

Aluminum Detoxification by Humic Substance Extracted from Compost of Organic Wastes

Sugeng Winarso¹, Eko Handayanto² and Abdullah Taufiq³

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ABSTRACT

Aluminum Detoxification by Humic Substance Extracted from Compost of Organic Wastes (S Winarso, E Handayanto and A Taufiq): Humic substance could control the activity of metal as well as exchangeable aluminum (Al_{exch}) on acid soil. The humic substance extracted from compost of agricultural waste is rarely conducted. The objective of research was to evaluate the effect of humic substance concentration and sources to pH and Al suspension. The research had been conducted in the Soil Laboratory of Agricultural Faculty of Jember University from April to July 2009. The humic substance used in these researches was extracted from compost of rice straw (RS), soybean straw (SS), cassava starch solid waste (CSSW), and empty bunch of oil palm tree (EBOPT). The humic substance concentration treatments were 0, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250, and 300 ppm. Result of the analysis showed that characteristic of humic substance was difference depending on the source material used. The humic substance extracted from SS contains total base cations (K, Na, Ca, Mg) higher (1.17%) compared with CSSW (1.07%), OPT (0.87%), and RS (0.69%). While the humic substances extracted from RS contain total organic acid (Acetic, Fumeric, Cetoglutamic, Succinic, Propionic, Butiric, Ocsalic, and Citric Acid) higher (157 ppm) compared with EBOPT (129 ppm), SS (115%), and CSSW (108%). Among these organic acids, acetic acid was highest concentration (> 34.51% of total acid). The addition of humic substance increased pH and decreased aluminum concentration of the suspension. The higher pH increment and Al concentration reduction took place in the suspension treated with humic substance from SS compost. The correlation between decreasing Al concentration with humic substance concentration which explained chelation was higher ($r = 0.97$) than decreasing Al concentration with increasing pH which explained precipitation ($r = 0.93$). Based on these research results, it can be concluded that humic substance extracted from agricultural waste have a good prospect as a soil ameliorant to increase soil pH, detoxify soil aluminum, and increase soil P availability on acid soil.

Keywords: Aluminum, chelate, compost, humic substance

INTRODUCTION

Previous researches showed that humic substance affect soil characteristic, water, and environment. The role of humic substance in the soil that affect or control the metal activities and other pollutant (like pesticide) were studied by previous researchers, for example Cu (Karlsson *et al.* 2008), Uranium (Singhal *et al.* 2006), Hg and Pb (Cruz-Guzma *et al.* 2003), and pesticide (Li *et al.* 2003).

Aluminum (Al) content in the soil is very high, but the solubility is very low. The Al solubility will

increase as the soil acidity increase (Lindsay 1979). Aluminum concentration on Ultisol Kentrong Banten was more than 6.02 cmol kg⁻¹ (Winarso 2009), and this concentration could be toxic to plant. High Al concentration not only has a negative effect on plant root growth, but also potentially retard nutrient absorption, like Mg (Sverdrup and Warfvinge 1993).

Humic substance decreases Al concentration in acid soil through chelation process. Winarso *et al.* (2009) reported that humic substance extracted from rice straw compost decreased exchangeable Al on Ultisol through precipitation due to soil pH increased

¹ Faculty of Agriculture, University of Jember (UNEJ). Jl. Kalimantan 33 Jember - Post Code 68121; e-mail: sgwinarso@yahoo.co.id

² Faculty of Agriculture, University of Brawijaya (UB); e-mail: ekohanda@telkom.net

³ Balitkabi Malang; e-mail: ofic_rilet@yahoo.com

and/or through chelation by functional group, especially carboxylate.

The objective of the research was to evaluate the effect of humic substance addition, that was extracted from compost of rice straw, soybean straw, cassava starch solid waste and oil palm tree, to pH and Al suspension.

MATERIALS AND METHODS

Extraction of Humic Substance

The humic substance used in the research was extracted from the compost of rice straw (RS), soybean straw (SS), cassava starch solid waste (CSSW) and empty bunch of oil palm tree (EBOPT). Composting these organic materials and extracting the humic substance were conducted without any chemical addition that might affect humic substance characteristic. Aerobic composting was conducted by controlling aeration and water content condition. The humic substance was extracted mechanically by pressing the composted material. Chemical extraction by addition of NaOH solution did not execute to prevent outside material to become part of humic substance compound. Characteristic of humic substance was based on organic acids analysis (acetic acid, citric acid, oxalic acid, propionic acid, butyric acid, succinic acid, fumaric acid, and cetoglutamic acid) using HPLC at Laboratory of PT Bogor Agro Lestari; pH (pH meter Jenway); C-organic (Walkley and Black method); N (Kjeldahl method); P, K, Na, Ca, Mg, Fe, Cu, Zn, and Mn (wet ashing with $\text{HNO}_3 + \text{HClO}_4$, measured using Spectrophotometer for P and Atomic Absorption Spectrophotometer for the other ones).

Experiment Setup

The research consisted of two experiments. The first experiment aimed to evaluate the effect of addition of humic substance extracted from some agricultural wastes on suspension pH. The experiment was conducted at Soil Laboratory of Agricultural Faculty of Jember University on April to July 2009. The humic substance concentration used were 0, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250, and 300 ppm with total suspension volume of 100 ml. The suspension was shaken two hours a day during a week in ambient temperature, and then the suspension pH was measured.

The second experiment aimed to evaluate the effect of addition of humic substance extracted from some agricultural wastes on pH and Al suspension. The experiment was conducted in the same place and time as the first one. The humic substance concentration used were 0, 50, 75, 100, 150, 200, 250, and 300 ppm. Aluminum used to express metal come from AlCl_3 pure analysis (pa) with concentration of 2 mM. The suspension was shaken two hours a day during a week in ambient temperature, and then the suspension pH was measured directly. Aluminum was measured based on titration method from *N* KCl extraction.

Data Analysis

All of humic substance concentration treatments were replicated 3 times and the value were average. Regression equations and pattern of two variables relationships were analyzed simply with Microsoft Office Excel 2007.

RESULTS AND DISCUSSION

Characteristics of Humic Substance

Result of humic substance analysis indicated that humic substance extracted from compost of RS, SS, CSSW, and EBOPT showed different chemical characteristic (Table 1). The humic substance extracted from SS contains total base cations (K, Na, Ca, Mg) higher (1.17%) compared with CSSW (1.07%), OPT (0.87%), and RS (0.69%). While the humic substances extracted from RS contain total organic acid (Acetic, Fumaric, Cetoglutamic, Succinic, Propionic, Butyric, Oxalic, and Citric Acid) higher (157 ppm) compared with EBOPT (129 ppm), SS (115%), and CSSW (108%). Among these organic acids, concentration of acetic acid (CH_3COOH , aliphatic and single carboxylate) was the highest i.e. 34.51% of total acid for humic substance from SS and >40% of total acid for humic substance from RS, CSSW and EBOPT.

Acetic acid, Fumaric acid, Cetoglutamic acid, Succinic acid, Propionic acid, Butyric acid, Oxalic acid, and Citric Acid are organic acid that contain double as well as single chain carboxylic functional group ($-\text{COOH}$) (Hart *et al.* 2003). If this functional group dissociates its proton (ion H^+), it becomes negative (anion compound) and it can chelate Al in the soil suspension (Essington and Anderson 2008).

Table 1. Characteristic of humic substance extracted from compost of some agricultural wastes.

Variable	Unit	Humic substance from compost of			
		Empty bunch of oil palm tree	Cassava starch solid waste	Rice straw	Soybean straw
Acetic acid	ppm	56	46	94	39
Citric acid	ppm	18	10	12	16
Oxalic acid	ppm	20	16	17	22
Propionic acid	ppm	2	4	6	9
Butyric acid	ppm	1	tt	1	tt
Succinic acid	ppm	21	11	16	18
Fumaric acid	ppm	9	21	11	8
Cetoglutamic acid	ppm	2	tt	tt	1
pH		8.60	4.60	7.60	8.70
C-organic	%	0.32	1.69	0.17	0.17
C/N ratio		23.2	30.2	15.0	6.8
N	%	0.01	0.06	0.01	0.03
P ₂ O ₅	%	0.02	0.02	0.01	0.01
K ₂ O	%	0.11	0.06	0.06	0.10
NaO	%	0.01	0.02	0.01	0.02
CaO	%	0.62	0.68	0.49	0.92
MgO	%	0.13	0.31	0.13	0.13
Fe	ppm	11.0	68.3	1.3	6.0
Cu	ppm	tt	tt	tt	tt
Zn	ppm	0.75	9.00	2.38	3.50
Mn	ppm	298	295	679	834
Mo	ppm	163	101	71	121
B	ppm	305	148	250	314

The highest acetic acid concentration (carbon alifatic chain) (Table 1) indicates that decomposition process does not complete yet. Ait Baddi *et al.* (2003) reported that aromatic degree of humic substance extracted from compost of *olive mill* waste increased with increasing period of decomposition or the compost maturity. After 12 months decomposition, humic acid from this humic substance contains high aromatic structure and the reverse for alifatic structure. Winarso (2009) reported that humic substance from rice straw composted during a year contains succinic acid (aromatic and dicarboxilate) higher (20.9%) compared with other organic acid.

The existing of organic acids containing functional group was in line with the hypothesis from Stevenson (1982) and Buffle *et al.* (1977) about the model of humic acid and fulvic acid structure that are fraction of humic compound. Until the moment, there is no agreement about humic acid and fulvic acid structures. Beside that, procedure of humic

substance fractionation to humic acid, fulvic acid and humin; extraction and purification recommended by “*The International Humic Substances Society*” are based on chemically dilution process in the acid-base system.

The pH of humic substance originated from compost of many agricultural wastes varied from pH 7.6 to 8.7, except from CSSW which pH value of 4.6 (Table 1). High pH seems correlated with high Ca, Mg, K and Na content (Table 1). Among the cation, Ca content was dominant (>70% of the total base cation) followed by Mg, K and Na. In case of Ca and Mg content, humic substance originated from compost of many agricultural wastes contains Ca and Mg ten times higher compared with K-Humat Plus 26% (produced commercially by Omnia Australia). It also contains other macro and micro nutrient (N, P, Fe, Zn, Mn, Mo, and B).

The composition of basic cation in the humic substance originated from compost of many

agricultural wastes was better than the commercial one. The basic cation in the commercial humic substance dominated by Na rather than K, Ca, and Mg (Cerdan et al. 2007). Na is non essential element for plant, and on high concentration in the soil it can destroy plant root due to plasmolysis. Beside that, it also can disperse soil colloids and therefore soil become sensitive to erosion and compaction.

Based on these characteristic, the humic substance originated from compost of many agricultural wastes might have multiple function: it could be as fertilizer, acid soil ameliorant, and for amelioration of soil contaminated by metal around the mining area.

Aluminum Detoxification by Humic Substance

Addition of humic substance originated from compost of RS, SS and EBOPT increased pH suspension as humic substance concentration increased (Figure 1). Higher pH increment took place at concentration below 50 ppm, while pH level at concentration above 50 ppm to 350 ppm was relatively constant (pH about 8.5). Addition of humic substance originated from compost of CSSW could not change suspension pH, since it had low pH (pH = 4.6). Humic substance originated from compost of SS had higher pH (8.7) and therefore increased pH higher than the other one. It means that humic substance originated from compost of SS, RS and EBOPT can be used as acid soil amandement like Ultisol and Oxisol.

Addition of humic substance originated from SS at concentration of 200 ppm caused initial Al concentration in the suspension as much as 2 mM

became undetectable (value = 0) (Figure 2). Significant decreased in Al concentration also took placed by addition of humic substance originated from the other sources. Aluminum concentration reduction was caused by precipitation as $Al(OH)_3$ due to pH increment, and/or chelation (linkage by more than one deprotonized functional group, especially carboxilate and some phenolate or other ones). This phenomenon indicated that humic substance originated from compost of agricultural wastes is highly potential to netralize Al.

The correlation value between extracted Al with humic substance concentration indicated that reduction in Al concentration was caused by chelation by functional groups of humic substance and then precipitated due to pH increment (Figures 2 and 3). Among the correlation values, correlation value between concentration of humic substance from compost of SS with extracted Al was higher ($r = 0.97$). Relationship between humic substance concentration and extracted Al was quadratic, and equation with higher determination coefficient was from RS, *i.e.* $y_p = 7E-06 X^2 - 0.004 X + 0.808$; $R^2 = 0,947$. Skyllberg (1999) stated that complex Al-organic matter valid at $pH < 4.2$ and in the unsaturated $Al(OH)_3$ solution.

Addition of 2 mM $AlCl_3$ in the water decreased solution pH to nearly 4. Addition and humic substance concentration increment increased pH, except in the treatment with addition of humic substance originated from compost of SS (Figure 3). This result was in line with the previous research without any Al addition Al (Figure 1). Figure 3 also showed relationship between pH with Al extracted with KCl

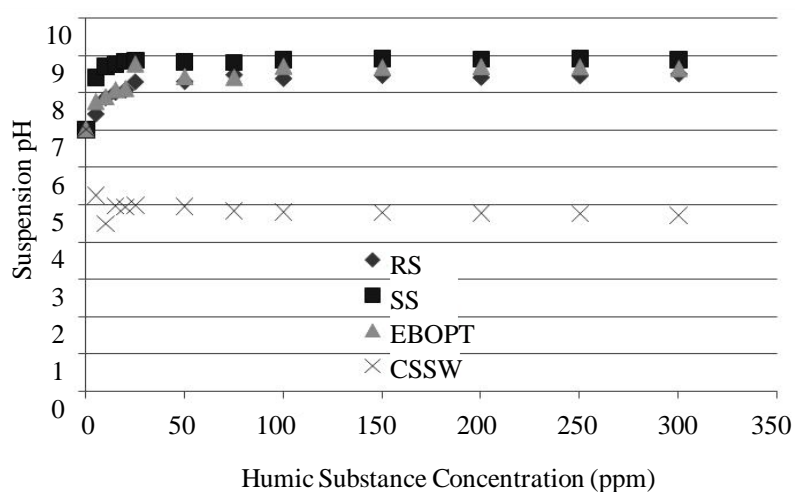


Figure 1. Effect of humic substance concentration to suspension pH.

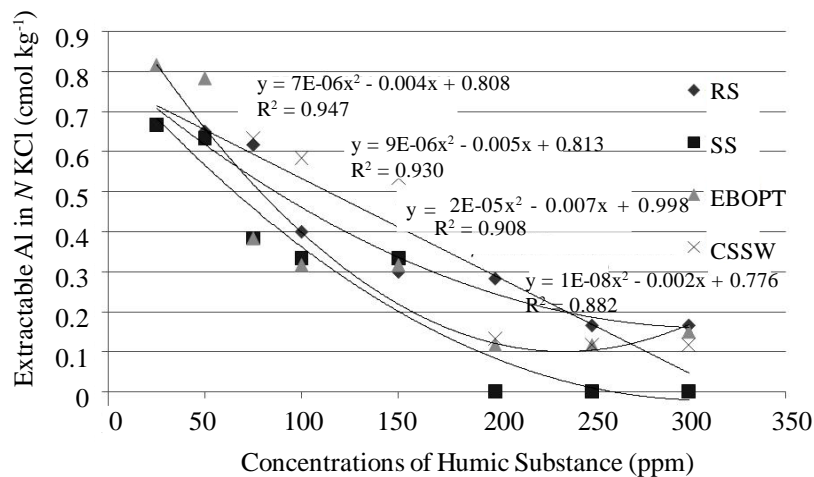


Figure 2. Relationship between concentrations of humic substance originated from compost of some agricultural wastes with extractable Al in N KCl in the suspension containing 2 mM AlCl₃.

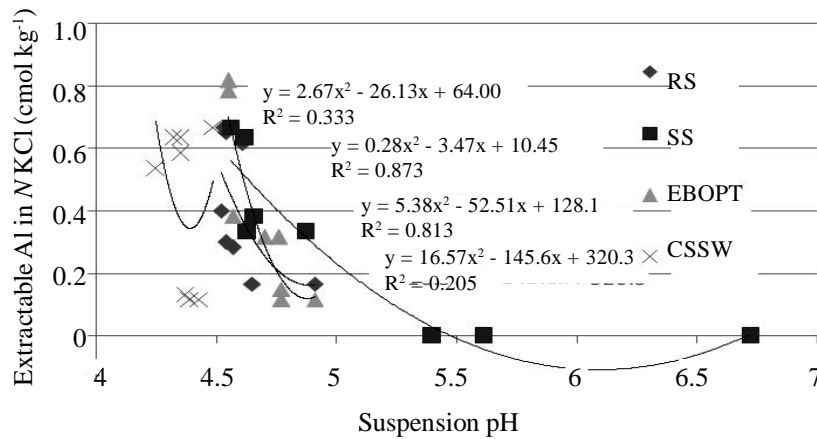


Figure 3. Relationship between pH with extractable Al in N KCl in the suspension containing humic substance originated from compost of some agricultural wastes and 2 mM AlCl₃.

from suspension containing humic substance originated from some compost sources and 2 mM AlCl₃. The equation between these two variables was quadratic, but had lower coefficient determination (R²) compared with R² between humic substance and Al (Figure 2). The highest correlation value took place between humic substance originated from SS compost (r = 0.93), followed by humic substance originated from EBOPT compost (r = 0.90), RS compost (r = 0.58) and CSSW compost (r = 0.45).

Based on these explanations, correlation value, and relationship between Al and humic substance concentration indicated that reduction of Al concentration was primarily due to chelation by functional groups of humic substance rather than by

precipitation due to pH increment. This close relationship between humic substance concentrations with Al measured at pH in the range of 4 to 5.5. Winarso (2009) showed that Al detoxification on Ultisol (Al_{-exch} undetected) by humic substance and CaCO₃ effective on pH at about 5.5.

The results indicated that Al chelation and precipitation by humic substance originated from some agricultural wastes compost can be used to control metal element on land metal-contaminated. So that, it needs further research to know effective concentration on certain pH and certain metal element, since low humic substance concentration will promote metal mobilization especially in the water canal.

CONCLUSIONS

Characteristic of humic substance was difference depending on the source material used. The humic substance extracted from soybean straw contains total basic cations (K, Na, Ca, Mg) higher (1.17%) than that extracted from cassava starch solid waste (1.07%), empty bunch of oil palm tree (0.87%), and rice straw (0.69%). Humic substance extracted from rice straw contains total organic acid (Acetic acid, Fumaric acid, Citoglutamic acid, Succinic acid, Propionic acid, Butiric acid, Oxalic acid, and Citric acid) higher (157 ppm) compared with the other. Among these organic acids, acetic acid was the highest concentration (>40% of total acid) except in the humic substance from rice straw compost (34.51%).

The addition of the humic substance decreased aluminum concentration of the suspension. Higher reduction of Al took place in the suspension treated with 200 ppm humic substance from soybean straw compost. Al detoxification by humic substance in various pHs below 5.5 levels primarily due to chelation rather than precipitation.

Further research to identify optimum concentration of humic substance to detoxify metal element in the soil and phosphorous desorption in acid soil.

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