

*Full Length Research Paper*

# Effect of pH and concentration on the complexation of calcium ions with humic acid extracted from composted oil palm bunches.

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The reaction (complexation) between calcium ions at certain concentrations (1.000, 0.500, 0.250 and 0.125 M) and pH (2, 4, 6, and 8) and humic acid obtained from composted oil palm (*Elaeis guineensis Jacq*) bunches were investigated in this study. The results obtained showed that at maximum total calcium concentrated (1.000 M) few or no  $\text{Ca}^{2+}$  was complexed to the humic acid at pH 2 and 8 respectively, while some degree of complexation was exhibited at pH 4 and 6. Similarly, at 50% total calcium level, more  $\text{Ca}^{2+}$  reacted with the humic acid at pH 4 and 6 respectively. Interestingly, all the points on the plotted graph of  $\text{Log}_{10} [\text{Ca}^{2+}]$  versus  $\text{Log}_{10} [\text{Ca}_T]$  converged at the lowest total  $\text{Ca}^{2+}$  concentration. Furthermore, the study revealed that depending on the total  $\text{Ca}^{2+}$  concentration, effective interaction occur at and between pH 4 and 6 with the humic acid. This feature can be employed in regulating the release or retention of  $\text{Ca}^{2+}$  by the application of the humic acid in calcareous or limestone rich soils.

**Key words:** Humic acid complexation,  $\text{Ca}^{2+}$ , pH.

## INTRODUCTION

Humic substances are products of the transformation of organic matter. They may be defined as a mixture of high molecular weight macromolecules (0.500 – 100 K Dalton) of natural origin (Zara et al., 2006). A typical humic acid molecule contains aromatic rings and aliphatic chains that host numerous carboxylic, phenolic, hydroxyl, and other functional groups (Oviasogie and Aisueni, 2004; Kantar and Karadagli, 2005)

Humic substances exist in recycled nutrient streams used for crop production and so their effects on plant growth and nutrient chemistry are being evaluated (Mackowaik et al., 2001). A benefit of humic acid in agricultural systems is its ability to complex metal ions. Humic acid ion form aqueous complexes with micronutrients. Since humic acid binds to soil colloidal surfaces, it is not easily leached (Spark et al., 1997a). Metal complexation by humic substances can play an important role in regulating the toxicity, bio-availability, and transport pro-

erties of systems (Cao et al., 1995). Since relevant conclusions both trace and alkaline earth metals in soil and aquatic are reached using experimental conditions which are similar to those of natural ecosystems, in particular without the addition of species which could disturb the free equilibria, one important condition that affect the complexation behaviour of humic acid is pH (Takahanshi et al., 1997; Spark et al., 1997b; Oviasogie and Isemla, 2005). In this study, the complexation of  $\text{Ca}^{2+}$  by humic acid extracted from composted oil palm bunches as a function of pH and metal ion concentration were investigated.

## MATERIALS AND METHODS

### Extraction of humic acid

Humic acid was extracted from freshly prepared mature and processed composted oil palm bunches according to the method by Kononova (1966). Briefly, 6 L of 0.1 M NaOH was added to 400 g (dry weight) compost in a plastic container. The mixture was shaken for 24 h and centrifuged (3000 rpm) for 30 min. The supernatant was carefully transferred into a glass beaker, acidified with  $\text{H}_2\text{SO}_4$

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**Table 1.** Concentration of total calcium ions.

[Ca <sub>T</sub> ] M	Log <sub>10</sub> [Ca <sub>T</sub> ]
0.125	-9.030 × 10 <sup>-1</sup>
0.250	-6.020 × 10 <sup>-1</sup>
0.500	-3.010 × 10 <sup>-1</sup>
1.000	0.000

(pH 2) and then centrifuged for 30 min at 8000 rpm. The precipitate (humic acids) was separated from fulvic acids by filtration, dissolved in 0.1 M NaOH and then dialysed against water (pore diameter 20 A). The final humic acid solution was then freeze dried to obtain a brown powder.

**Complexation reactions**

Analytical grade CaCl<sub>2</sub> obtained from BDH was used for the complexation reaction. 1.000, 0.500, 0.250 and 0.125 M concentrations of CaCl<sub>2</sub> solutions were prepared using distilled/deionized water. 50 ml each of these solutions was transferred into polyethylene containers each containing 0.5 g of the humic acids. The pH values of the various mixtures were adjusted to read 2, 4, 6 and 8 on the Jenway 3020 glass electrode pH meter. The tubes were put in the Reedolph 2010 shaker and agitated for 24 h. After agitation, the mixture in the tubes were centrifuged for 1 h at 800 rpm and the supernatants analyzed after filtration on Whatman no. 1 filter paper for uncomplexed Ca<sup>2+</sup> using the Bulk Scientific GVP 210 atomic absorption spectrophotometer. All samples were prepared and analyzed in triplicates.

**Amount of Ca complexed was calculated as follows**

Amount of Ca<sup>2+</sup> complexed = known amount of Ca<sup>2+</sup> - Amount of Ca<sup>2+</sup> present in supernatant solution after complexation.

**RESULTS AND DISCUSSION**

The data obtained were analyzed using a single ligand model.

$$[MeL] = \sum(K_i \times [Me] [L]_i)_{i=1,2 \dots n} \dots\dots\dots (1)$$

Where (MeL) stands for bound-metal concentration, [Me] stands for free metal concentration, Li is the ith ligand concentration, and Ki is the conditional binding constant corresponding to ith ligand. Charges are omitted for simplicity. The conditional formation constant for this complexation at a constant pH is:

$$K = \frac{[MeL]}{[Me] [L]} \dots\dots\dots (2)$$

[Me] and [MeL] are respectively, the free and bound concentration of Ca metal, and [L] is the free concentration of ligand. [Me] concentration was calculated by subtracting metal-humic concentration from labile metal concentration and [MeL] and [L] values were then determined using the mass balance equations:

$$L_t = [L] + [MeL] \dots\dots\dots (3)$$

$$Met = [Me]_L + [MeL] \dots\dots\dots (4)$$

Where [Me]<sub>L</sub> is the labile metal concentration. Substituting equation 3 in eqn.2 and rearranging

$$[MeL] = \frac{K L_t [Me]}{1 + [Me]} \dots\dots\dots (5)$$

A nonlinear regression method can be employed to determine K and L<sub>t</sub> parameters in the functions of [MeL] = f (Me). In the fitting processes of the complexation reaction, free metal concentration instead of bound metal concentration was used as the independent variable, while Met was the dependent variable, according to Cabaniss and Shuman (1988). Applying the above computation to the present study,

$$[CaHA] = K_i [Ca^{2+}] [HA_i] \dots\dots\dots (6)$$

Where (CaHA) represents calcium-humic acid concentration and (Ca<sup>2+</sup>) stands for free metal concentration, [HA<sub>i</sub>] is the ith humic acid concentration and K<sub>i</sub> is the conditional binding constant corresponding to ith humic concentration.

The conditional formation constant can be obtained by applying the equation

$$K = \frac{[CaHA]}{[Ca^{2+}] [HA]} \dots\dots\dots (7)$$

Where [Ca<sup>2+</sup>] and [CaHA] represent free and humic-bound concentration of Ca metal respectively given the total concentration of calcium [Ca<sub>T</sub>].

Applying the mass balance expression of equations (3) and (4) respectively,

$$HA_t = [HA] + [CaHA] \dots\dots\dots (8)$$

$$Ca_T = [Ca^{2+}] + [CaHA] \dots\dots\dots (9)$$

where [Ca<sup>2+</sup>] is the labile metal concentration. Substituting equation (8) into (7) and rearranging,

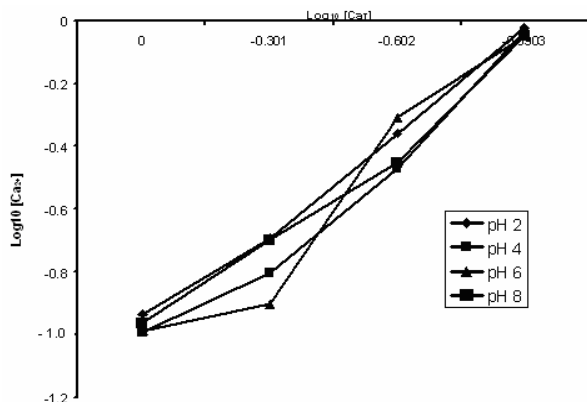
$$[CaHA] = \frac{kHA_t[Ca^{2+}]}{1 + k[Ca^{2+}]} \dots\dots\dots (10)$$

As analogous to equation (5), in the present complexation reaction, free calcium concentration [Ca<sup>2+</sup>] instead of bound metal concentration was used as the independent variable, while Ca<sub>T</sub> was the dependent variable (Shuman, 1988). Consequently, a graphical plot of log<sub>10</sub> [Ca<sup>2+</sup>] against log<sub>10</sub> [Ca<sub>T</sub>] was made.

Table 1 shows the total concentration of calcium ions in solution while Table 2 is the amount of uncomplexed (labile) calcium ions at the various pH values. The plot of Log<sub>10</sub> [Ca<sup>2+</sup>] versus Log<sub>10</sub> [Ca<sub>T</sub>] is shown in Figure 1. At maximum total calcium concentration (IM), little or no Ca<sup>2+</sup> was bound to the humic acid at pH 2 and 8, while some degree of complexation was exhibited at pH 4 and 6. This trend continued at 50% (0.500 M) total calcium

**Table 2.** Concentration of uncomplexed calcium ions at various pH values.

pH	[Ca <sup>2+</sup> ]M	Log <sub>10</sub> [Ca <sup>2+</sup> ]
2	0.116	-9.355 x 10 <sup>-1</sup>
	0.203	-6.925 x 10 <sup>-1</sup>
	0.438	-3.585 x 10 <sup>-1</sup>
4	0.944	-2.502 x 10 <sup>-1</sup>
	0.102	-9.913 x 10 <sup>-1</sup>
	0.157	-8.041 x 10 <sup>-1</sup>
	0.339	-4.698 x 10 <sup>-1</sup>
6	0.926	-3.338 x 10 <sup>-1</sup>
	0.103	-9.871 x 10 <sup>-1</sup>
	0.198	-7.033 x 10 <sup>-1</sup>
	0.492	-3.080 x 10 <sup>-1</sup>
8	0.896	-4.769 x 10 <sup>-1</sup>
	0.109	-9.625 x 10 <sup>-1</sup>
	0.200	-6.989 x 10 <sup>-1</sup>
	0.353	-4.522 x 10 <sup>-1</sup>
	0.898	-4.672 x 10 <sup>-1</sup>

**Figure 1.** Plot of Log<sub>10</sub> [Ca<sup>2+</sup>] versus Log<sub>10</sub> [Ca<sub>T</sub>]

concentration which showed that relatively more Ca<sup>2+</sup> complexed with the humic at pH 4 and 6 while almost the same binding behaviour was exhibited at pH 2 and 8. At fairly moderate Ca<sup>2+</sup> levels, various degrees of complexation were displayed at all the pH investigated especially at 4 and 8. Interestingly, all the points on the graph seem to have converged at the lowest total Ca<sup>2+</sup> concentration, which equally exhibited almost negligible complexation between Ca<sup>2+</sup> and humic acid.

A few important reasons can be adduced for these observations. Firstly, at extremely low pH, humic acid is precipitated in solution (Ghabbour and Davies, 2000) with a few available charged sites and reduced surface area of complexation hence the negligible reaction at pH 2. On the contrary, at basic pH, humic acid is very soluble in solution with available binding sites. The little or no complexation observed in the present study may be attributed

to a very high saturated level or amount of Ca<sup>2+</sup> ions present in solution thereby making complexation difficult. At pH 4 and 6 the reverse trend was observed. This trend is very significant because it shows that humic acid obtained from composted palm bunches can be used as amendment to regulate the release of calcium in calcareous or lime stone rich acid soils, for effective uptake of calcium by plants. The convergence of the points at extremely low metal concentration may be attributed to one or a combination of the following: (i) the extreme binding site heterogeneity (ii) the variable stoichiometry of the binding reactions, and (iii) the effect of electrostatic interactions (Koopol et al., 2001). These factors account for the considerable complexity in understanding metal humic interactions.

## Conclusion

From the findings in the present work, it can be seen that the total metal concentration and pH are two very important factors that affect humic metal interactions. Most importantly, humic acid obtained from composted oil palm bunches can be effectively utilized in regulating calcium dynamics in the soil-water ecosystem.

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