ROLE OF HUMIC MATERIALS FROM *SUBBITUMINOUS* IN IMPROVING SOIL CHEMICAL PROPERTIES OF OXISOLS

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ABSTRACT

One way to improve the soil chemical properties is adding ameliorant, for instance humic substance, to the soil. There were many kinds of organic matter as source of humic matter. This research was aimed to study the capability of humic substance derived from non-productive coal (*subbituminous*) powder which was extracted with solvent from fertilizer, salt and base (Urea, KCl, NaCl, and NaOH) and then it was used to improve the soil chemical properties of Oxisols. The improvement of chemical properties of Oxisol can be achieved by adding humic substance from *subbituminous*. Urea can be used to substitue the role of NaOH in solving humic materials and improving soil chemical properties of Oxisols. Humic materials which are extracted by Urea on recommendation 125 % and *subbituminous* in concentration 0.5 % to improve soil chemistry properties of Oxisols.

Key words: subbituminous powder; humic substance; fertilizer, salt and base solvent

INTRODUCTION

Oxisol is acid mineral soils which cover about 14.11 million Ha or 7.5 % from Indonesian total land area, it is distributed in Sumatera, Kalimantan and Papua (Pusat Penelitin Tanah and Agroklimat, 2004). Oxisol is low productivity soils for the crop since it has acidic reaction and high phosphorous (P) sorption. The solubility of Aluminum (Al) and Iron (Fe) is high, it is causing toxicity for the crop, so that inhibit the plant growth, stunted, limiting formation of rice seedling due to limited root development.

The plant growth is inhibited by low pH in soil solution of acid mineral soils. In this condition, the membrane permeability of plant cell is depend on H⁺ and Ca²⁺ concentration in the adjacent medium. This H⁺ effect is as counter balance by Ca²⁺ which is more effective in soil with lower pH. Ca²⁺ ion is require for maintaining the membrane integrity that may affect its permeability by binding negatives charges of plasmalemma with the cell wall. The present of Ca²⁺ in soil solution stimulated the uptake of K⁺ but the internal Ca²⁺ of the root is not influence the K⁺ uptake (Mengel and Kirkby, 1982).

If there is no calsium (Ca) and potassium (K) in plant cell cytoplasmic (Ca and K deficiency), the plant membrane will not prevent the adsorption of Al and Fe to the plant inner cell. It caused Al and Fe toxicity to the plant. High amount of Al and Fe in root cell membrane will inhibit the phosphorous (P) absorption. The effort to prevent Al and Fe toxicity and nutrient deficiency of plant can be done by adding organic matter into the soil in form humic substance which was extracted from non-productive coal (*subbituminous*), it contained about 31.5 % of humic substance (Rezki, 2007). Humic substance had some important roles to improve physical, chemical and biological properties of soils (Stevenson, 1994 and Tan, 2011).

Herviyanti *et. al* (2009) reported that humic substance from *subbituminous* which came from Bonjol Pasaman district, West Sumatera increased P fertilizing efficiency and marginal land productivity which was planted by corn. The humic substance had the same capability with compost, but the amount of coal needs was one third of the amount of compost, because the concentration of humic substance in coal was higher than compost (31,5 % compared 11 %).

Humic substance from non-productive coal was extracted with alkali solution on concentration 0.1 to 0.5 N. NaOH solution was one of alkali solution that was frequently used. This research used alkali solution as the solvent, i.e macro fertilizers like Urea and KCl which were commonly used by farmer. By using Urea and KCl fertilizers, humic substance obtained would contain some nutrients, so that it would be more efficient in organic matter and fertilizer application to the acid mineral soils. This research also used NaCl that was obtained from sea water and it is also alkali, so that the sea water can be used as a solvent for non-productive coal.

The background and the urgency of this research had clearly explained above, so that this research had been done with the purpose was to study the capability of humic substance derived from *subbituminous* which was extracted with Urea and KCl fertilizers, NaCl and NaOH to improve soil chemical properties of Oxisol.

MATERIALS AND METHOD

Research Design

The solubility test of *subbituminous* which was obtained from extraction of organic and inorganic solvent (Urea, KCl, NaCl, NaOH) with the best dosage from previous research by Herviyanti *et. al.*(2013) on Oxisol used Factorial Design in CDR with 3 replication.

The 1st factor were four doses of humic substance which was extracted from *subbituminous*, they were 0,125; 0,25; 0,375; and 0.5 %.

The 2nd factor were four kind of humic substance that was obtained from extraction using Urea, KCl, NaCl and NaOH, and the best dose from Herviyanti's research were 125 % for Urea and KCl solvent and 0.25 N for NaOH and NaCl solvent.

Research Implementation

Non-productive coal was taken from Bonjol Pasaman District, West Sumatera in 1-2 m depth from soil surface. This coal type was *subbituminus* based on research Ahmad *et al.* (2006). And then, the coal was mashed by porcelain mortar in 63 μ m sieving.

The soil was taken from Padang Siantah Lima Puluh Kota District, West Sumatera, on depth 0-20 cm from soil surface; it was done by composite soil sample. The soil sample was prepared in air dry, it was mashed (2 mm), the soil was prepared homogeneously. Finally, soil water content was determined.

Humic substance from *subbituminous* was extracted by Urea, KCl, and NaCl (1:5), it means 100 g coal powder was dissolved in 500 ml solvent (Urea, KCl, and NaCl). This treatment was based on NaOH comparation which was usually used to extract humic substance from non-productive coal. The extraction would produce NH₄-humic, K-humic, and Na-humic. The soil had prepared 1 kg weight, and it was stored in treatment pot, and then the humic substance was applied to the soil as treatment doses had design before.

The observation

Some observation had been done after the incubation of soil and humic substance mixture on each experimental unit. Parameters observed were soil organic carbon (organic-C) with Walkley and Black method, total nitrogen (total N) with Kjeldahl method, cation exchange capacity (CEC) with Leaching method by NH₄Oac pH 7 solvent, and pH by electrometric with glass electrode. Soils nutrient content determined were K, Fe, and P. The nutrient contents were determined by KCl 1 N extraction method for K and Fe, and Bray II method for P. The data were analyzed by statistical method.

RESULTS AND DISCUSSION

Soil Organic Carbon

As seen in Table 1, humic substance had donated soil organic carbon to Oxisol, the highest average was 1.96 %, if it is compared with control, it was increase to 1.24 %. NaOH was a stronger solvent for humic substance, but the soil organic carbon value with addition of humic substance from NaOH extraction was same as Urea, KCl, and NaCl solvent.

Humic matter obtained from *subbituminous* by NaOH solvent increased the soil organic carbon content because humic matter contains some humic fraction like humic acid and fulvic acid, that it can donate higher soil organic carbon content on Oxisol. It was known that NaOH is the strongest alkali solution to extract humic substances to humic substance fraction. Fractionation of humic substances will result some functional group like total acidity, CO₂, phenolic OH group from each humic and fulvic acid fractions. Humic substances fraction will donate variation content of C, O, H and N of each fraction. If these were given to the soil, so those elements would influence reaction and chemical properties of the soil.

Cation Exchange Capacity (CEC) of Soil

The effect of humic matter from *subbituminous* showed in Table 2. There was no interaction of solvent used and doses on CEC. However, the average value of humic matter addition showed that there was a significant different between solvent, where the CEC of humic matter with Urea and NaOH solvent showed the higher average value of KCl and NaCl solvent. If soil CEC with humic matter addition value was compared with control, the CEC value increased about 9.44 me/100 g.

One of soil properties was CEC that determined from mixing humic substance and Oxisol, it can be seen that CEC value was increase, it was caused by the humic molecule attained a high negative charge as a result of functional groups dissociation that released is proton or H⁺ ion in aromatic group, alifatic, like carboxyl, carbonyl and fenolic from humic matter of *subbituminous*. This CEC value was influenced by soil solution pH and it would be increase if the pH value was higher, then H⁺ dissociation is raising in low pH comes from carboxyl, and higher pH (pH=9) comes from fenolic group (Tan, 2011).

Soil pH

Table 3 showed the effect of humic matter addition from *subbituminous* on Oxisols. pH showed no interaction from both factor (kind of solvent and doses). However, the higher average value of pH was found in doses 0.5 % from humic matter with the pH value 5.07.

The effective solvent to influence pH was NaOH solvent and this pH value was almost same with pH of Urea solvent. Compared with soil pH control, this value increased as much as 0.34 pH unit. The increase of soil pH was influenced by H⁺ dissociation, because the development of negative charges, so that at low pH values the humic molecule was capable to attract cations, which was lead to cation exchange reactions (Tan, 2011).

The available of Phosphorous (P)

There was no interaction between solvent and doses of humic matter that given to soil on P-available Oxisols. However, the average value of Pavailable was raised if this value compared with control. Urea solvent had given a higher value of P-available from other solvent, it was 6.60 ppm higher than NaCl solvent, even though this value was same as KCl and NaOH solvent. The highest average value of P-available according to humic matter doses from *subbituminous* was dose 0.375 %, this value was same as 0.5 %, if this value compared with dose 0.125 % and 0.25 %, so it would go up 7.38 ppm (Table 4). All value of P-available were higher than control (Table 4). The addition of humic substance from *subbituminous* improved the soil chemical properties that was bring out many functional group of soil organic carbon and there an impact on soils CEC. It would brought out negative charge from functional group of humic matter as consequents of H^+ ion dissociation that it could release P anion (H₂PO₄⁻) and could inhibit the sorption of P ion by Al and Fe oxide via formation of metal-organo complex (Tan, 2011).

The available of P mechanism in soil depend on total acidity H⁺ ion dissociation from dissolved humic matter with any kind of solvent, it would determine exchange capacity of organic compound resulted from presence of ion H⁺ that was come from functional group of aromatic, alifatic, and carboxyl (R-COOH), hydroxil fenolic group. It can be clearly explained by the reaction below:

 $R-COOH \iff R-COO^- + H^+ ---- dissociation H^+$

 $R-COO^{-}M^{+} === electrostatic bound$

An increase of soil quality could be reached with addition of humic matter from *subbituminous*.

Total Nitrogen

The addition of humic matter was not significant according to kind of solvent and humic matter doses. Compared with control, total N of Oxisol was

higher with Urea solvent. Total amount of nitrogen is in form organic and inorganic nitrogen in coal powder.

The primary source of nitrogen in Oxisol is urea that it is used as solvent (Table 5). In soil, urea is dissolve as $N-NH_4^+$, because there is an addition of H^+ from H_2O as reaction below:

$$(NH_2)_2 - C = O + H_2O \longrightarrow NH_3 + R - OH + E$$

(urea)
$$+H_2O \longrightarrow NH_4^+ + OH^-$$

As can be seen in the reaction above that urea dissolved could be donated N- NH_4^+ as soon as possible. Besides that, donated N is possible comes from organic N from organic substances in from coal powder (Havlin, 1999).

Exchangeable of Potassium (K-exch)

The content of K-exch on Oxisol had no interaction between the humic matter addition of some solvent and dose. Exch-K content by kind of solvent with humic material was higher on KCl solvent compared with NaOH and NaCl, but almost same with urea solvent. Exch-K content with humic matter addition was higher than \pm 0.12 % compared with control. Addition of KCl solvent to dissolve humic matter will release K in soil solution because KCl had higher K content (50 % to 52 %).

The available of K on Oxisol was more influenced by clay mineralogy in Oxisol, the clay fraction on Oxisol was dominated by phylosilicate clay 1:1 and

Al/Fe Oxide and the mixing of both. Oxisol had a good aeration, it was caused by the desilicification (loss of Si) from the clay mineral 1:1 to form hematite and goetit, and the present of both secondary minerals will differ Oxisol and Ultisol. Oxisol had gibbsite and goetite minerals in its clay faction dominantly. Then, it can be concluded that soil exchange lattice were most of Al and Fe abundant and H⁺ ion dominantly, that caused low pH in soil solution, the surface if lattice had filled by Al and Fe (trivalent cation) and it will repelled bases cation like K⁺, Na⁺, Ca⁺², Mg²⁺ and these cations will be leached out of soil solution. So, it will cause K deficiency in soil solution and this is the prevalent condition because a higher Al saturation repelled K bound in soil solution.

Exchangeable of Iron (Fe- exch)

From the Table 7, it can be seen that the addition of humic matter had no interaction between kind of solvent and humic matter on Fe-exch. However, each of variables had given the significant influence on Fe-exch. The humic matter addition with NaCl and Urea solvent decreased the content of Fe-exch as much as 22.81 ppm and 18.73 ppm compared with control. The declined of Fe content with addition humic matter by using Urea and NaCl solvent was bigger compared with NaOH and KCl solvent. While, the dosage of humic matter 0.5 % had highest capabilities to decline the content of exch-Fe compared with other dosage.

Finally, the content of Fe in soil solution will be reduced by chelate or complex of humic molecule. The solubility of humic substance in soil solution would complex some metal element like Al and Fe to form metal organo complex. This complex would reduce the solubility and the exchangeable of Fe in soil solution since this formation will resist the soluble Fe to exchange, and ion Fe can be prevented to be sorbed by root into the cell of plant.

The solubility test of *subbituminous* powder with urea solvent had same result with NaOH solvent that usually used to dissolve humic matter from coal powder or other humic matter sources in many variation of concentration (Herviyanti *et. al.*, 2013). The achievement of this research was Urea could substitute the NaOH role to dissolve coal powder from *subbituminous* that it was used to be applied on Oxisol.

CONCLUSION

The improvement of Oxisols chemical properties can be achieved with addition of humic matter from *subbituminous* powder. Urea was able to substitute the role of NaOH, it dissolved the humic substance and improve the Oxisols chemical properties. In fertilizers technology application and the organic matter addition, humic material from *subbituminous* which are extracted with Urea solvent on reccomendation 125 % in concentration 0.5 % can be used to improve the chemical soil properties of Oxisol.

ACKNOWLEDGMENTS

The authors acknowledge for the fund had received from Research Institutes and Agricultural Development of the Agricultural Ministry, through Partnership Research and Development National Agricultural, budget year 2013-2014.

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Table 1. The treatment effect of humic matter from *subbituminous* with some solvent on soil organic carbon (%)

	H				
- Kind of solvent	0.125	0.25	0.375	0.5	Average
Urea	1.69	1.73	1.91	1.82	1.79 a
KC1	1.63	1.85	1.98	2.04	1.87 a
NaOH	1.82	1.98	2.02	2.04	1.96 a

	Control	0.72			_
Average	1.72 A	1.82 A	1.93 A	1.94 A	
NaCl	1.73	1.71	1.81	1.89	1.78 a

Table 2. The treatment effect of humic matter from subbituminous with some solvent on soil CEC (me /100 g^{-1})

Vind of		_			
Kind of solvent	0.125	0.25	0.375	0.5	Average
Urea	31.39	40.50	33.63	41.62	36.79 a
KCl	28.45	19.48	28.87	31.95	27.19 b
NaOH	31.11	33.21	32.79	32.23	32.34 ab
NaCl	26.21	29.99	31.11	26.63	28.48 b
Average	29.29 A	30.79 A	31.60 A	33.11 A	
	Control	21.47	7		

Table 3. The treatment effect of humic matter from subbituminous with some solvent on soil pH

Kind of					
solvent	0.125	0.25	0.375	0.5	Average
Urea	4.77	5.11	4.86	5.29	5.01 ab
KCl	4.67	4.94	4.51	4.88	4.75 cd
NaOH	5.13	4.97	5.17	5.45	5.18 a
NaCl	4.71	4.81	5.03	5.03	4.89 bc
Average	4.79 B	4.91 AB	4.85 B	5.07 A	
	(Control	4.67		

Kind of		Humic Matte	er Dosage (%)	_
solvent	0.125	0.25	0.375	0.5	Average
Urea	17.53	17.53	38.48	20.49	23.51 a
KCl	15.70	15.7	21.42	17.24	17.52 ab
NaOH	18.06	18.06	19.5	19.52	18.78 ab
NaCl	16.09	16.09	17.53	17.91	16.91 b
Average	16.85 B	16.85 B	24.23 A	18.79 AB	

Table 4. The treatment effect of humic matter from subbituminous with some solvent on available P Oxisol (ppm)

Table 5. The treatment effect of humic matter from subbituminous with some solvent on total nitrogen (%)

Kind of]	Humic Matte	r Dosage (%)		
solvent	0.125	0.25	0.375	0.5	Average
Urea	0.14	0.14	0.11	0.12	0.13 a
KCl	0.09	0.12	0.11	0.11	0.11 a
NaOH	0.12	0.12	0.11	0.14	0.12 a
NaCl	0.11	0.11	0.12	0.11	0.11 a
Average	0.11 A	0.12 A	0.11 A	0.12 A	
Control	1 : 0.09				

Table 6. The treatment effect of humic matter from subbituminous with some solvent on exchangeable K (me $(100 \text{ g})^{-1}$).

Kind of .	Kind of Humic Matter Dosage (%)					
solvent	0.125	0.25	0.375	0.5	Average	
Urea	0.44	0.57	0.48	0.60	0.53 ab	

Average	0.48 C	0.57 A	0.56 AB	0.52 B	
NaCl	0.43	0.65	0.49	0.51	0.52 b
NaOH	0.53	0.50	0.60	0.44	0.52 b
KCl	0.49	0.55	0.66	0.54	0.56 a

Table 7. The treatment effect of humic matter from subbituminous with some solvent on exchangeable Fe (ppm).

Kind of	Kind of Humic Matter dosage (%)						
Solvent	0.125	0.25	0.375	0.5	Average		
Urea	75.95	58.69	57.99	39.36	57.99 bc		
KCl	65.59	67.89	59.15	59.61	63.06 a		
NaOH	56.16	74.11	51.78	55.24	59.32 ab		
NaCl	43.73	60.76	63.75	47.41	53.91 c		
Average	60.36 B	65.36 A	58.17 B	50.40 C			
	Control	= 76.7	72				

The number on the same line is followed by a same uppercase and on the same collum is followed by same lowercase is no difference on significant level 5 % according to BNJ.