

Chemical properties of Oxisols treated with humic materials from sub-bituminous coal

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Abstract

One way to improve soil chemical properties of Oxisols is by adding ameliorant, for instance humic substance (HS), to the soil. As there are many kinds of organic matter being a source of humic matter, to investigate a specific type of humic substance for improving the soil chemical properties of Oxisols is necessary. This research was aimed to study the capability of humic substance derived from non-productive coal (sub-bituminous) powder which was extracted with Urea, KCl, NaCl, and NaOH and then it was used to improve the soil chemical properties of Oxisols. The improvement of chemical properties of Oxisols was expected to be achieved by adding humic substance from sub-bituminous. Urea could be used to substitute the role of NaOH in solving humic materials and improving soil chemical properties of Oxisols. Humic materials which were extracted by Urea 0.2 g (kg)^{-1} of soil and sub-bituminous in concentration 0.5 % to improve soil chemical properties of Oxisols.

Keywords: Sub-bituminous powder, humic substance, fertilizer, salt and base solvent

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Introduction

Oxisol is an acid mineral soils which covered about 14.11 million ha or 7.5 % of the total land area of Indonesia and is widely distributed in Sumatra, Kalimantan and Papua (The Research Center of Soil and Agroclimate, 2004). Oxisol is one of low productive soils for crop growth since it is acidic and has high phosphorous (P) sorption (Fink et al., 2016). The solubility of aluminum (Al) and iron (Fe) was high and could be toxic for the crop and inhibit plant growth and development (Pietraszewska, 2001; Jones and Ryan, 2017)

The plant growth is inhibited by the low pH of soil solution from acid mineral soils (Jones and Ryan,

2017). In this condition according to Mengel and Kirkby (1982), the membrane permeability of plant cell is dependent on H^+ and Ca^{2+} concentration in the adjacent medium. High H^+ concentration competitively inhibit Ca^{2+} uptake. High extracellular Ca^{2+} may affect cell wall permeability by bridging negative charges on the cell wall and cell membrane. The presence of Ca^{2+} in soil solution stimulates the uptake of K^+ but the internal Ca^{2+} of the root is not influenced by K^+ uptake. If Ca and K are deficient in plant cell cytoplasmic, the plant membrane will not prevent the adsorption of Al and Fe to the plant inner cell causing toxicity to the plant. High amounts of Al and Fe in root cell membrane will inhibit the phosphorous (P) absorption.



An effort to prevent Al and Fe toxicity and nutrient deficiency of plant can be done by adding organic matter into the soil in the form of humic substance which was extracted from non-productive coal (sub-bituminous) containing about 31.5 % of humic substance (Rezki et al., 2007). Humic substance has some important roles to improve physical, chemical, and biological properties of soils (Stevenson, 1994; Tan, 2011).

The presence of humic substances in soil is necessary for sustainable agriculture, due to their ability to improve the soil properties, to enhance soil aggregate stability and to increase soil resistance to erosion, to ensure the enhancement of biological activity and to obtain higher crop yields. In addition, humic materials have ability to sequester soil pollutants and may be used in soil remediation. Among many other roles, solid HSs act as pH buffers and metal binders, and they are places to sequester plant hormones, fertilizers, nutrients, pollutants, and soil toxins (Ghabbour et al., 2012).

Herviyanti et al. (2009) reported that humic material from sub-bituminous coal from the Bonjol Pasaman district of West Sumatra improved the efficiency of P fertilizer and the productivity of marginal land planted with corn. It was equally as effective as compost, but the amount of coal required was one third the amount of compost, because the content of humic material in coal was higher than that in compost (31.5% compared to 11 %).

Urea solution has alkaline conditions when it produces humic acid. Urea in concentration 0.5 M had maximum yields of humic acid extraction. The characteristics of extracted humic acid with Urea had more functional groups, aliphatic structures and the great degree of saturation; otherwise humic acid extracted by Urea had a small size, but in general, there was no differences between the characteristics of extracted humic acid by other solvent. Finally, more research on the Urea as a new extractor could be recommended.

Humic materials from non productive coal are usually extracted with alkaline solvent (0.1 to 0.5 N. NaOH). In this study, the solvents derived from macro nutrient containing fertilizers (Urea and KCl) which are used to by farmers, were tested since it could improve fertilizer use efficiency of both organic and inorganic matter types of fertilizer. Sodium chloride (NaCl) was also tested since it is easily obtained from sea water which is alkaline too.

Material and Methods

Soil, to a depth of 20 cm, was collected from the Padang Siantah Lima Pulu Kota District, West Sumatra, then air dried, ground, sieved (2 mm gauge sieve) and weighed 1 kg for each pot. The soil had chemical properties as follow: Organic-C 0.72 %, CEC 13.51 cmol(+) kg⁻¹, pH 4.67, available-P 9.98 ppm, total-N 0.09 %, K-Exch 0.44 cmol(+) kg⁻¹, Fe-Exch 76.72 ppm. Sub-bituminous coal was collected from the Bonjol Pasaman District, West Sumatra at a depth of 1-2 m below the soil surface (Ahmad *et al.*, 2006). The coal was ground and passed through a 63 µm sieve. Humic material was extracted from the sub-bituminous coal powder (100 g) using 500 mL Urea, KCl (0.25 N), NaCl (0.25 N) or NaOH (0.25 N) with the pH of each solution was 8.20, 7.71, 7.29 and 9.76. The extraction would produce NH₄-humic, K-humic, or Na-humic salts.

The physicochemical properties of treated Oxisol was examined in triplicate using a completely randomized factorial design with four doses of humic material (0.125, 0.25, 0.375 and 0.5% calculated on the basis of dry weight of coal powder extracted per kg of soil treated. The amount of solvent applied was adjusted as necessary to 125 % of the recommended application rate for Urea fertilizer (375 kg/ha = 7 g/kg of soil) and KCl (250 kg/ha= 4.7 g/kg of soil) or 0.25 N for NaOH and NaCl (Herviyanti et al., 2013).

Soil organic carbon (organic-C) was determined by the Walkley and Black method, total nitrogen (total N) by the Kjeldahl method, cation exchange capacity (CEC) using leaching method with ammonium acetate at pH 7. The K content was determined by leaching, Fe using 1 N KCl and P using the Bray II method, pH was measured using a glass electrode. Statistical analysis was performed using the F-test at the 0.05 level of significance.

Results and Discussion

Soil organic carbon

As seen in Table 1, humic substance increased soil organic carbon content. The highest mean value was 1.96 % compared to the control, and it increased to 1.24 %. The NaOH solvent was considered as the strongest solvent for humic substance, but the soil organic carbon value with addition of humic substance from NaOH extraction was the same as Urea, KCl, and NaCl solvent.



All of the four humic extractors were equally effective in increasing the organic carbon content of the soil (Table 1) and the average value across all treatments was significantly different from the control. Equal effectiveness across all solvents was unexpected because NaOH is generally considered to be a stronger solvent for humic material than the other (Urea, KCl, and NaCl) (Tan, 2011). Since a crude humic extract was used, both the humic acids and fulvic acids are contributing to this increase in organic carbon.

Humic matter obtained from Sub-bituminous by NaOH solvent increased the soil organic carbon content because humic matter contains some humic fraction like humic acid and fulvic acid, so that it can donate higher soil organic carbon to Oxisol. It is known that NaOH was the strongest alkaline solution to extract humic substances to humic substance fraction (Stevenson, 1994). Fractionation of humic substances will produce some functional group like total acidity, CO₂, phenolic OH group from each humic and fulvic acid fractions. Humic substances fraction will donate variable content of C, O, H and N of each fraction. If these humic substances were given to the soil, so those elements would influence reaction and chemical properties of the soil.

Table-1: Organic carbon content (% w/w) following treatment of Oxisols with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
Urea	1.69	1.73	1.91	1.82	1.79 a
KCl	1.63	1.85	1.98	2.04	1.87 a
NaOH	1.82	1.98	2.02	2.04	1.96 a
NaCl	1.73	1.71	1.81	1.89	1.78 a
Average	1.72 A	1.82 A	1.93 A	1.94 A	

The organic carbon content of untreated Oxisols was 0.72%. Treatment with humic materials are expressed as a% by weight if coal powder extracted per kg of soil treated. Number on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at 5% level (HSD)

Cation exchange capacity (CEC) of soil

The effect of humic matter from Sub-bituminous showed in Table 2. There was no interaction between solvent types as well as the doses used and soil CEC. However, the average value of humic matter addition

showed that there was a significant difference between solvent types. The CEC values of humic matter solved with Urea and NaOH showed the highest average value. If the soil CEC with humic matter addition value was compared to control, the CEC value increased about 9.44 cmol(+) kg⁻¹.

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

Table-2: Cation Exchange Capacity (cmol (+) kg⁻¹) of Oxisols following treatment with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
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	

The cation exchange capacity of the untreated Oxisols was 21.47 cmol (+) kg⁻¹. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

Soil pH

Table 3 presents the effect of humic matter addition from Sub-bituminous on Oxisols characteristics. The pH values showed no interaction from between factors (types and doses of solvent). However, the highest mean value of pH was found in dose 0.5 % from humic matter with the pH value was 5.07.

The effective solvent to influence pH was NaOH, and the pH value was almost the same as pH of Urea solvent. Compared to pH of soil control, this pH value



increased by 0.34 unit. The increase of soil pH was influenced by H⁺ dissociation, because of development of negative charges. Therefore, at low pH values, the humic molecule was capable of attracting cations, which were led to cation exchange reactions (Tan, 2011).

Table-3: Soil pH following treatment of Oxisols with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
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	

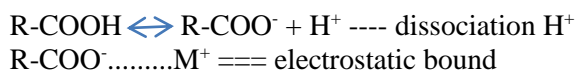
The pH of the untreated Oxisols was 4.67. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

The available of phosphorous (P)

There was no interaction between solvent and doses of humic matter that was given to soil on P-available of Oxisols. However, the average value of P-available was higher than the control. Urea solvent gave higher value of P-available (6.60 ppm) than the other solvents used, it was higher than NaCl solvent, even though this value was the same as KCl and NaOH solvent. The highest mean value of P-available according to the doses of humic matter derived from Sub-bituminous was found at dose 0.375 %. This value was the same as that at the dose 0.5 % (7.38 ppm) and higher than those at doses 0.125 % and 0.25 % (Table 4).

All of the values of P-available were higher than that of control (Table 4). The addition of humic substance from Sub-bituminous improved the soil chemical properties that have many functional groups of soil organic carbon. It would be brought out negative charge from the functional groups of humic matter as the consequence H⁺ ion dissociated that could release P anion (H₂PO₄⁻) and could inhibit the sorption of P ion by Al and Fe oxides via formation of metal-organo complex (Tan, 2011).

The availability of P mechanism in soil depends on the total acidity (H⁺ ion) dissociation from the dissolved humic matter with any kind of solvent. It would determine the exchange capacity of organic compound resulted from the presence of ion H⁺ from aromatic, aliphatic, and carboxyl (R-COOH), hydroxyl phenolic functional groups. It can be clearly explained by the reaction below:



An increase of soil quality could be reached with addition of humic matter from Sub-bituminous.

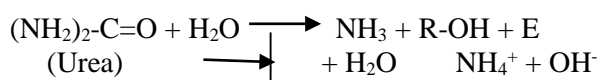
Table-4: P-available (ppm) in Oxisols following treatment with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
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	

Available P in the untreated Oxisols was 9.98 ppm. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

Total nitrogen

The addition of humic matter was not significant according to kind of solvent and doses of humic matter. Compared to the control, total N of Oxisol was higher with Urea solvent. Total amount of nitrogen in coal powder is in form of organic and inorganic nitrogen. The highest source of nitrogen in Oxisol was Urea because it was used as solvent (Table 5). In soil, Urea is dissolved as N-NH₄⁺, because there is addition of H⁺ from H₂O as reaction below:



As it can be seen in the reaction above that Urea dissolved could instantly donate N-NH₄⁺. Besides that,



donated N is possible to come from organic N from organic substances in from of coal powder.

Table-5: Total nitrogen (% w/w) in Oxisols following treatment with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
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	

Total nitrogen in the untreated Oxisols was 0.09 %. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

Exchangeable of potassium (K-exch)

There was no statistically significant difference in exchangeable potassium across all treatments (Table 6). Although additional potassium was added with the KCl solvent, the exchangeable potassium averaged across treatments was indistinguishable from those where Urea was the solvent. Averaged across all four application rates, exchangeable potassium following addition of the Urea extract was indistinguishable from that measured in samples treated with the NaOH extract. Giving humic materials dissolved with KCl produce K-exch higher than NaOH and NaCl solvents, but is relatively the same as Urea solvents. K-exch with humic matter 0.5 % dosage was higher than ± 0.12 % compared with control. Addition of KCl solvent to dissolve humic matter will donate K into soil solution because KCl have a higher K content (50 % to 52 %). [Table 6]

The availability of K on Oxisol was more influenced by clay mineral in Oxisol, the clay fraction on Oxisol was dominated by phyllosilicate clay 1:1 and Al/Fe oxides and the mixing of both. Oxisol had a good aeration, it caused the desilicification (loss of Si) from the clay mineral 1:1 to form hematite and goethite, and the present of both secondary minerals will differ Oxisol and Ultisol. Oxisol had gibbsite and goethite minerals in its clay fraction dominantly. Then, it could

be concluded that most of Al and Fe abundant and H⁺ ion were dominantly at soil exchange lattice. It caused low pH in soil solution, if lattice had been filled by Al and Fe (trivalent cations), they will repel basic cations 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.

Table-6: K-exch (cmol (+) kg⁻¹) in Oxisols following treatment with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
Urea	0.44	0.57	0.48	0.60	0.53 ab
KCl	0.49	0.55	0.66	0.54	0.56 a
NaOH	0.53	0.50	0.60	0.44	0.52 b
NaCl	0.43	0.65	0.49	0.51	0.52 b
Average	0.48 C	0.57 A	0.56 AB	0.52 B	

Exchangeable of K in the untreated Oxisols was 0.44 cmol (+) kg⁻¹. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

Exchangeable of iron (Fe-exch)

No significant differences in exchangeable Fe were observed across all treatments (Table 7) but the average values, for each solvent and for each rate of application regardless of solvent, were significantly different from the control (p=0.05). The largest decrease were seen at the highest application rate (0.5%) and with NaCl or Urea extracts (26.32, 22.81 ppm and 18.73 ppm, respectively). This decrease in exchangeable Fe was presumably due to the formation of organometallic complexes with humic materials in the extracts. Such Fe-humic complexes can improve Fe uptake by plants (Kulikova et al., 2005), so this decrease in exchangeable Fe may not have a detrimental effect on plant growth. The averaged value of iron exchangeable across all four application rates, exchangeable potassium following addition of the Urea extract was indistinguishable from that measured in samples treated with the NaOH extract. Finally, the content of Fe in soil solution will be reduced by



chelation 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 roots to get into the cell of plant.

The solubility test of Sub-bituminous powder with Urea solvent had the same result as 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 that Urea could substitute the NaOH role to dissolve coal powder from Sub-bituminous that it was used to be applied on Oxisol.

Table-7: Fe-exch (ppm) in Oxisols following treatment with humic matter extracted from Sub-bituminous coal

Solvent	Treatment				Average
	0.125	0.25	0.375	0.5	
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	

Exchangeable of Fe in the untreated Oxisols was 76.72 ppm. Treatments with humic materials are expressed as a % by weight of coal powder extracted per kg of soil treated. Numbers on the same line followed by the same upper case letter and in the same column followed by the same lower case letter are not significantly different at the 5 % level (HSD).

Conclusion

The improvement of Oxisols chemical properties can be achieved with addition of humic matter from Sub-bituminous powder. Urea was able to substitute the role of NaOH, it dissolved the humic materials and improved the Oxisols chemical properties. In fertilizers technology application and the organic matter addition, humic material from Sub-bituminous 0.5 % dosage which was extracted with Urea solvent 0.2 g (kg)⁻¹ can be used to improve the chemical soil properties of Oxisols.

Contribution of Authors

Herviyanti: Conceived idea, conducted experiment and write up of article

Chan A: Helped in experiment

Yusnaweti: Helped in experiment, compilation of results and statistical analysis

Prasetyo TB: Helped in experiment, compilation of results and statistical analysis

Harianti M: Helped in experiment and article write up

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