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The Properties of Humic Acids Extracted from Four Sources of Organic Matters and Their Ability to Bind Fe^{2+} at New Established Rice Field

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ABSTRACT

The Properties of Humic Acids Extracted from Four Sources of Organic Matters and Their Ability to Bind Fe^{2+} at New Established Rice Field (Herviyanti, TB Prasetyo, F Ahmad and Darmawan): In order to identify the properties of humic acid extracted from four kinds of organic matters (a peat soil, a stable manure, a compost of rice straw and a municipal waste) and their potentiality to bind Fe^{2+} at new established rice field, a series of experiment was done in Soil Laboratory Faculty of Agriculture, Andalas University Padang. First step was characterization of functional groups and other chemical properties of humic acids, and their reaction with Fe^{2+}. The second step was to examine the ability of humic acids to bind Fe^{2+} solution at new established rice field by conducting incubation experiments. The experiment used a completely randomized design with three replications. The 450 ppm Fe solution was treated with 0, 50, 100, 150, 200, 250, 300, 350, 400, and 450 ppm humic acids and incubated for 24 hours. While top soil samples taken from Sitiung, West Sumatera were treated with 0,100, 200, 300, and 400 ppm humic acids, flooded with deionized water, and incubated for 6 weeks. The result showed that the functional group and other chemical characteristic of humic acid from rice straw compost and peat soil were better than those of manure and municipal waste compost. Functional group of both humic acids was dominated by COO^-. High reactivity of the humic acid had been found when humic acids were added to Fe solution with ratio 1 : 1. Use of humic acid extracted from peat soil with the levels from 0 to 100, 200, 300, and 400 ppm decreased the Fe^{2+} concentration from 1.361 ppm to 910, 860, 831, and 776 ppm, respectively at new established rice field. While the use of humic acid extracted from rice straw compost with the same levels as above decreased the Fe^{2+} concentration from 1361 to 770, 701, 612, and 600 ppm, respectively, after four weeks of flooding.

Keywords: Dissolved iron, functional groups, humic acid, new established rice field, organic matter

INTRODUCTION

To convert the decreasing of rice field as consequences of land use change from agriculture especially rice field into non-agriculture purposes, many new rice field has been established in marginal soils such as Ultisols and Oxysols. The most common problem occur on those soils are Fe-toxicity and deficiency of macro nutrient especially phosphorous (P) to the plant. Herviyanti *et al.* (2005) reported that Ultisols from Sitiung I were characterized by low soil base saturation (15.46%), cation exchange capacity (15.20 c-mol(+) kg^{-1}), total nitrogen (0.07%), organic carbon (1.99%), and available phosphorus (4.63 ppm). On the other hand, the aluminum (Al) saturation was high (49.89%) as well as exchangeable Fe content was also high (57.32 ppm)

Regarding land use system of rice field, the high content of exchangeable Al will not create any problem although soil is under submerged condition. Different situation will occur with Fe. Submerged condition will promote reduction of stable Fe^{3+} into soluble Fe^{2+}, which the excess amount of this cation will harm plant growth and significantly influence rice productivity. Many experiments have been conducted to conquer the Fe toxicity problem such

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as addition of organic matter, water management and use of tolerant rice varieties.

Taher (1990); Hartatik *et al.* (1997); and Widowati *et al.* (1997) stated that, controlling Fe-toxicity using water management (intermittent drainage) at new established rice field could be happen through leached and oxidation of Fe^{2+} into insoluble Fe^{3+}. Water management during rice growth decreased Fe^{2+} and Mn^{2+} content in soil, as well as alleviated Fe and Mn content in plant tissue, but it also leached alkaline cations (Ca, K, and Mg). Intermittent drainage at new established rice field Inceptisols in Muarabeliti could decrease of Ca and K-exch at cultivation soil, while at Ultisol Tatakarya it could decrease Mg-dd and based saturation (Nursyamsi *et al.* 2000)

The addition of 1 Mg ha^{-1} of lime and 5 Mg ha^{-1} of manure and N, P, K fertilizer increased yield of rice 1-2 Mg ha^{-1} at new established rice field in Bangkinang Riau (Jalid and Hirwan (1987); Burbey and Yusril (1989) *cit* Wiwik *et al.* 2006) and application of 20 Mg ha^{-1} manure at flooding soil increased P available. But the addition of organic matter in the paddy soil caused a negative effect, because the organic matter decomposition under an aerob condition can produce phenolic acid and methane which will be toxic to the crop (Prasetyo 1996; Tan 1998). Beside that, the organic matter that usually applied were manure, compost, green manure, etc which need high amount about 20-40 Mg ha^{-1} which causing difficulties for the farmer to the application and transportation. So, an applicable technology was needed, which benefit to plant growth and practically *i.e.* by producing humic acid that can improve the soil fertility only about 0.4-1.2 Mg ha^{-1}. Organic matter that is applied to the soil will become humic acid in the longtime (± 2 years). Application of humic acid will accelerate amelioration process, especially for the high iron soils that will be need for paddy soil.

Humic acid has an important role to improve soil fertility, either in chemical, physical, or biological process, improve soil structure, increase water holding capacity, soil cation exchange capacity, and decrease solubility of toxic elements such as Fe by formation metal-organo complex or chelate (Stevenson 1994, Ahmad 1989, and Tan 2003). Humic acid can be extracted from plant residue, organic fertilizer, and various organic matter having been decomposed like a peat soil, a stable manure, a compost of rice straw and a municipal waste. The best and suitable source of organic matter and applicative method however has not yet been found.

The main objectives of this study were to get the suitable humic acid sources extracted from four kinds of organic matter and to examine the ability of each organic matter to bind Fe^{2+} in new established rice field soil.

MATERIALS AND METHODS

The study was conducted in Laboratory of Soil Science, Faculty of Agriculture, Andalas University Padang, West Sumatera from June 2005 to February 2006. Top soil sample (0-20 cm) of new establish rice field soils (Ultisol) was taken from Sitiung, Dharmasraya Regency, West Sumatera Province, Indonesia. Humic acids used in this study were extracted from manure, peat soil, rice straw compost and municipal waste compost with NaOH 0.1 N (modification of Tan method 1996). The organic-C content, total N, lignin, CEC and functional groups characteristic of humic acid were analyzed by Infrared Spectroscopy.

To examine their ability to bind Fe^{2+}, a series of solution which contained 0, 50, 100, 150, 200, 250, 300, 350, 400, and 450 ppm of humic acids extracted from four sources of organic matter were added to 450 ppm Fe^{2+} solution. After 24 hours incubation, Fe concentration in the solution was determined by Atomic Absorption Spectrophotometer (AAS).

To study the ability of humic acids to bind Fe^{2+} in soil solution, the best result in previous step was applied into a new established rice field. Soil sample was compositely taken from the rice field at 0 – 20 cm depth. After dried, refined and sieved, 1.5 kg of soil sample was put into PVC (11 cm in diameter, 30 cm in high while base of the pipe was covered by PVC cover), treated with humic acids and submerged with deionized water, and let it for 6 weeks. The levels of humic acids were 0, 100, 200, 300, and 400 ppm. This experiment used a completely randomized design with three replications. The parameter observed were (a) characterization of the functional groups and chemical properties of humic acids, (b) reaction of humic acids and soluble Fe^{2+}, and (c) analysis of Fe^{+2} in soil solution every week (6 times). The sample of Fe^{2+} had taken from fresh soil in PVC, put into erlemeyer (100 ml) which contained 50 ml buffer solution pH 2.8 (136.08 g $NaCH_3COO$ was diluted with deionized water ± 1,000 ml, and to decrease pH 0.1 *N* HCl was added) (Hidayat 1978).

RESULTS AND DISCUSSION

Functional groups and chemical properties of humic acid

Infrared spectroscopy was used to identify of functional groups of humic acid and its spectra based on main absorption type of humic substances in the specific wave number was read. The identification result of humic acid extracted from the organic matters were shown in Figure 1 and Table 1.

Figure 1 showed that the spectra of humic acid from peat soil was relative similar to those form rice straw compost. The humic acid from both organic matters had functional groups as follow: 1) O-H and N-H at wave number 3377.6 and 3400 cm^{-1} respectively, 2) C=O from functional group of carbonyl at wave number 1713.4 cm^{-1} and 3) C=C aromatic, C=O double bundle H that conjunction with carbonyl vibration and COO^{-} at wave number 1631.1 and 1625,2 cm^{-1} respectively, as well as anti-simetric bundle COO^{-} at wave number 1419.6 and 1407.8 cm^{-1}. The humic acids of manure and municipal waste compost had also similar spectra, since strong absorption was found at wave number 2919.2 and 1096.4 cm^{-1}, respectively. It was that almost similar to humic acid spectra that was identified by Kemp and Mudrochova (1975 *in* Tan 2003).

According to transmittance result, it showed that the highest absorbance was found at humic acid from rice straw compost, followed by peat soil, manure, while the lowest one was found at municipal waste compost. Low transmittance at rice straw compost and peat soil showed that these two organic matters had high humic acid concentration while the other organic matters had low humic acid concentration. The low concentration of humic acid at municipal waste compost was due to it was made from organic matter with low in lignin concentration (31.63 %). It made the decomposition process was faster (1.5 month) than rice straw compost (3.5 month) which contained lignin 48.03% (Table 1). Peat soil decomposition result from wood which contained lignin 15.69% higher than its content in manure. Decomposition of organic compound which was low in lignin content would result organic acids which was easy to oxidation (aliphatic form). The organic compound which was high in lignin content would result organic acid which was difficult to oxidation (aromatic form). Therefore, functional bundle of humic acid in peat soil and rice straw compost had more stabile and higher concentration than those in manure, and municipal waste composts. The high on lignin, protein and cellulose contents at carries substance, the higher in humic compound contents (MacCarthy 2001; Tan 2003).

Lignin was source and base to make humic and fulvic acids. It would decompose with degradation processes into set of base such as monomer alcohol coniferil (Tan 1998). Stevenson (1994) stated that lignin decomposition resulted modification of lignin or quinone, protein decomposition resulted acid or amino compound, and carbohydrate decomposition resulted glucose. Modification and polymerization of glucose, amino acid, quinone, and lignin created the structure of humic acid.

Figure 1 showed that humic acid from rice straw compost and peat soil had aromatic rings C=C, C=O bundle of H conjunction with carbonyl vibration and COO^{-}. The humic acid from municipal waste compost

Table 1. Chemical characteristic of humic acids extracted from rice straw compost, municipal waste compost, peat soil, and manure.

Sources of Humic Acid	pH	Organic-C (%)	Total N (%)	C/N	Humic acid (%)	CEC (c mol kg^{-1})	Lignin (%)
Rice straw compost	3,75 b	45,40	2,41	18,84 ab	5,00 b	126,71 a	48,03
Municipal waste compost	4,03 a	51,07	3,78	13,51 c	1,40 c	64,95 c	31,63
Peat soil	3,32 c	55,70	2,48	22,46 a	9,20 a	96,60 b	59,98
Manure	3,79 b	50,40	6,20	8,10 d	1,50 c	57,42 c	44,29
SD (%)	0,69			2,78	3,33	4,94	

Note: The numbers in same columns followed by the same caharacter is not significantly different at 5% level with DNMRT.

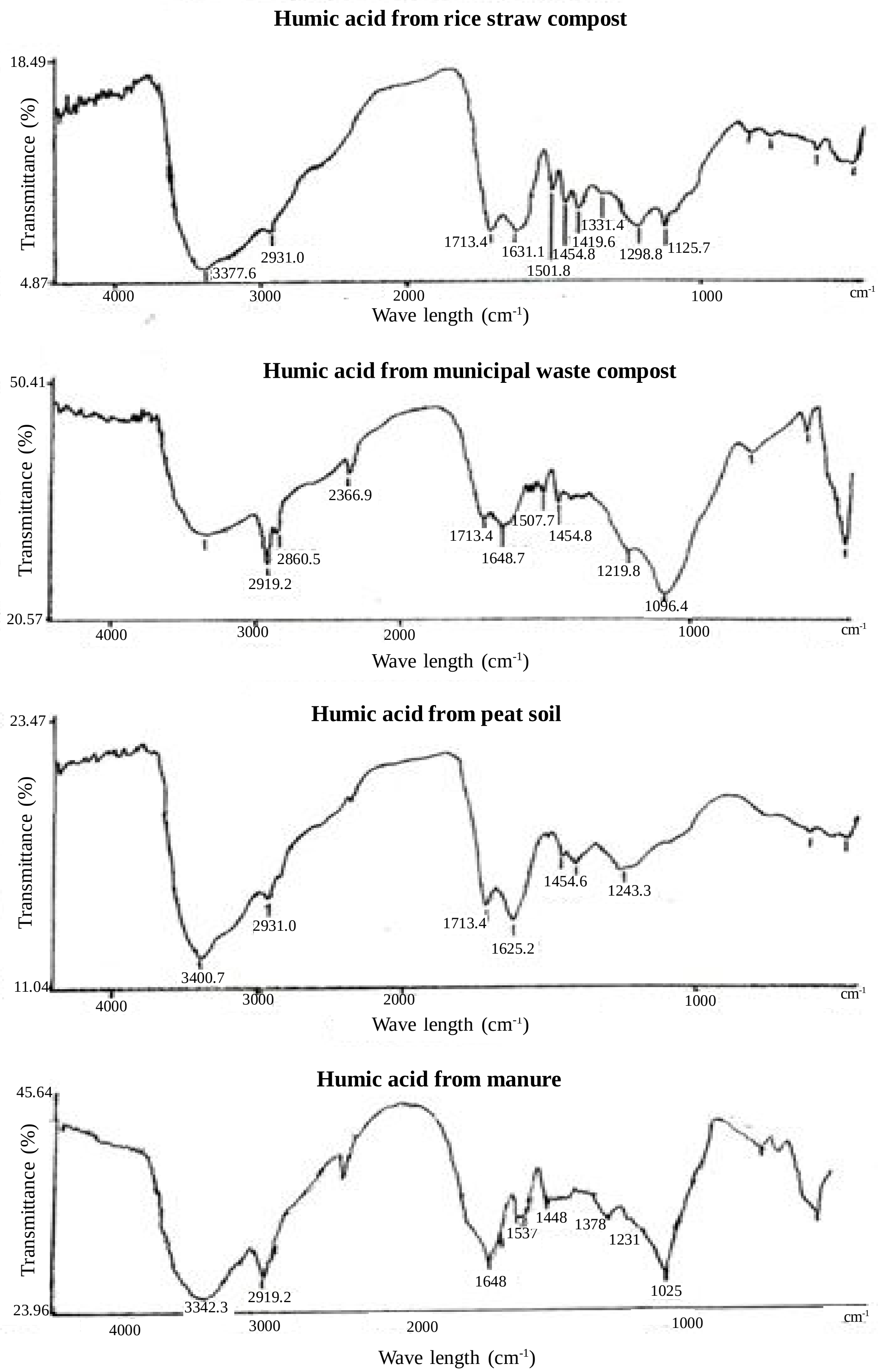

Figure 1. Functional groups characteristic of humic acid extracted from different source of organic matters with Infrared Spectroscopy.

and manure, however, did not have it. Beside that, antisymetric COO^- bundle was also not found at humic acid from municipal waste compost. Bundle of COO^- was determined at reactive humic acid, because COO^- bundle frequently increased with increasing its reactivity. Functional groups at humic acid consisted of several complex groups, but its ability to reduce Fe^{2+} was different. McKnight *et al.* (2001) stated that carboxyl (COOH) was a primary group for complexing humic substances.

Table 1 showed that chemical character of humic acid from peat soil and rice straw compost had pH lower than those from municipal waste compost and manure. Dominant functional group of humic acid from peat soil and rice straw compost was COO^- which had significantly effect to total acidity, because COO^- group was low in pH and high in solubility at pKa 3-6 (Stevenson 1994).

Humic acid from municipal waste compost and manure had low in C/N ratio, because it had high in total N content, although its organic-C content almost similar to those from peat soil and rice straw composts. The high in total N content might correlate to source of municipal waste compost from various of organic matters such as vegetable containing high N nutrient from fertilizer. That similar case was found in manure.

Table 1 also showed that CEC of humic acid from rice straw compost was higher than those from municipal waste compost and manure. It was about 61,76 and 69,29 c mol kg^{-1} respectively. This result was in agreement with identification of functional group (Figure 1), which showed that the most reactive functional groups was found at humic acid from rice straw compost. Compare to humic acid from peat soil, the CEC of humic acid from rice straw compost was also high about 30,11 cmol(+) kg^{-1}. It might be due to decomposition of rice straw produced aromatic organics acid which had molecular weight lower than those from peat soil. Beside that, humic acid from rice straw compost had relatively more reactive functional group and negative charge capacity. Marsi (1997) reported that humic acid fraction from rice straw had high component of negative charge 127,83 c mol kg^{-1} in average, and contained 20,49 % of organic-C and 1,743 % of N. The chemical characterized of humic acid from rice straw compost had high potency in increasing soil fertility of marginal soil such as Ultisol. According to Stevenson (1994) source of CEC of humic acid was negative charge from functional groups such as phenolic and carboxylic.

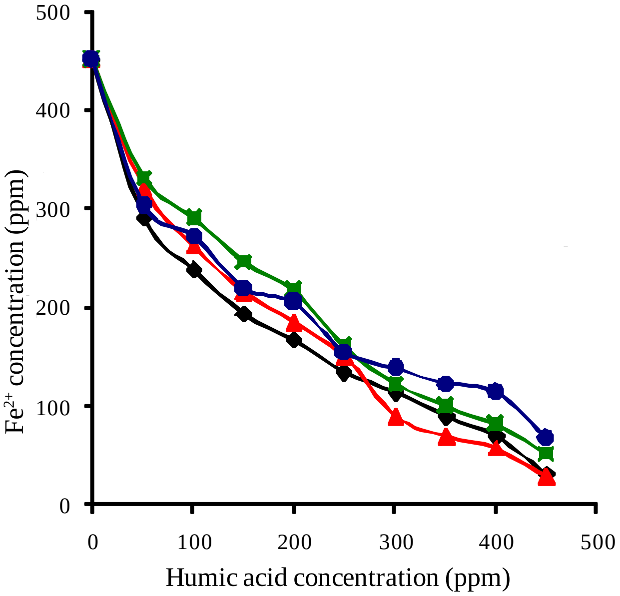

Figure 2. Ability of humic acid at several concentration (0-450 ppm) to decrease soluble Fe^{2+}. —◆— = humic acid of peat soil, —▲— = humic acid of rice straw compost, —✱— = humic acid of municipal waste compost, and —●— = humic acid of manure.

Ability of Humic Acid to Reduce Fe^{2+} Soluble

The reaction result of humic acid extracted from four kinds of organic matters at several concentrations (0, 50, 100, 150, 200, 250, 300, 350, 400, and 450 ppm) to decrease Fe^{2+} in solution at 450 ppm Fe were showed in Figure 2. The humic acid curves had similar trend so that had similar ability to bind Fe^{2+}, where the higher humic acid concentration the higher ability to bind Fe^{2+}. Addition of humic acid 450 ppm decreased Fe^{2+} in solution about 418.19 ppm for humic acid from peat soil; 421.27 ppm for humic acid from rice straw compost; 397,58 ppm for humic acid from municipal waste compost, and 382,94 for humic acid from manure. High reactivity had been found when humic acid (four types) added to Fe solution with 1 : 1 ratio.

The concentration of Fe^{2+} decreased with increased of humic acid concentration. It was caused by reaction of organo-metal complex's between humic acid and Fe. The higher addition of humic acid, the higher organo metal complex's formed from

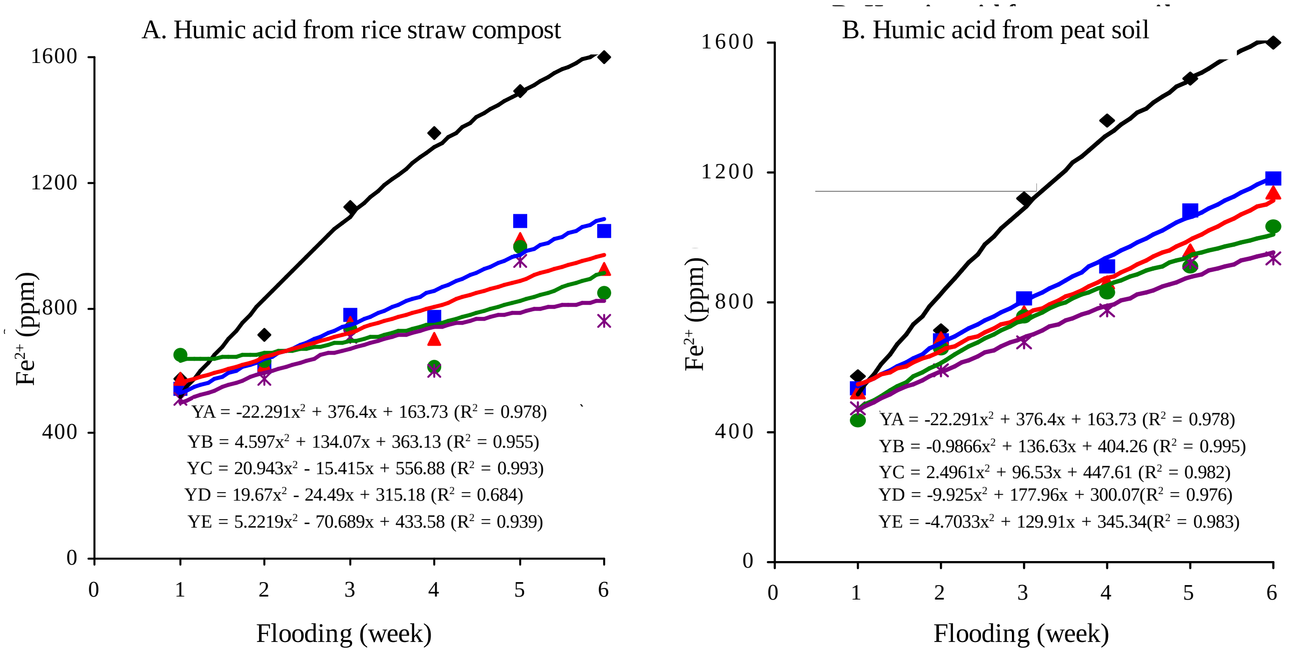

Figure 3. Effect of humic acid from rice straw compost and peat soil on Fe^{2+} concentration in new stablished rice field soil. ◆ = 0 ppm (A), ■ = 100 ppm (B), ▲= 200 ppm (C), ● = 300 ppm D), ✳= 400 ppm (E).

functional group of COOH and phenolic-OH (Schnitzer 1986; Tan 2003).

Figure 2 also showed that humic acid from peat soil and rice straw composts were more effective to bind Fe^{2+} compare to humic acid from manure and municipal waste composts. Chemical characteristic of both humic acids were relatively fines than those from manure and municipal waste composts. Beside that humic acid concentration from rice straw composts and peat soils were higher than those from the others. Base on functional groups and chemical characteristics of humic acid from tested organic matters, the humic acid from two kind of organic matters (rice straw compost and peat soil) was chosen for the next experiment using soil sample taken from a new rice field soil.

Fe^{2+} concentration in new established rice field soil treated with humic acid from rice straw compost and peat soil at 0, 100, 200, 300, and 400 ppm level and flooded for six weeks was showed in Figure 3A and 3B, respectively. Figure 3 showed, that Fe^{+2} concentration in new established rice field increased during 1 – 6 weeks flooding. Increasing of Fe^{+2} concentration in soil solution with flooding was caused by changed from oxidation to reduction condition which $Fe(OH)_3$ changed to become $Fe(OH)_2$. At 1st and 2nd weeks of flooding, the difference of Fe^{+2} concentrations between control and humic acid at various level was not clear, due to reduction process was not perfect yet. At the following weeks, the difference of Fe^{2+} concentration was more clear due to reduction process was more effective. The use of humic acid from both organic matters significantly decreased Fe^{2+} concentration in tested soil. The different effect of humic acid from two kind of organic matter, however, was not clear (Figure 3A and 3B).

Use of humic acid at various level could bind Fe^{2+} to become organo-metal complex's through binding with functional group of humic acid. The functional group of humic acid could be dissociation to became active. The negative charge was available, then bound Fe^{+2} in soil solution. According to Piccolo (2002) and Lutzow *et al.* (2006), a substantial fraction of the mass of humic acid is in the carboxylic acid functional group, which endows these molecules with the ability to bind positively charged multivalent ion (Fe^{2+}). Beside that Tan (2003) stated, humic substances would be effective to bind micro nutrient such as Fe, Cu, Zn and Mn. Huang and Schnitzer (1997) stated that, the capability of humic acid to decrease cation concentration such as Fe at Ultisol based on its reaction with metal to make organo-metal complex's compound. Increased of humic acid concentration caused decrease of Fe^{+2} concentration too.

Decreasing of Fe^{+2} concentrations with humic acid treatment at the fourth week flooding was bigger than other weeks. Use of humic acid extracted from peat soil with level from 0 to 100, 200, 300 and 400 ppm decreased the Fe^{2+} concentration at new established rice field soil from 1361 ppm to 910, 860, 831, and 776 ppm, respectively. While the use of humic acid from rice straw compost with the above levels decreased the Fe^{2+} concentration from 1361 to 770, 701, 612, and 600 ppm, respectively after four weeks of flooding.

In general, ability of humic acid from rice straw compost to bind Fe^{2+} was more hidher than humic acid from peat soil. The suitable of functional group and chemical characteristic both type, humic acid from rice straw compost have functional group more reactive (Fig 1) and higher CEC (Table 1) than humic acid from peat soil.

CONCLUSIONS

The functional groups and other chemical characteristics of humic acid from rice straw compost and peat soil were better than those of manure and municipal waste composts. Functional group of both humic acids was dominated by COO^- that very determined reactivity of humic acid. High reactivity of the humic acid had been found when humic acids were added to Fe solution with ratio 1 : 1.

Use of humic acid extracted from peat soil with level from 0 to 100, 200, 300, and 400 ppm decreased the Fe^{2+} concentration from 1,361 ppm to 910, 860, 831, and 776 ppm respectively at new established rice field soil. While the use of humic acid extracted from rice straw compost with the same levels as above decreased the Fe^{2+} from 1,361 to 770, 701, 612, and 600 ppm, respectively after four weeks of flooding.

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