to form carbonic acid (H_2CO_3). The carbonic acid produced will dissociate to form CO_2 and H_2O. The carbon dioxide (CO_2) produced will be released into the atmosphere, so the final result of this lime reaction is H^+ ions whose activity is decreasing and the more OH^- dissolved in the soil, which can increase soil pH. This is supported by research by Angelita et al. (2020) regarding the improvement of post-nickel soil quality with the use of mycorrhiza and OEFB biochar, it was found that the use of mycorrhizae and biochar could improve the chemical properties of post-nickel soil by increasing soil pH and decreasing Al-dd from 2.61 cmol kg^{-1} to 1.58 cmol kg^{-1}. The results of the analysis of exchangeable bases showed that B3K3 gave the highest effect compared to other treatments, which was indicated by an increase in Ca, K, and Na as well as a decrease in Mg. Based on the analysis of the ratio of Ca/Mg in the soil obtained a ratio of <1, which means the number of cations Mg>Ca. This will cause a nutrient imbalance (Anda, 2012). This imbalance is influenced by several factors such as parent material, soil pH and the ratio with other cations in the soil. According to Hutabarat (2015), ultramafic rocks are characterized by a high content of magnesian olivine (Mg_2SiO_4) and low content of SiO_2 (less than 45%). In addition, it is also influenced by soil pH, where these exchangeable bases will be optimally available at pH 6.5-7.5. This right is in accordance with the opinion of Munawar (2018) that the Ca, Mg and K elements are mostly available in soils with a pH greater than 6. According to Hanafiah (2014), the availability of elements is also influenced by the ratio between cations, Ca is influenced by high Al and H activities, Mg is influenced by high K and Al contents, and K is influenced by Ca and Mg contents.

The improvement of the chemical properties of soil fertility given biochar is supported by the quality of the biochar. The results of the analysis of the biochar used showed that the levels of organic C, total N and C/N ratio of the biochar were 18.26%, 0.86% and 21.2%, respectively. This value means that the quality of OEFB biochar is quite good and fits the standard requirements for soil amendment. According to the Decree of the Minister of Agriculture of Indonesia no: 28/Permentan/SR.130/B/2009 concerning the minimum technical requirements for organic and soil amendment, organic C is >7%, total N is <6%, and the C/N ratio is 8-15% (Soil Research Center, 2009).

Crop growth and biomass yield

The treatment with the highest effect on plant height, number of leaves and dry weight was found in the B3K3 treatment and was statistically significantly different from the other treatments (Table 2). The increasing dose of biochar and calcite was accompanied by an increase in the value of the measured parameters. It was influenced by the addition of biochar and $CaCO_3$, which significantly affect the chemical properties of soil fertility improvement. Biochar contains essential nutrients, can increase soil pH and availability of P and reduces Fe, Mn and Al. This is in accordance with Gani (2019); besides containing macro and micronutrients, biochar is also able to improve soil physical, chemical and biological properties; biochar can increase pH, organic C, available P, total N and soil CEC.

Table 2. Effects of biochar and calcite on growth and biomass yield of *Mucuna* sp. grown for 48 days on post-nickel mining soil.

Treatments	Plant Height (cm)	Number of Leaves (Strand)	Dry Weight (g)
BIK1	0.00 b	0.00 b	0.00 b
BIK2	4.33 b	1.00 b	0.16 b
BIK3	4.67 b	1.67 ab	0.19 b
B2K1	1.17 b	0.67 b	0.06 b
B2K2	4.00 b	1.67 ab	0.39 b
B2K3	3.67 b	1.00 b	0.43 b
B3K1	3.33 b	1.00 b	0.14 b
B3K2	6.67 b	3.33 a	0.34 b
B3K3	15.83 a	3.67 a	1.15 a

Notes: Numbers followed by the same letters (a, b, c, d) mean no significant difference in the treatment of biochar and $CaCO_3$ in the HSD test of 0.05. B1 = biochar 2.5% soil weight, B2 = biochar 5.0% soil weight, B3 = biochar 7.5% soil weight. K1 = 1.5 t calcium carbonate ha^{-1}, K2 = 3 t ha^{-1}, K3 = 4.5 t calcium carbonate ha^{-1}.

According to Tambunan et al. (2014), most of the Ca^{2+}, Mg^{2+} and K^+ cations in the soil in which biochar was added were not bound by electrostatic forces but as dissolved salts and were therefore easily available and absorbed by plants. This is also supported by Tarigan and Nelvia (2020), that the application of OEFB biochar and mycorrhizae had a significant effect on the growth of sweet corn. Another study conducted by Muhammad (2019) found that the addition of biochar and manure had a very good effect on plant height, plant fresh weight and plant dry weight. Biochar is safe to use in the long term (Gani, 2019). Biochar keeps the balance of carbon-nitrogen and retains water and nutrient available to plants.

Conclusion

The use of a combination of biochar 7.5% by weight of soil and 4.5 t $CaCO_3$ ha^{-1} (B3K3) significantly improved the chemical properties of post-nickel mining soil (enhancing soil pH, organic C, available P, cation exchange capacity, basic cations, and reducing exchangeable Al). The B3K3 treatment had a significant effect on the growth and biomass yield of *Mucuna* sp. as indicated by the highest plant height, number of leaves and plant dry weight compared to other treatments.

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