

Original Research Article

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Characterization of Metal Ion Complexes with Humic Fractions of Farmyard Manure by Potentiometric Titrations

D. Rajashekhar*, M. Srilatha, P. Chandrasekhar Rao, S. Harish Kumar Sharma and K. Bhanu Rekha

Department of soil science and Agricultural chemistry, College of Agriculture, PJTSAU, Rajendranagar, Hyderabad - 500 030, Telangana, India

*Corresponding author

ABSTRACT

Keywords

Farmyard manure (FYM), Humic acid (HA), Fulvic acid (FA), Metal ions and Potentiometric titration

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The present study was carried out at the laboratory, Department of Soil Science and Agricultural Chemistry, College of Agriculture, Rajendranagar to characterize the complex formation of humic fractions with metal ions. The results observed that increase in pH of humic and fulvic acid when titrated with 0.1 N NaOH indicates higher buffering capacity of these fractions. Potentiometric titration curves obtained for both humic and fulvic acids are sigmoidal in shape indicating their weak acid nature. Absence of inflection indicates the formation of metal complexes. Among all the metal ions does not show any inflection with both humic and fulvic acid indicating metal ion forms more stable complexes with these humic fractions. In case of Zn shows greater stability at pH 8.0 and above. Thus these humic fractions can be used as carrier materials especially supply of micronutrients to in crop nutrition as these also prevents the loss of nutrients from leaching by forming complex with metal ions like cationic micro nutrients.

Introduction

The humus formation is a composite of the individual processes like, mineralization, decomposition, humification and putrefaction (Choudhuri *et al.*, 2010).

The quantitative changes in soil humus are determined by the relation between the processes of synthesis and decomposition of the organic matter. They are dynamic and are expressed specifically under particular soil, climatic conditions and systems of agriculture (Koteva and Kostadinova, 2014). Investigations into humus focus not only on

direct management, but also into sustainable management practices that define the dynamic of humus in the soil. It is known that many factors have an impact on the humification and mineralization of humus in soil, of which precipitation is one of the most important. Humification and mineralization takes place slowly under conditions in which the amount of precipitation is high and the temperature is low (Tajnssek *et al.*, 2013). Humic substances (HS) are the major source of energy and nutrients for soil biota. They are also charge carriers and play vital role in complexing organic compounds and adsorbents in controlling the toxicity, transport and fate of a

variety of pollutants (Ahamadou *et al.*, 2013). These are yellow or brown to black coloured, acidic, poly disperse substances of relatively high molecular weight (Stevenson, 1982). Based on solubility, the humic substances are broadly divided into three classes. (a) Humic acid (alkali soluble and acid insoluble) (b) Fulvic acid (acid and alkali soluble) and (c) Humin (insoluble in both acid and alkali) (Waiker *et al.*, 2004; Kar *et al.*, 2007; Srilatha *et al.*, 2013; Ramalakshmi *et al.*, 2013 and Nagamadhuri *et al.*, 2013).

One of the most prominent features of humic substances is its complex formation through the functional groups, like carboxylic (–COOH), phenolic (–OH), amino (–NH₃) and carbonyl (C=O) (Datta *et al.*, 2001, Srilatha, 2001, Kar *et al.*, 2007 and Ghabbour and Davies, 2009) with polyvalent metal ions, *viz.* Cu²⁺, Zn²⁺, Mn²⁺ and Fe²⁺ etc. with different stability constants *i.e.* solubility in water, depending on the nature of metal ions and organic ligands. The complex formation reactions between metal ions and humic substances are helpful in understanding the problems of plant nutrition (Stevenson *et al.*, 1993). During complexation, numerous compounds including humic acid and fulvic acid are involved which control the distribution and supply of micronutrients to plant roots and interact with metal ions through their functional groups forming metal complexes of varying stabilities.

The magnitude of pH drop on addition of metal ion to aqueous solution of humic acid and fulvic acid are indicated by potentiometric titrations. Potentiometric measurements have been extensively used to provide information on contribution of metal complexes. From several studies it was indicated that the pH effect is as much a property of metal complex as its absorption intensity. Potentiometric measurements have been claimed to be convenient way to study the metal -HA and

metal -FA interactions (Erdogan *et al.*, 2007; Mina *et al.*, 2004 and Pandeya and Singh 2000). Potentiometric titration curves information along with the buffer effects obtained in titration curves were taken as an indication of complex formation. These potentiometric titration curves are simple, rapid and provide information on relative tendencies of metals to form complexes. Keeping this in view the present study was conducted to characterize humic and fulvic acids in presence and absence of metal ions by using potentiometric methods.

Materials and Methods

The present study was carried out at the laboratory to characterize the complex formation of humic fractions with metal ions at Department of Soil Science and Agricultural Chemistry, College of Agriculture, Rajendranagar.

Humic acid (HA) and fulvic acid (FA) components of humus are extracted from farmyard manure using the classical fractionation procedures based on their solubility characteristics (Kononova, 1966).

For potentiometric titrations, one hundred milligrams of HA/FA were dissolved in 25 ml of distilled water and was titrated against 0.1 N NaOH potentiometrically on digital pH meter to pH 12.0. For potentiometric titration of HA/FA both in presence and in absence of metal ions, humic acid/fulvic acids were dissolved in 0.1 N NaOH to give a final concentration of 5 mg sample per ml of 0.1 N NaOH. Ten ml of above solution was taken in to 100 ml beakers, to which 25 ml of 0.1 N KCl was added in each case. Then the pH of the sample was adjusted to 3.0 by the addition of 0.1 N NaOH (or) 0.1 N HCl, after which the volume of solution in each case was made up to 50 ml with 0.1 N KCl. The NaOH was added in increments of about 0.05 ml and the

change in pH of the system was recorded by digital pH meter.

For the potentiometric titration in the presence of metal ion, 4 ml solution of 0.05 N of appropriate metal ions (Zn (II), Cu (II), Mn (II) and Fe (II)) was added to the sample to supply 100 μ moles of metal ions. Similarly 100 μ moles of metal ions were also titrated alone for comparison.

Results and Discussion

Potentiometric titration of humic acid and fulvic acid

Potentiometric titrations have been used to characterize the acidic functional groups in humic and fulvic acids. Potentiometric titration curves of humic acid and fulvic acid presented in figure 1. There was a gradual increase in pH with the addition of NaOH indicating high buffering capacity of these humic fractions.

The curves obtained for both humic acid and fulvic acid were sigmoidal in nature and suggested that these substances behave as weak acid polyelectrolytes. These results were in consistence with results reported by Ramalakshmi *et al.*, (2013), Ghatak *et al.*, (2004) and Nagamadhuri *et al.*, (1998).

Titration of metal ions with alkali

The presence of inflections in the titration curves indicated the oxidation of metal ions and formation of metal hydroxides. The two inflections in the curves at Cu (II) at pH 4.6 and 8.2, at pH 8.6 for Zn (II), at pH 3.9 and 8.1 for Fe (II) and at pH 6.2 for Mn (II).

It is evident that corresponding metal hydroxides were formed as indicated by inflection in titration curves (Fig. 2). These results are in line with those reported for

Cu(II) (Schnitzer and Skinner, 1963; Stevenson, 1977), Zn(II) (Srilatha, 2001), Fe(II) (Relan *et al.*, 1990) and Mn(II) (Schnitzer and Khan, 1972).

Titration of humic acid and metal humates

Titration curves of humic acid and corresponding metal-humates are shown in (Fig. 3). The close perusal of graph indicated no inflection in the titration curve of humic acid and a close look at the titration curves of metal-humates indicated that the formation of metal hydroxides was suppressed when metal ions are added to humic acid and the absence of inflection was taken as an index of complex formation.

In the case of Zn complexes, the greatest stability was found for pH values of 7.0 and 8.0, which correspond to those of neutral and alkaline soils. This fact suggests the intervention of strongly acidic carboxyl and phenol groups in the complexing process at these pH levels. At pH 6.0, stability was also important although lower than at alkaline pH levels. Stability at pH 9.0 decreased significantly, probably because of the competition between the complexing process and the formation of the insoluble hydroxide of Zn *i.e.*, Zn(OH)₂ (Mina *et al.*, 2004).

The displacement in curve of humic acid in presence of metal ion was wider at higher pH and the reverse was true at lower pH. The reduction in pH on addition of humic acid in the presence of various metal ions followed the order Cu (II) > Mn (II) > Fe (II) > Zn (II).

Titration of fulvic acid and metal-fulvates

The titration curves of fulvic acid and metal fulvates are presented in (Fig. 4). The apparent monobasic character of fulvic acid was evident from the sigmoidal shape of their titration curves.

Fig.1 Potentiometric titration curves of humic acid (FYM-HA) and fulvic acid (FYM-FA)

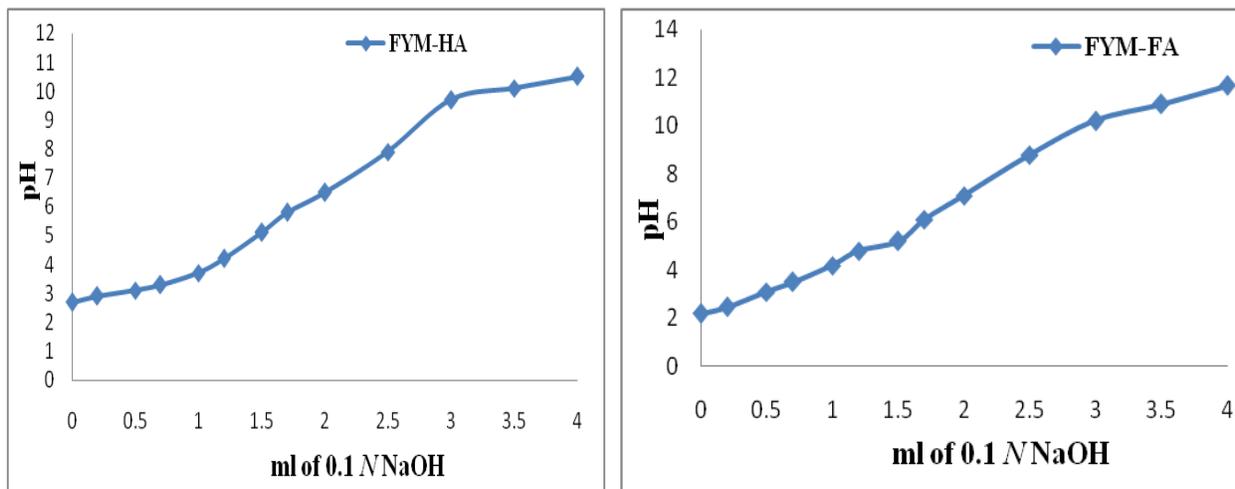


Fig.2 Potentiometric titration curves of metal ions

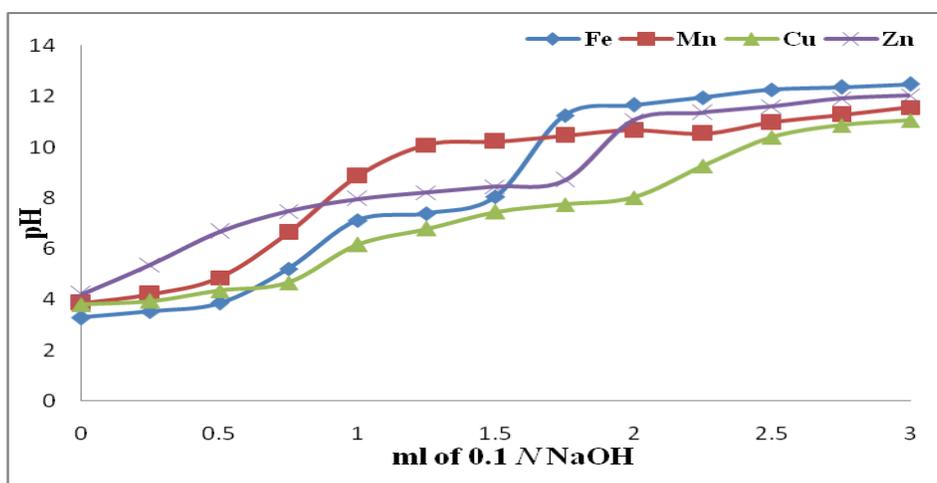


Fig.3 Potentiometric titration curves of humic acid and metal humates

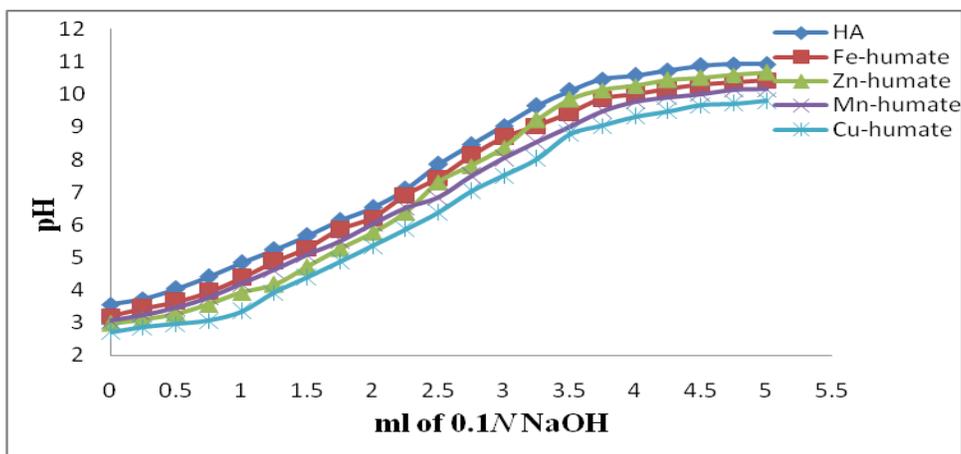
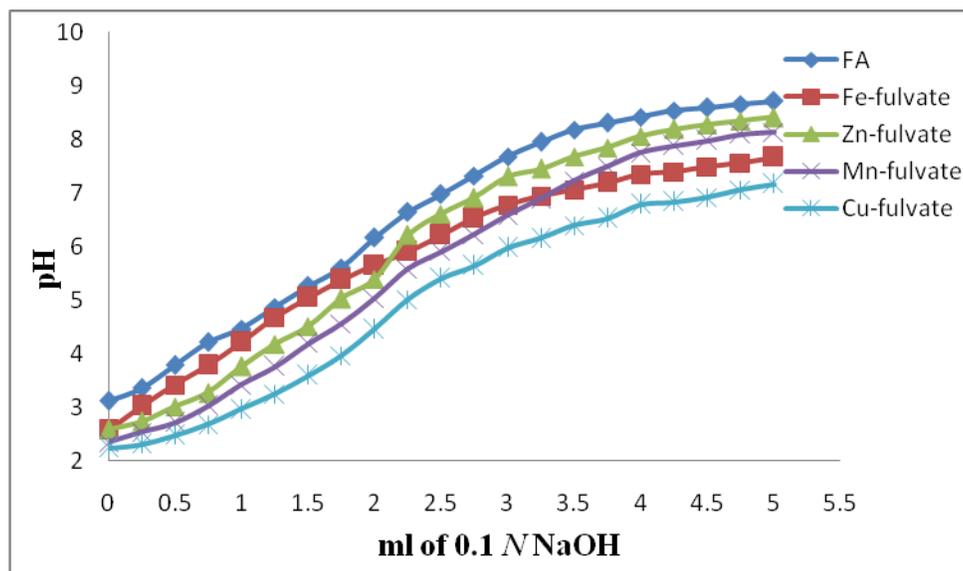


Fig.4 Potentiometric titration curves of fulvic acid and metal fulvates



Absence of inflection corresponding to formation of metal hydroxides indicates the formation of metal complexes. The potentiometric titration curves of fulvic acids in the absence and presence of Zn show that all the points of titration curves, the pH of the fulvic acid zinc complex was less than the corresponding pH of fulvic acid alone.

Humic acid/ fulvic acid contains large number of functional groups. Several H^+ ions are displaced during complexation leading to drop in pH of solution. Similar results were also reported by Pandeya and Singh, (2000). The pH drop can ascribed to that Fe forms a complex with fulvic acid ligands which will be accompanied by a drop in the pH of the system. The drop in the pH of the solutions may thus be attributed to the formation of fulvic acid iron complexes and release of protons from the functional groups.

From the comparison of metal-humic substance complexes, it is clear that displacement of curves of fulvic acid was higher than that of humic acid. This could be attributed to higher hydrophobic nature of fulvic acid as compared to humic acid and

thus fulvic acid has greater tendency to form complexes with metal ions. Similar results were also reported by Reddy *et al.*, (1999).

From the potentiometric curves it is evident that the reduction in pH on addition of humic acid in the presence of various metal ions followed the order) Cu (II) > Mn (II) > Fe (II) > Zn (II) while fulvic acid in presence of metal ions followed the order Cu (II) > Mn (II) > Fe (II) > Zn (II). Among the metals Fe metal ion forms a stable complex indicating the absence of inflection in potentiometric curves booth in humic and fulvic acids.

From the comparison of metal-humic substance complexes, it is clear that displacement of curves of fulvic acid was higher than that of humic acid due to higher hydrophobic nature of fulvic acid as compared to humic acid and thus fulvic acid has greater tendency to form complexes with metal ions.

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