



P-ISSN: 2349-8528

E-ISSN: 2321-4902

IJCS 2017; 5(5): 1463-1466

© 2017 IJCS

Received: 21-07-2017

Accepted: 23-08-2017

M Eshwar

Dept. of soil science and
Agricultural chemistry, college of
Agriculture, PJTSAU,
Rajendranagar, Hyderabad,
Telangana, India

M Srilatha

Dept. of soil science and
Agricultural chemistry, college of
Agriculture, PJTSAU,
Rajendranagar, Hyderabad,
Telangana, India

K Bhanu Rekha

Department of Agronomy,
Agricultural College, Palem,
Nagarkurnool, Telangana, India

S Harish Kumar Sharma

Dept. of soil science and
Agricultural chemistry, college of
Agriculture, PJTSAU,
Rajendranagar, Hyderabad,
Telangana, India

Characterization of metal complexes with humic fractions by potentiometric titrations

M Eshwar, M Srilatha, K Bhanu Rekha and S Harish Kumar Sharma

Abstract

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 the metal -humate and metal -fulvates Fe does not show any inflection with both humic and fulvic acid indicating Fe metal ion forms more stable complexes with these fractions. Thus these humic substances can be used as carrier materials especially supply of micronutrients in crop nutrition as these also prevents the loss of nutrients from leaching by forming complex with metal ions like cationic micro nutrients.

Keywords: Humic acid (HA), Fulvic acid (FA), Metal ions and potentiometric titration

Introduction

Humic substances are considered as the most important constituents of soil. They form the largest fraction of soil organic matter (OM) and play pivotal role in improving soil productivity. Humic substances are formed by the decomposition of plant and animal residues by microorganisms. They are colloid-sized, polymeric substances having dark colours. On account of their wide range of molecular sizes and properties, humic substances are usually fractionated to obtain materials with similar properties. The three fractions of humic substances are: i) fulvic acid (FA), (ii) humic acid (HA) and (iii) humin. Among these humic fractions, FA is most soluble in both acid and alkali. HA is the fraction which is soluble only in alkali. The most insoluble fraction of humus is humin, which is neither soluble in acid nor alkali.

Humic acid (HA) and fulvic acid (FA) make up an important part of soil organic matter and their binding capacity affects the fate of metal ions (especially micronutrients). These humic substances play an important role in mobility of nutrients (Stevenson, 1994 and Srilatha, 2001) [12, 10]. Soil organic matter fractions are capable of forming complexes with metal ions and the ability of these humic substances to form stable complexes with metal ions can be accounted for their high content of oxygen containing functional groups *viz*, carboxylic, phenolic aliphatic and alcoholic -OH groups. The complex formation reactions between metal ions and humic substances are helpful in understanding the problems of plant nutrition (Stevenson *et al.* 1993) [13]. During complexation, numerous compounds including humic acid (HA) and fulvic acid (FA) are involved which control the distribution and supply of micronutrients to plants 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) [1, 3, 6]. 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.

Correspondence

M Eshwar

Dept. of soil science and
Agricultural chemistry, college of
Agriculture, PJTSAU,
Rajendranagar, Hyderabad,
Telangana, India

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.

Material 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 in the year 2016-17.

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 fig 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 consistency with results reported by Ramalakshmi *et al.* (2013)^[7]; Ghatak *et al.* (2004)^[2] and Nagamadhuri *et al.* (1998)^[4].

Titration of metal ions with alkali

The inflections in the titration curves indicated the formation of metal hydroxides. The inflections in the curves at pH 10.5 for Cu (II) and Mn (II), at pH 10.9 for Zn (II) where as two inflection points for Fe (II) at pH 5.08 and 9.6 were observed. In case of Fe complexes, a clear stability was observed at pH 8.0. The stability at pH 6.0 and 7.0 was similar and was also important. At pH value of 9.0, a clear reduction in stability was observed. Such a pronounced increase in stability at pH 8.0 could reflect the role of phenolic groups those most markedly acidic in nature-in the complexing process, in addition to carboxylic groups (Mina *et al.* 2004)^[3]. The fall in stability at pH 9.0 suggests that other factors exert an important influence on the complexing process apart from the increase in the ionization of the phenolic groups. Such factors are probably directly associated with the conformational changes accompanying the increase in pH and with formation of Fe (OH)₄⁻ that might cause a significant change in the model of chemical interaction between Fe and the complexing groups (Ghatak *et al.* 2004 and Pandeya and Singh 2000)^[2,6].

The pH drop for the metal ions followed the order Mn (II) > Zn (II) > Fe (II) > Cu (II).

It is evident that corresponding metal hydroxides were formed as indicated by inflection in titration curves (Fig. 2). Similar to those reported for Cu (II) (Ghatak *et al.* 2004^[2] and Stevenson, 1977)^[11] Zn (II) (Mina *et al.* 2004^[3] and Zende and Raman, 1978)^[15] Fe (II) (Mina *et al.* 2004)^[3] and Mn (II) (Srilatha, 2001^[10]; Sujana Reddy *et al.* 1999^[14] and Sailaja and Rao 2000)^[9].

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 illustrations (or) 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. The inflections in the curves for metal humates shows, at pH 10.3 for HA-Cu (II), at pH 10.3 for HA-Mn (II) and two inflection points for HA-Zn (II) at pH 6.6 and 8.45 respectively.

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 Fe (II) > Zn (II) > Mn (II) > Cu (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. 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 Fe show that all the points of titration curves, the pH of the fulvic acid iron complex was less than the corresponding pH of fulvic acid alone.

The inflections in the curves of metal -fulvate shows, two inflection points for FA-Zn (II) at pH 7.63 and 10.19, two inflection points for FA-Cu (II) at pH 6.15 and 10.08 and at pH 8.5 for FA-Mn (II). The order of magnitude of pH drop with addition of fulvic acid follows the order Fe (II) > Cu (II) > Zn (II) > Mn (II). Absence of inflection of Fe in presence of humic acid (fig 3.0) and fulvic acid (fig 4.0) clearly indicated that Fe metal ion formed complexes with these fractions (Mina *et al.* 2004^[3]; Sailaja, 1999^[8] and Nand Ram and Raman, 1988)^[5].

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)^[6]. 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 Sujana Reddy *et al.* (1999)^[14].

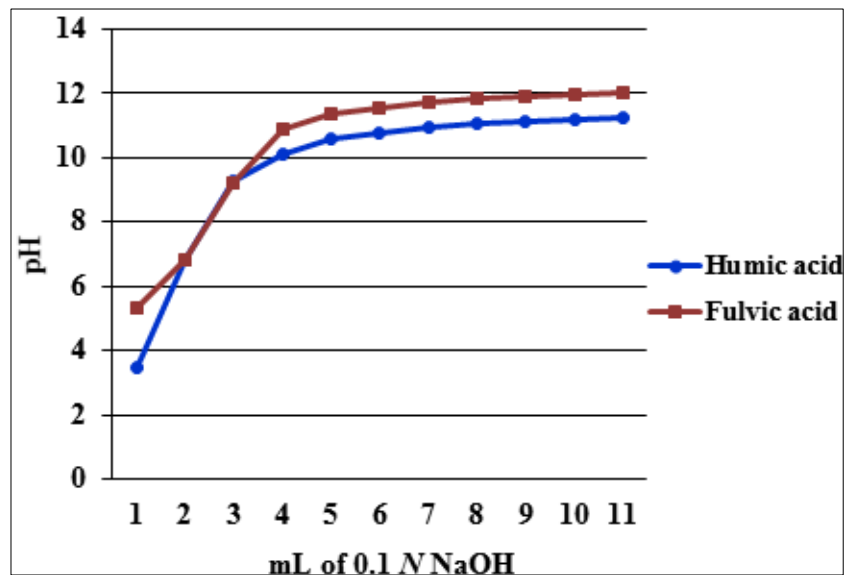


Fig 1: Potentiometric titration curves of humic and fulvic acid

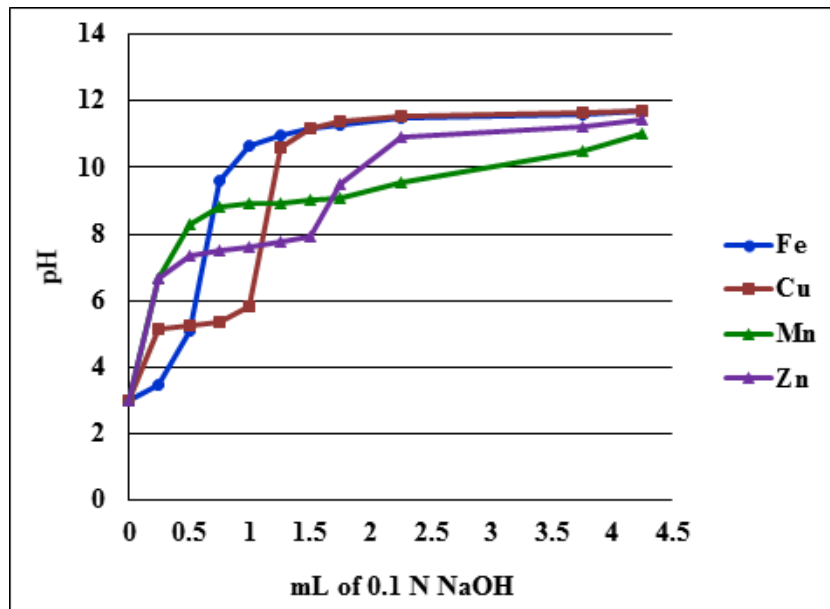


Fig 2: Potentiometric titration curves of metal ions

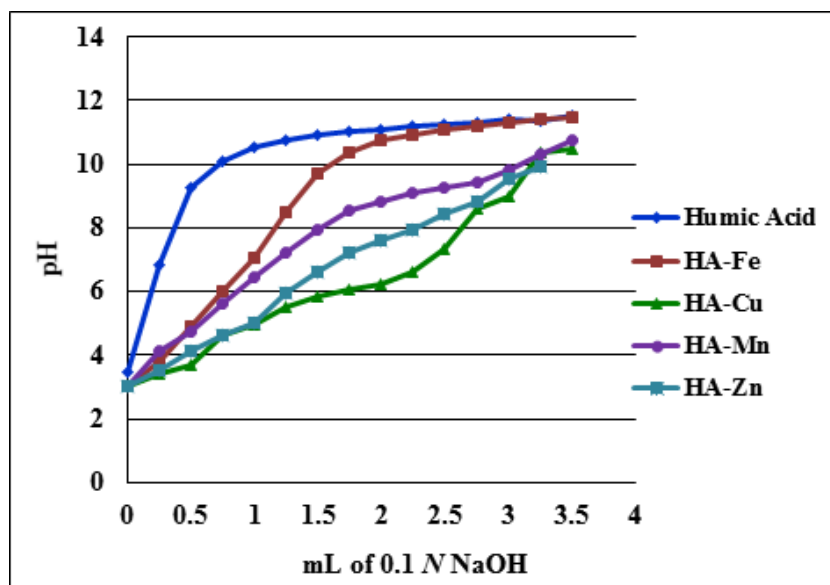


Fig 3: Potentiometric titration curves of humic acid and metal humates

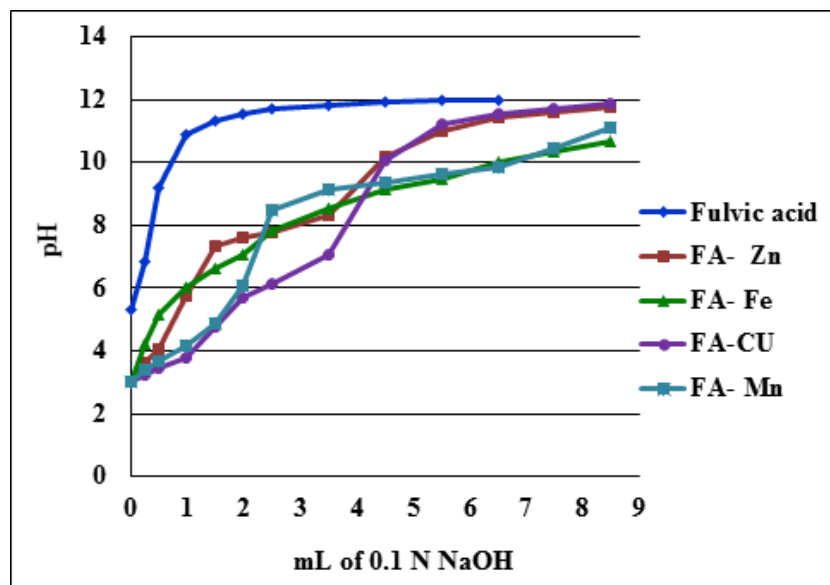


Fig 4: Potentiometric titration curves of fulvic acid and metal fulvates

Conclusions

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 Fe (II) > Zn (II) > Mn (II) > Cu (II) while fulvic acid in presence of metal ions followed the order Fe (II) > Cu (II) > Zn (II) > Mn (II). Among the metals Fe metal ion forms a stable complex indicating the absence of inflection in potentiometric curves both 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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