EFFECT OF HUMIC ACID ON SOIL CHEMICAL AND PHYSICAL CHARACTERISTICS OF EMBANKMENT

Munawar Ali[1] and Wanti Mindari[2]

[1]Department of Environmental, Faculty of Civil and Environmental Engineering, University of Pembangunan Nasional "Veteran" East Java, Indonesia
[2]Department of Agrotechnology, Faculty of Agriculture, University of Pembangunan Nasional "Veteran" East Java, Indonesia
E-Mail: munawar1960@gmail.com[1]

ABSTRACT

The effectiveness of the treatment of pathogens disease in fish using chemicals is very limited because of the stress of toxic ions. A treatment of humic acid of 50-90 mg /L on a farmland has been able to reduce illness and death compared to a mixture of formaldehyde and blue-green methylene. Humic acid is suspected to be able to increase yield, through improved conditions and resistance to diseases, health, and cultural vitality, either by itself or combined with cation species toxic. Humic acid can balance the soil cation so that the soil pH reached 7-8, through a chelate of Al, Fe, Ca or exchanged with NH_4, Na and K. Humic acids were extracted from compost plants with a weak base of 0.1 N NaOH and precipitated at pH 2. The concentration of AH 0- 400 ml was applied to three soil types with an area of 0.12 m^2 and 15 cm thickness. The results showed that the application of 100-200 ml HA/0.12 m^2 gave optimum yield in improving the physical-chemical characteristics of the soil embankment. Soil pH reached a value of 7-8, cation exchange to 60% saturated, and soil bulk density was reached in the range of 1.1- 0.97 g / cm^3.This condition is suitable for fish or shrimp in the embankment.

Keywords: cation, embankment, humic acid, pH, soil

INTRODUCTION

The low levels of fertility and quality of soil embankment are due to fluctuations in salt content, organic sediment, plankton, and soil structure (Machmudin, 2009). The pH of water is not affected since high biological activity rarely reaches > 8.5, but the pH of water of fish or shrimp embankment may reach 9 or more (Boyd, 2002). The seven primary ions: sodium, potassium, potassium, magnesium, chloride, sulfate and bicarbonate have a great contribution towards salinity within (Boyd, 1990). Calcium ions (Ca), potassium (K), and magnesium (Mg) is the most important ions in propping up the level of living shrimps (Davis et al. 2004). The ideal range of saturation of Ca, Mg and K are 60-80%, 10-25%, and 3-5%, respectively, of the CEC soil. Magnesium is recommended to be given when saturation is below 15%, or the ratio of Mg/K < 2:1. Osman *et al* (2010) found that the concentration of chemical compounds increases in the Outlet and declines in the Inlet. Heavy metals and inorganic anion varies significantly ($P < 0.05$) depending on the type of fish and the location of the relative abundance of cultivation. Sequence elements: sediment > > fish water. The order of heavy metals and inorganic anions in water: Fe-Mn-Zn > Pb >Cu > Cd, whereas in sediments are: Fe >Mn-Zn > Cu >Pb > Cd.

Alkalinity is a buffer important to control embankment soil pH and changes of dissolved cations. Ion solubility or salinity in the embankments water for shrimp cultivation is in a range of 15-30 g/l. The addition of organic fertilizers has increased the production of shrimp in 2011 only by 5% while in 2012 there was an increase of 22 %. An alternative solution is to use a buffer to keep the pH value from changing (Tan, 1988). Alkalinity acts as a buffer for the pH fluctuations as well as stabilizing the tapping solution of pH and determines the natural fertility of the waters (Boyd, 2002). Humic acid (HA) is a major component of humic substance, produced from the biodegradation of dead organic matter, containing carboxyl and phenolic so that it behaves functionally as dibasic acid or sometimes as a tribasic acid. Functional groups which most contribute to surface charge and reactivity. The presence of carboxylic groups and phenolic gives the ability to form a complex with HA ions such as Mg^{2+}, Ca^{2+}, Fe^{2+}, and Fe^{3+}. The ability of humic acid to adsorb cations follows the lipotrophic sequence, i.e., $Al^{3+} = (H^+) > Fe^{3+} > Fe^{2+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$ (Tan, 1998). Sorption of NH_4^+ is similar to Na^+ (Nursyamsi et al., 2009). Sorption and maximum buffering capacity of the NH_4^+ and Na+ are relatively different. Cation adsorption by HA occurs through the exchange of cations in solution or that adsorbed by clay-humic. Adsorption of cations or metals by HA can be through (a) direct adsorption (Ca^{2+} that release PO_4^{3-}), (b) complexation of Cu^{2+} or outer-sphere interactions for hydrated Mg^{2+} , (c) serving as a cation bridge through direct or indirect chelation, and (d) interaction with Ca^{2+}-HA aggregates or with amine groups (Sharma and Kappler, 2011). Clay or humic materials have a strong affinity to weak acids containing phenolic hydroxyl, a carboxyl group, or amino sulfonyl. Alkaline cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) are primarily retained by simple cation exchange with COOH groups (RCOONa, RCOOK) (Zhang et al., 2013).

Humic acid (HA) is a derivative product of decomposed organic material that is soluble in alkali but insoluble in acid (Mikkelsen, 2005; Pena-Méndez et al., 2005). A typical structure molecule of HA may consist of six carbon aromatic rings of the basis of di- or tri-hydroxyl phenols linked by -O-, -NH-, -N-, - S-, and contain -OH group and quinone (O- C_6H_4-O-) (Tan, 1998). Humic acid (HA) is a cyclic organic compound having high molecular weight, long-chain, and active carboxyl group (- COOH) and phenolic (-OH), which are amphoteric, binding of cations/anions at certain pH dependent charge (Stevenson, 1994; Bohn et al., 2001; Pena-Méndez et al., 2005; Khaled and Fawy, 2011). Carboxylate of some carboxyl group is released below pH 6 leaving a negative charge on the functional group: R-COOH = R-COO- + H^+ (Pettit, 2011). Dissociation of H+ from amide (= NH) can also increase the negative charge. Humic acid levels in compost, manure, straw, and others are relatively low (<1%), while that in coal deposits "Leonardite" is relatively very high (~ 15%) (Humintech, 2012). Mindari *et al*. (2013) obtained HA extracts from compost, coal and peat with 0.5 N NaOH and its deposition to pH 2, respectively of 2.6%, 4.6%, and 7.6%. Goff (1982), Lebo *et al*. (1997), Anaya-Onala (2009), and Chen *et al*. (2009) obtained HA at least 60-80% and has a high solubility. Nur Hasinah et al. (2008) reported that reduction of the duration of the extraction time from 24 hours to 12 hours gave AH a similar character. Characteristics of humic acids can be analyzed from the ratio of the value of E4 / E6 which is the value of absorbance at 465 nm (E4) and the absorbance of 665 nm (E6). Kononova (1966) and Chen *et al*. (1977) believed that the ratio of E4 / E6 was associated with the degree of condensation of aromatic carbon lattice. Weak ratio values indicate weak condensation of high levels of humic aromatic components while strong ratio indicates the proportion of higher aliphatic structure. The ratio value of E4 / E6 is primarily governed by the size of the molecule or molecular weight or particle, which is correlated with the concentration of free radicals with O, C, CO_2H and total acidity (Chen et al., 1977), but it does not depend on the concentration of humic acid or fulvic. The structure of humic acids has a range of E4 / E6 ratios about 3.3-5.0 (Pansu and Gautheyrou, 2006).This study was aimed to examine the effect of humic acid on the soil cation concentration, pH, EC, and soil bulk density (SBD) at the embankment.

METHODOLOGY

The experiment was conducted from April 2015 to July 2015 in the glasshouse and laboratory, consisting of two activities.

Extraction and characterization of humic acid as buffering agent

Humic acid were extracted from compost with 0.5 1 NaOH solution (1:5) through the 24-hour agitation and precipitation with 6 N H_2SO_4 up to pH 2 in accordance with the method of Stevenson (1994). The extracted humic acid was purified by adding a mixture of HCl and HF (2:1 by volume) which were then forwarded with water up to 3 times by centrifugation or settling in the separator tube. The humic acid precipitate was heated at 40ºC to obtain concentrated HA. The humic acid having a pH 2 adjusted to a pH of 6 for the application.

Organic-C content of the humic acid was determined using the method of Walkey and Black. The percentage of humic acid was calculated by the gravimetric method at a temperature of 100ºC. The value of E4 and E6 were analyzed by diluting humic acid with 0.05 N $NaHCO_3$ (1 mL of humic acid: 10 mL), and then each of which was analyzed at a wavelength of 465 and 665 nm using a Spectro Pharo 100. The ratio of E4 / E6 was obtained by dividing the value of E4 with E6 (Kononova, 1966; Chen , *et al*, 1977). The E4 / E6 ratio value of less than 5 shows the character of humic acid while that of more than > 5 is fulvic acid (Tan, 2003). CEC value of the humic acid was analyzed by saturation 1N NH4OAc at pH 7. The C organic content and CEC were analyzed according to the previous method in organic materials that have been oven-dried at 70°C as proposed by Pansu and Gautheyrou (2006). CEC was analyzed by saturation 1N Ammonium Acetate. The pH and EC values were analyzed in pasta humic acid 1:1.

Experiment: Effect of humic acid on soil pH, cation, and bulk density

The experiment was arranged according to a factorial completely randomized design (CRD) where the first factor 1 was five dose of humic acid : 0,100, 200, 300, 400 ml/1200cm^2 (100 ml/1200cm2= 889 mg/kg). The second factor was three types of embankment. Each treatment was repeated three times. The soil used for this experiment was topsoils (0-20 cm depth) collected from Gununganyar Village of Surabaya. Soil sampling sites located as far as 2-3 km from UPN Surabaya. They were taken from three different levels of fertility, i.e.: slow to moderate permeability (2.2-25.5 mL / h), clay texture (60- 62%), pH 7.9-8.55, EC 6.8-7.8 mS / cm, and 1.88–2.96% organic C. Samples were taken when the embankment is still saturated with water, and then placed in a plastic chamber of 30x40cmx15 cm^3 capacity.

The buffer made of humic acid extracts was blended with NPK fertilizer. The buffer-based humic acid liquid was given according to the dosage then evenly mixed and incubated for 1 month at a room temperature. Water with a salinity of less than 1 mS/cm was added to the soil to approximate field capacity. After incubation, soil samples were taken for analysis of cations of soil and soil pH. The chemical characteristics of the embankment: pH, EC, heavy metals Pb, Cu, Cd, bases, and heavy soil content farms. Character humic acids were analyzed by NMR, pH, EC and Redox with soil paste method, and cations using ammonium acetate extract. After 1 month of incubation, the soil samples were analyzed for changes in pH, EC, and redox. At 2 months of incubation, the soil samples were analyzed for their soil bulk density change.

After a month of incubation, 50g of soil subsample was collected from each pot, air-dried and sieved to pass through 0.5 mm sieve for chemical analysis. The soil chemical characteristics analysis includes pH, EC, and soil bases.

Data analysis

Observations data were summarized in the chart treatment of the results. A regression treatment was performed on the results to assess the optimal dose to the buffer embankment fertility levels. LSD 5% was used to assess the best materials for fish embankment land buffer. The statistical analysis was performed using Excel. The regression and correlation treatment of the results were used to assess the buffer dose optimization.

RESULT AND DISCUSSION

Characteristics of Humic Acid

The humic acid used in the experiment is presented in table 1 and figure 1. Humic acid was extracted by NaOH and precipitated with H_2SO_4 until pH reached 2. This is similar to the characteristics of peat containing higher organic- C, humic acid, CEC, and smaller E4 / E6 ratio than others (Mindari, 2013).

Table-1. Characteristics of humic acid materials

Sources of Humic Acid	**pH**	**Org-C (%)**	H-NMR ppm	**Humic Acid (%)**	**Ratio E4/E6**	**CEC (me/100g)**
Compost Of leaf	6	25.15	20.000	5.50	3.31	85.72

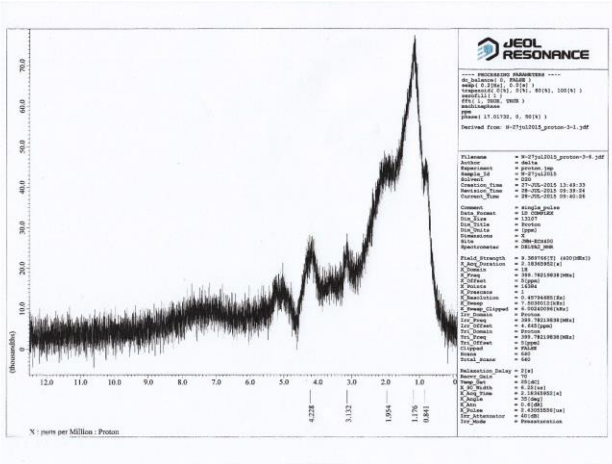

Figure-1. H-NMR humic acid contains concentration of H

Compost saturated with NaOH caused the **site** to be oxidized to molecules saturated with Na, which was ready to be exchanged with all ions in the soil. A highly oxidized organic matter, in which parts of its chemical structure are oxidized, will create site adsorption to bind micro nutrients, microflora, and the molecules. According to Tan (2003), Miklesen (2005), positive ions bind to oxidized site adsorption to provide space for the entry of negatively charged molecules which causes them to absorb micronutrients.

The addition of NPK to compost -HA is suspected that AH-NH_4^+ and -K^+ exchanged to soil -Na^+ and soil-Ca^{+2} caused reduced soil salinity. This reduction of Na was because of K^+ replaced them on the surface of adsorption colloid so the proportion of K was increased. Because the three ions have a similar valence, their exchangeability is determined by the affinity of the cations (Tan, 2003). Fosfat Ion ($H_2PO_4^-$) adsorbed in the positive charge of HA will eventually be released into the soil solution if needed by plants or biota. In line with the increasing charge, the addition of cations also increased CEC. The ability of K^+ to exchange H^+ potential of missel made the solution become baser. These humic pH were around 6, which was the same as the original pH buffer of 6.3-6.5. The addition of K^+ -NPK fertilizer formed K^+ -humic, that were easier or more preferably adsorbed to the colloid surface than NH_4^+ - NPK fertilizer (Nursyamsi et al., 2009). Because of the ability of colloid to absorb NH_4^+ or K^+ is similar, the addition of one of the ions will exchange the others in the same amount.

The higher the dose of humic acid, the higher the CEC value. This was because of the addition of cations will increase them in the mineral surface and between minerals. Colloids do not only adsorbed ions but also absorbed water, so that increased water reserves. HA absorb more than absorbents used to date (Pena-Méndez et al, 2005).

Effect of humic acid on soil pH, cation, and bulk density

The value of humic acid pH was adjusted to 6 for application to soil embankment. The application of humic acid+NPK significantly affected soil pH (Figure 1), soil cation exchange (Ca, Mg, K, Na) (figure 2 and Table 2) and soil EC on three types of the fish embankment.

The soil reaction greatly affects the availability of nutrients to plants. Under neutral soil pH, nutrients are available in considerable amounts. However, if the soil pH is more than 8.0, nitrogen, iron, manganese, boron, copper, and zinc will be less available to plants (Tan, 1998).

Saline intrusion on soil causes (a) fixation or absorption of other nutrients in the soil by the compounds and silica carbonate or oxide Fe, Ca, and Mg, and (b) disturbance in the balance of $Ca^{2+,}$ Mg^{2+}, Na+, and K^+ in the soil, among others, further strengthen the aggregate stability (Mikkelsen, 2005;

The downward trend in soil pH of all three types of soil is almost the same, but the first soil changed faster compared to the second and third ones. The reduced pH value of the soil was due to the replacement of the soil solution of salt ions with H + humic acid which caused the pH of the solution is lowered (Khaled and Wafy, 2011).

The applications of AH 0-400 ml dose /0.12m^2 lowered the soil pH to 0.8 units on soil 1, 0.6 units on soil 2, and 0.7 unit on soil 3. The addition of humic acid will exchange H + cations to cause lower soil pH. The soil cation exchange has a capability to greatly influence the content of clay and organic matter. The higher the content of clay and organic matter, the smaller the pH change, as in the case on soil 2. The EC value of the soil greatly influenced the accumulation of salt concentration in the soil solution. EC values are correlated with soil pH, wherein if the soil pH dropped due to the decreased levels of salt concentration as shown in Figure 2. The high value of farm land EC may be due to the high content of Na, K, Ca and Mg soil. The addition of humic acid will release H + into the soil solution H + humic where its position was replaced by cation salt, then decrease the salt concentration in the solution so that the value of EC was reduced. Therefore, if the suitability for pond soil pH is between 7 and 8, the pH of HA administration of 100 ml is sufficient for embankment repairs.

The dose of application of HA was up to 400 ml for 5kg **soil** significantly decreased soil pH, cations exchange. The results of analysis of cations embankments with the application of a humic acid with a dose of 400 ml /12m^2 or an equivalent of 3-6g/kg soil have a pH value between 7 and 8 which is suitable for embankments. Cation exchange was a little bit changed and can reach the portion corresponding to the cation saturation. There was an interaction between the

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dose and the type of soil in affecting the soil cation exchange. The best treatment combination was 400 ml to soil type 3, 100-200 ml HA to soil type 2, and 200 ml to soil type 3 to reach a saturation ca 60% ideal for soil.

Along with the release of H by humic, the cations present in the solution and adsorbed colloid surface soil will be exchanged. The value of the exchanged cations and anions causes particles to loose or ease the incorporation of solid particles added to the soil pore space. The changes in soil porosity affect the flow of water and soil nutrients. Overall, the trend of changes in the soil cation decreases with increasing humic acid applications. The soil 1 embankment with the provision of another soil humic acid was suspected to have ugly structures that need some improvement. Humic acid can increase the aggregate stability (Pena-Méndez *et al*, 2005) by improving the saline soil physic.

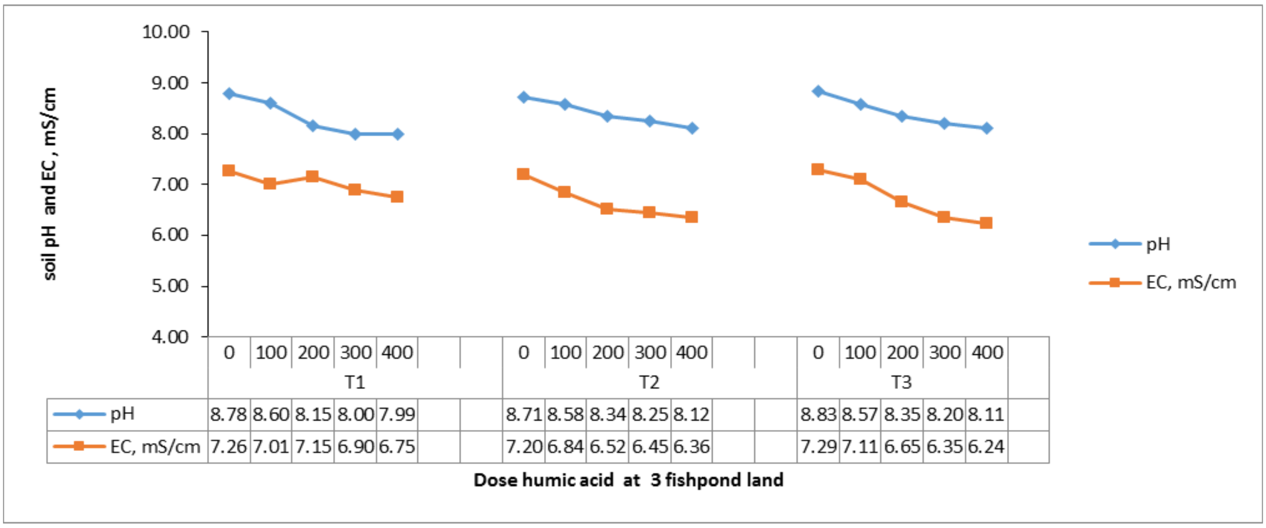

Figure-2. The value of soil pH and EC at 1 month after humic acid +NPK application

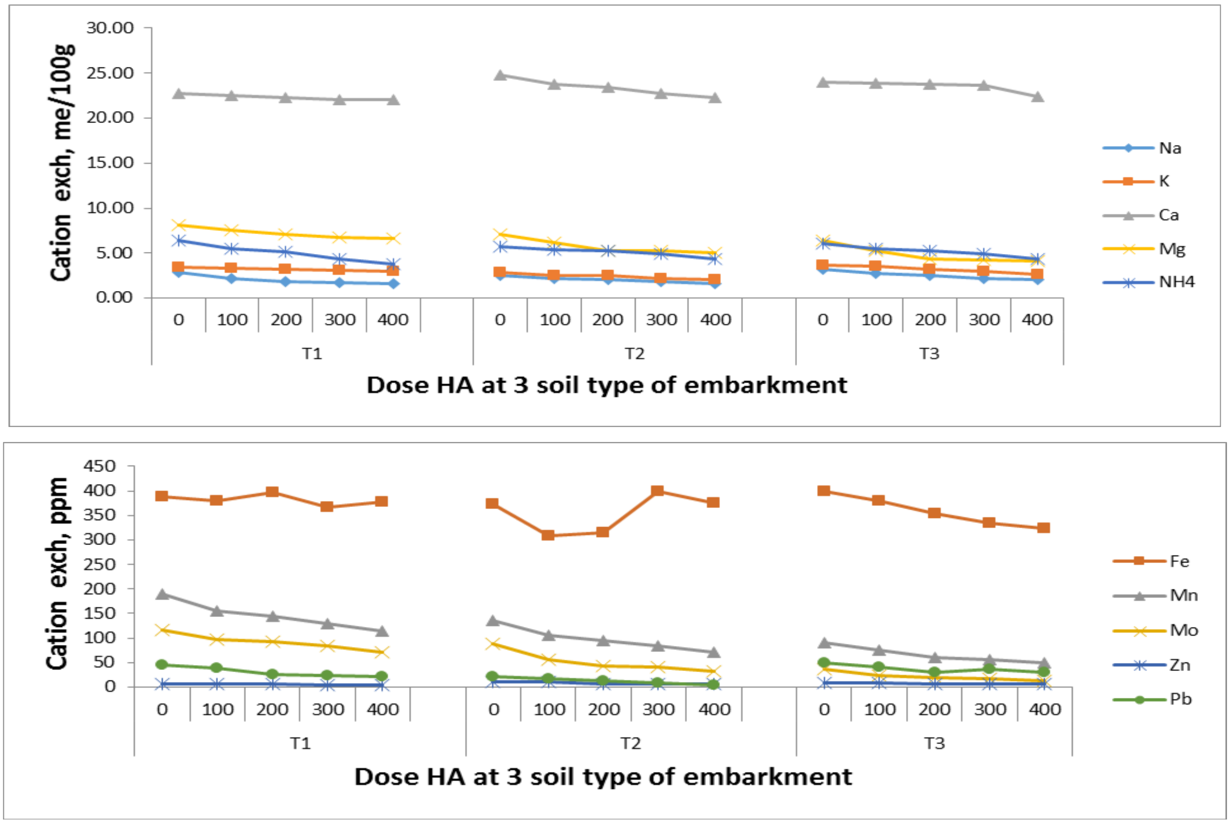

Figure-3. The value of soil cation after 4 weeks of HA application at 3 types of embankment
(Above: macro cations, Bottom: micro cations)

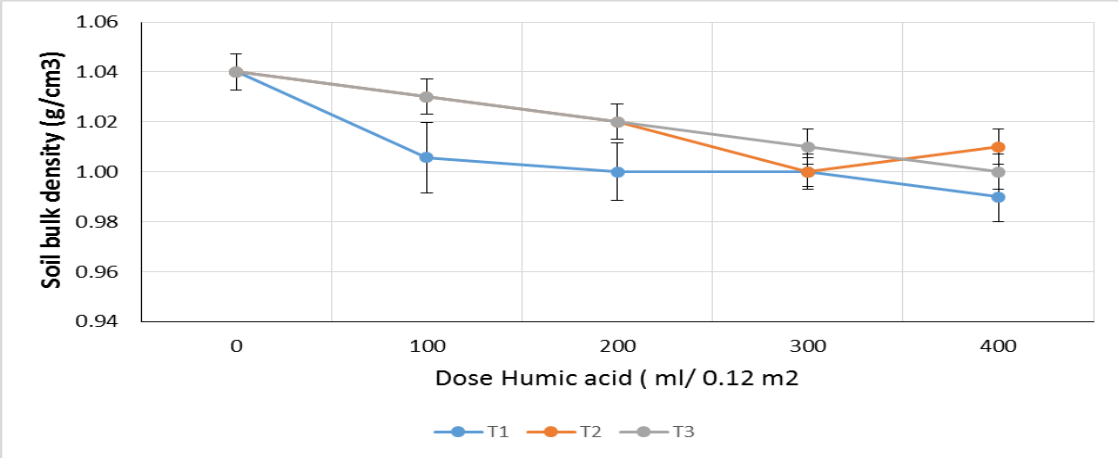

Figure-4. Soil bulk density of embankment after application of HA +NPK

Table-2. Percent saturation cations on 3 type of soil embankment after application AH 0-400 ml / 100g

Type of embarkment	Soil cation (me/100g)	Dose of humic acid (Ml/0.12 m2)				
		0	100	200	300	400
1	Na	6.62	5.32	4.67	4.59	4.45
	K	7.96	8.05	8.16	8.11	8.08
	Ca	52.17	54.80	56.30	58.21	59.29
	Mg	18.56	18.35	17.93	17.66	17.99
	NH4	14.70	13.48	12.94	11.43	10.18
2	Na	5.94	5.45	5.38	4.95	4.67
	K	6.53	6.32	6.45	5.90	5.73
	Ca	57.62	59.29	60.83	61.51	63.07
	Mg	16.49	15.55	13.74	14.25	14.29
	NH4	13.42	13.39	13.59	13.39	12.25
3	K	7.27	6.80	6.41	5.83	5.86
	Na	8.44	8.67	8.32	7.96	7.28
	Ca	55.50	58.28	60.76	62.06	62.88
	Mg	14.76	12.91	11.15	11.15	11.65
	NH4	14.03	13.33	13.37	13.00	12.33

CONCLUSION

The humic acids extracted from compost has a CEC of 60-156 me/100g, organic-organic C content of 20-30%, pH value of 6.0, in black color, and slow soluble in water. HA applications up to 400 ml for 5kg soil significantly lowered the soil pH, cation exchange, and bulk density. The pH value of about 8 and about 60% Ca saturation was achieved in the administration of 400 ml HA for soil type 1, 100-200 ml for soil type 2, and 200 ml for soil type 3.

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