INTRODUCTION

Oxisols (acidic soil) has areas for about ± 14.11 million ha or 7.5% of the total land area in Indonesia. Many problems will be faced when it is used as agricultural land, such as heavy metal toxicity of aluminum (Al) and iron (Fe) as well as nutrient deficiencies, especially phosphorus (P) in plants (Goyer, 1997). In acidic soils (especially soil with pH less than 5.5), Al is the dominant ion that will react with phosphate. In these soils the first products formed would be amorphous Al phosphates. The amorphous Al phosphates are gradually changed into compounds that resemble crystalline variscite (an Al phosphate). This reaction will result in very insoluble compounds of phosphate that are generally not available to plants (Petzet, Peplinski, & Cornel, 2012). Therefore, the addition of P fertilizer less beneficial for the crop and the result is low efficiency of P fertilizing.

The addition of organic matter with P-fertilizers might be more efficient to increase P solubility and uptake by plant. Components of organic materials that play a role in the process of improving soil chemical properties are humic substances (HS) (Sparks, 2003). HS was used in this research due to its rapid reaction, active in soil, with some electric charge and cation exchange capacity (CEC) as compared to clay minerals. The component of HS were humic acid dan fulvic acid, which humic acids are colloids and behave somewhat like clays, even though the nomenclature suggests that they are acids and form true salts. When the cation exchange sites on the humic molecule are filled predominantly with hydrogen ions, the material is considered to be an acid and is named accordingly. However, it has no great effect on pH because the acid is insoluble in water (Senn & Kingman, 1973). The functional groups of the HS act as acids or bases, as anion and cation changers and specific absorbent for the nutritive and harmful substances (Rodrigues, Novotny, Knicker, & de Oliveira, 2019).

This HS was extracted from low rank coal (ex : Sub-bituminous). Rezki, Ahmad, & Gusnidar (2007) reported that Sub-bituminous coal taken from Pasaman, West Sumatra can be used as a source of organic material because it contains HS

ARTICLE INFO

Keywords: Humic Substances, Oxisol, P-fertilizer, Rice, Sub-bituminous

ABSTRACT

Humic Substances (HS) sources of Sub-bituminous can be used as soil amandement. The purpose of this research was to examine the residual effects of HS combined with P-fertilizers and the method of incubation to improve Oxisols fertility and rice production. The experiment consisted of 2 factors, including: 1) incubation methods (i.e. I₁ = HS incubated 1 week, then incubation of P fertilizers 1 week; I₂ = HS and P- fertilizers directly incubated into the soil 2 weeks; and I₃ = HS and P-fertilizers mixed 1 week, then incubated to soil 1 week), and 2) residual effect of HS with P-fertilizers combinations (i.e. H₁ = 800 ppm + 100%; H₂ = 800 ppm + 75% R; H₃ = 400 ppm + 100% R; and H₄ = 400 ppm + 75% R). All treatment was compared to the tradition of fertilization by the local farmers and control. The results showed that the combination of residual effects (HS and P-fertilizers) with the incubation method decreased exchangeable Al, as consequently increased the available P in Oxisols. The HS addition increased the efficiency of P fertilizers up to 25%, as well as increased rice production in averaged 3.9 t/ha (i.e. treatment H₄).
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as much as 31.5% (21% humic acid and fulvic acid 10.5%) and were extracted with 0.5 N NaOH. Sub-bituminous coal percentage humic acid (21%) was higher than the percentage of humic acid contained from other organic materials, such as municipal solid waste compost (1.4%), manure (1.6%), rice straw compost (5%), and peat soil (9.2%) (Herviyanti, Prasetyo, Ahmad, & Saidi, 2012). Therefore, the Sub-bituminous coal as a source of HS can be used as soil organic matter to improve soil fertility. The potential of coal in Indonesia is very abundant, especially on the islands of Kalimantan and Sumatra (Lignite and Sub-bituminous). Indonesia has the coal reserves of 20.98 billion tons or 0.5% of the total coal reserves in the world and are dominated by Lignite by 59%, Sub-bituminous by 27%, and Bituminous reaching 14%, while Anthracite is less than 0.5%. According to Haryadi & Suciyanti (2018), West Sumatra has around 973.92 million tons (mined and after being mined) of coal. This HS was extracted from low rank coal (Sub-bituminous).

Stevenson (1994) and Tan (2011) stated that by using HS, it could control Al and Fe toxicity and increase the availability of P, through the formation of a chelate or complex organo-metal compounds between oxide and hidroxide of Al and Fe, so that the metal Al and Fe activities could be reduced and had no toxic for plants. According to Parvan, Rahmandad, & Haghani (2013) organic matter and the HS at the same time are the energetic substrate of the microflora activity in the rhizosphere and represent an important reservoir of chelate-type compounds, which have a great capacity to bind various metal ions (Al, Cu, Fe, Zn) and to form organo-metallic complexes with an important role in the formation of the soil characteristics and plant nutrition. A large number of nutritive ions (PO$_4^{3-}$ and SO$_4^{2-}$) are retained by chelating processes, in the form of various solubility compounds.

Humic substances directly can influence the growth of plant, nutrient uptake, and a number of other soil processes. Indirectly, HS can improve soil fertility by altering soil physic, chemical, and biological. HS can modify plant growth medium by improving soil structure, increasing CEC and water holding capacity for any soil type especially acidic mineral soil (Fiorentino, Spaccini, & Piccolo, 2006; Stevenson, 1994; and Tan, 2011). dos Santos, Lacerda, & Zinn (2013) stated that the HS have interesting properties to be used as fertilizers since they improve the physical and chemical structure of the soil and provide a source of organic carbon which is absorbable by the plants, whereas potassium is a primary nutrient for plants.

The application of HS has been studied by Herviyanti, Prasetyo, Ahmad, & Saidi (2012) from the first year of research. The result showed that the highest grain yield of paddy rice was on the treatment of 800 ppm HS + 100% P-fertilizer recommendation (300 kg/ha) which were incubated with I$_1$ (the mixture of HS and P fertilizer for 1 week and then incubated to the soil for 1 week) with grain yield 5.27 t/ha. This value was the best result because the yield grain production was the highest yield about 3.9 t/ha from Impago 6 (one of varieties of rice). The potential of rice grain yield could be reached was 5.81 t/ha (Sasmita et al., 2019) and the results were almost as good as 800 ppm HS + 75% Recommendation P fertilizers treatment. So that, with HS treatment 400 ppm were combined with 100% and 75% Recommendation of P-fertilizer and the incubation method. It showed that HS treatment was more economically for P fertilizing until 25%.

This research used plant indicator of paddy rice (Oryza sativa L.), because this crop is the prospective plant to grow in acid mineral soils and high responses on P fertilizing, where paddy was needed P by 120 kg SP-36 per ha or 19 kg P per ha (9.5 ppm). Paddy rice is the main crop plant in Indonesia. Based on the research background and the urgency that has been described, the research is conducted for the 2nd year, to study residual effects of HS from Sub-bituminous, which was combined with P-fertilizer in Oxisols. The objectives of examine the residual effects of HS combined with P-fertilizers and the method of incubation to improve Oxisols fertility and rice production. The hypothesis of this research was the treatment of HS from sub-bituminous and P-fertilizers with incubation method still has residual effect, so that plants can be used for the second planting season.

MATERIALS AND METHODS

Field experiment was done in a land farmer (Padang Siantah, 50 Kota district, West Sumatera), where residual effects research conducted in the first year experiment (2012). The designs of experiment have been conducted like first year, in the form of a 3 x 4 in block random factorial with tree replication. As the 1st factor was 3 ways incubation of HS from Sub-bituminous with P-fertilizers and the 2nd factor were four combination levels of HS
and P fertilizers which have best responses from greenhouse experiment by Herviyanti, Prasetyo, Ahmad, & Darmawan (2010). As a comparison, demonstration plots without HS and P-fertilizers (control) was made as well as the tradition of fertilization of the local farmers with 3 replications. Complete treatment is presented in Table 1.

Before the cultivation of the second season, ± 500 g of soil was collected for chemical analysis to show the nutrient residue from planting season 1. Soil analysis was conducted to determine the pH of H$_2$O (1:1) using a glass electrode, available P with Bray II methods, exchangeable-Al with the volumetric methods (Eviati & Sulaeman, 2009).

Soil cultivation was done by plowing and hoeing before planting. The size of plots was made about 3 m x 3 m and the distance between plots was about 1 m and 1.5 m as seen in Fig. 1. Five rice seeds per hole were planted with a planting spacing of 25 cm x 25 cm and covered with the soil. The harvest was done after 115 days to determine crop yield (weight of seed in 14% water content). The formula of water content by seed was 14%:

Water content of seed (X) = \[
\frac{\text{Heavy wet} - \text{Dry weight}}{\text{Dry weight} + 100\%} \times 100\%
\]

(1)

Dry weight remain (Y) = \[
\frac{\text{Dry weight}}{1 + X}
\]

(2)

Water content of dry weight by seed 14% = Y × 1.14

(3)

Plant growth analysis were determined the number of productive young plants by counting the number of panicles that produce pithy seeds which was measured when the plant at the maximum vegetative growth on 75 days after planting.

RESULTS AND DISCUSSION

pH and Al-exch of Oxisols

In Fig. 2, it can be seen that the interaction effect is not significant with the addition of HS and P-fertilizer ingredients in each incubation method carried out on the pH of Oxisol at the 2nd year, while for the two treatments of main effect was also seen not to have an effect on the pH of Oxisol, except compared to farmers’ traditions and controls. The soil pH was increase by 0.4 and 0.77 unit with the addition of HS and P-fertilizer at several doses compared to the farmer tradition and control in the 2nd year (Fig. 2A).

In Fig. 2B, the incubation method in the second year is lower than the first year, and the $I_3$ incubation method has a higher pH value in the first year compared to the second year. This was due to the contact with HS and P fertilizer to the soil in a short time, so the solubility of the H$^+$ ion decreases.

The soil pH in second year was lower than the first year in all treatment due to the increasing of ion H$^+$ solubility from HS, and soil organic addition from HS of Sub-bituminous coal. While the pH value in the tradition of farmers using chicken manure is equivalent to 10 t/ha.

Table 1. Combinations of residual effect of HS and P-fertilizers with incubation method

<table>
<thead>
<tr>
<th>Method of Incubation</th>
<th>Residual Effect Combination of HS + P-fertilizers (ppm + % Recommendation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1$: HS incubated 1 week, then incubation of P fertilizer for 1 week</td>
<td>$I_1H_1$ $I_1H_2$ $I_1H_3$ $I_1H_4$</td>
</tr>
<tr>
<td>$I_2$: HS and P fertilizer directly incubated into the soil 2 weeks</td>
<td>$I_2H_1$ $I_2H_2$ $I_2H_3$ $I_2H_4$</td>
</tr>
<tr>
<td>$I_3$: the blended HS and P fertilizer for 1 week, then its mixed material incubated to the soil for 1 week</td>
<td>$I_3H_1$ $I_3H_2$ $I_3H_3$ $I_3H_4$</td>
</tr>
</tbody>
</table>

Fig. 1. Plot design of all treatment in the field
In the first year the pH value was almost the same as the administration of HS in various combinations with P fertilizer, but slightly was more acid in the second year. This situation might be caused by the amount of manure given was quite a lot, so it produced many organic acids and contributed $H^+$. The addition of HS and combination P fertilizer had a lower pH value due to the suspected increase in soil organic carbon (SOC) and organic acid from the HS used and the effect of contact time on the soil. Schon, Mackay, Gray, Dodd, & van Koten (2015) stated that there is a negative correlation between SOC and pH. An increase in SOC implies a decrease in soil pH, which in turn decreases the microbial decay rate.

**Fig. 2.** Residuals effects of HS from sub-bituminous with P-fertilizers (A) and the way of incubation and (B) on the soil pH value and Al-exch (cmol(+)kg⁻¹)
Based on the results of statistical analysis, there was an insignificant effect on the amount of the addition of HS and P-fertilizer to the incubation method in the DNMRT Advanced Test at the level of 5%. The interaction effect was not significant with the addition of HS and P-fertilizer ingredients in each incubation method carried out on the Al-exch of Oxisols (Fig. 2). While for the two treatments, the main effect was also not seen on the Al-exch of Oxisols, except compared to farmers traditions and controls.

The effectiveness of decreasing Al-exch value is almost the same as in the first and second year (Fig. 2). While in Fig. 2A, the treatment of HS and fertilizer P was seen in the second year with higher Al-exch reduction occurred in the treatment (400 ppm + 100% Recommendation (R)) and in the first year there was a treatment (800 ppm + 100% Recommendation), amounting to 1.12 and 1.71 cmol(+)kg. A higher Al-exch decrease occurred in the method of Incubation I, by 1.41 and 1.09 cmol(+)kg when compared to controls in the first and second year (Fig. 2B). HS have the ability to reduce the content of Al3+ dissolved in interchangeable soil solutions. In this way, Al-exch can be reduced because these Al3+ ions are bound with HS. Reducing Al3+ and increasing soil pH with the application of HS and P-fertilizers which is organic acids (functional groups) of HS can react with Al3+ metals resulting complex organo compound or chelate. According to Huang & Schnitzer (1986), increasing the HS addition could increase carboxylic (-COOH) and phenolic (-OH) functional groups, therefore it could form complexes with Al3+ cations and this cation exchange will decrease. Soil pH is influenced by Al3+ where a decrease in Al3+ can increase soil pH when HS binds Al. Rodrigues, Novotny, Knicker, & de Oliveira (2019) stated that the functional groups deprotonation of HS will reduce hydrogen bond formation, between molecules and intra-molecules, so this mechanism will increase the repelling force between groups in humic acid molecules. This mechanism causes the surface of colloidal humic acid to have a negative charge and will become an exponential open system to increase the pH of the soil.

Available-P of Oxisols

Based on the results of statistical analysis, it showed that there was a significant effect on the amount of addition of HS and P fertilizer materials to the incubation method in the DNMRT Advanced Test at the level of 5%. Fig. 3 showed that the interaction effect is significant with the addition of humic substances and P-fertilizer ingredients in each incubation method carried out on the P-available of Oxisols.

Available P in the second year is lower than the first year of planting season (Fig. 3). The available P content was higher in the third incubation method treatment with a combination of humic and P fertilizer compared to the other treatment interactions. Herviyanti, Prasetyo, Ahmad, & Darmawan (2010) reported that of 400 and 800 ppm HS treatment can increase P availability by 20.99 and 22.22 ppm with 100% Recommendation P fertilizer. If the research data is compared to the results of soil analysis on control and treatment of traditional farmers in Fig. 3, the availability of P is only available 7.61 ppm and 12.54 ppm, so that the publicly available of P appears to be available in the second year was lower than the first year. This is caused by the P fertilizer given in the first year of planting has been absorbed by the plant while on the second planting was no longer given.

Humic Substances directly influenced the P available by mineralization processes and indirectly by releasing P fixation on soil colloids surface. According to Parvan, Rahmandad, & Haghani (2013), humic acid and fulvic acid have capability to increase the release of P and P inorganic solubility by chelate mechanism. Heckman, Lawrence, & Harden (2018) and Tan (2011) stated that organic acids like humic, citrate, tartrate, malate, and malonate acid will form complex compounds with hydroxide of Al and Fe which is not soluble and releasing phosphate ions to the soil solution and then it will increase available P and total P content.

Based on soil analysis, it has been suggested that the addition of HS combined with P fertilizers for all incubation methods can improve soil chemical characteristics of Oxisols, such as increasing soil pH and available P, and in other way reducing Al content. It is very significant if the results are compared to the traditional farmers treatment and control, so that the administration of HS and P fertilizers in several incubation methods is able to provide nutrients for a long time in increasing plant growth and production.
Plant Analysis

The Phosphorus Content in Plant (Stems + Leaves)

The results of the statistical analysis of plant P levels presented in Fig. 4 shows that the interaction effects of HS and P-fertilizer incubated in various ways were not significant for the P levels of upper part of the rice plant (stems + leaves). While the main effect of the combination of the dose of HS and P fertilizer and the way of incubation was real to the P level the upper part of the rice plant.

In Fig. 4A, it can be stated that the P content of rice in the treatment 800 + 100% Recommendation is higher by 0.006; 0.008; and 0.11% compared to the treatment of 800 + 75% Recommendation and 400 + 100% Recommendation and 400 + 75% Recommendation. Stevenson (1994) stated that P uptake of plants increases by increasing P solubility and decreases in soil Al-exch. According to Tan (2011), an increase in P content is caused by organic acids (humic acids) in Sub-bituminous coal which binds Al to form complex compounds so that the P element bound by Al is released and causes the P element to be available.

The same effect was also obtained in treatments I₂ and I₃ for P levels of rice plants (Fig. 3). When compared to controls, the P content of rice plants was still higher, even though P-fertilizer was not applied in the second year. While the way of farmers who provided chicken manure as much as 10 t/ha each planting season was only able to match the P level of plants in the second planting season. The results of plant P levels observations were obtained from all treatments as well as the increase in P available (Fig. 3) in the soil.

Number of Young Plants

An analysis of plant growth was carried out in the maximum vegetative period of 75 days after planting. Based on the statistical analysis results, there was an insignificant effect on the amount of addition of HS and P-fertilizer to the incubation method in the DNMRT Advanced Test at the level of 5%. In Fig. 4 and Fig. 5, it can be seen that the interaction effect is not significant with the addition of HS and P-fertilizers in each incubation method affected the number of productive tillers of rice. While for the incubation method showed no influence, but the treatment of HS and fertilizer P combination significantly affected the number of productive tillers of rice.
Fig. 4A and Fig. 5 showed that the treatment of 800 ppm + 100% Recommendation and 800 ppm + 75% Recommendation had a much higher number of productive tillers at 6.2 and 6.82 compared to the treatment of 400 ppm + 100% Recommendation and 400 ppm + 75% Recommendation. While, in the incubation method I₁, I₂, I₃ showed that the number of productive tillers looks almost the same as the value. This was due to the provision of HS and fertilizer of P only in the first year and was not carried out again in the second year.

**Fig. 4.** Residual effects of HS from sub-bituminous with P-fertilizers (A) and the way of incubation (B) on phosphorus content in plant, number of productive tillers, and the weight of seeds 14% water content (t/ha)
The numbers of young plant has been provided because the improving of soil characteristics (increasing pH, high available of P, and decreasing of Al-exch makes roots of plant can develop better and increase the absorption of nutrients (the correlation test presented in Table 2). The absorption of P in plant has been used for forming the roots and the growth of plant. Application of Grow Flow 45 H (humic acid multinutrient liquid fertilizer) at recommended dose increased the tuber yield by 9.3% as compared to chemical fertilizer (Selladurai & Purakayastha, 2016). The previous research reported that humic acid can results some of activity like plant growth hormones like Auksin. Suntari, Retnowati, Soemarno, & Munir (2015) reported that efficiency of urea-humic acid fertilizer at 100% recommended dosage (200 kg urea-humic acid) to the dry weight of effectively harvested crop with dry weight of effectively milled crop was 22% compared to the recommended urea fertilizer (200 kg/ha).

**Crop Yield (Weight of Seed in 14% Water Content)**

Variance analysis showed that there was no significant interaction between the effects of residual HS + P-fertilizer with its incubation method on seed weight 14% of water content (WC). The combination of HS and P fertilizer as the main factors significantly influenced the plant production, while the incubation method was not significant. It can be seen that the combination of 800 ppm HS + 100% Recommendation of P fertilizers resulted the highest dry weight of seeds 14% of WC as compared to other treatments.

![Fig. 5. The vegetative growth of rice at 75 days treatment with HS + P-fertilizers](image-url)
However, this data was not significant with the 800 ppm HS + 75% Recommendation P-fertilizer and can increase production of rice as 1.71 and 1.67 t/ha, compared to 400 ppm HS + 100% Recommendation P fertilizer treatment. While, the way of incubation showed similar result for all combination of HS and P fertilizers treatment. However, the highest production of plant was in I$_3$

This is seen in Fig. 4, the rice production in the second year almost the same as the first year. Fig. 4A shows that the combination of HS and P-fertilizer in the treatment (800 ppm + 100% Recommendation P fertilizer treatment) was able to increase production by 2.79 t/ha. Whereas the incubation method showed almost the same results for all combinations of HS and P-fertilizer treatment, but the highest crop production in the incubation method of I$_3$ by 5.08 t/ha (Fig. 4B). The value obtained is the best point because it exceeded the average rice production by Inpago 6 varieties (3.9 t/ha) and the production potential wanted to reach 5.81 t/ha (Sasmita et al., 2019).

Even though, those yield were almost the same as the yield obtained on treatment 800 ppm + 75% Recommendation. So that, for the treatment 400 ppm + 100% Recommendation and 75% Recommendation had shown the same result with all the way of incubation. So, it can be concluded that HS addition gave the efficiency use of P fertilizers up to 25%.

If this result is compared to the control and the tradition of farmer, residual effect of HS from Sub-bituminous and P-fertilizers combination on the way incubation can increase production of rice from 3.14 and 3.17 t/ha, and become 5.93 t/ha, where there were rise about 88.85% and 59.84%. It showed that P fertilizers in farmer site was 100% but root plants absorbed very little P, because without organic matter, P ion will be directly attracted by soil colloids. Al ion from soil colloids will be attracted by HS and it formed metal organo complex, and then P fertilizer precipitation could be reduced. While, the addition of manure needs more time to react with Al ion.

### CONCLUSION

Residual effects of HS from Sub-bituminous and P-fertilizers combination with the method incubation can decrease Al-exch and increasing available-P of Oxisols. The HS addition increased the efficiency of P fertilizers up to 25%, as well as increased rice production in averaged 3.9 t/ha (i.e. treatment 800 ppm HS + P-fertilizer 100% Recommendation). Using HS from Sub-bituminous combination with P fertilizers and the methods of incubation increased production of upland rice in the second planting season.

### ACKNOWLEDGEMENT

We thank to the Indonesian Directorate General of Higher Education (DGHE), Ministry of National Education Republic of Indonesia wich had provided funding to conduct National Strategic Research in 2012 and 2013.

### REFERENCES


Herviyanti et al.: Chemical Properties of Oxisols and Rice Production with Humic Substances ............................


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