



# Particle size, charge and colloidal stability of humic acids coprecipitated with Ferrihydrite



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## HIGHLIGHTS

- Colloidal properties of Ferrihydrite humic acid coprecipitated are investigated.
- Fe–HA coprecipitate increase in the size and negative charge compare with HA.
- $\zeta$ -Potential measurements revealed a increment of negative charge for Fe–HA at pH 4–8.
- At neutral alkaline pH the Fe–HA negative charge enhancing colloidal stability.
- Ferrihydrite–HA coprecipitate could play an important role in the carbon stabilization.

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## ABSTRACT

Humic acids (HA) have a colloidal character whose size and negative charge are strictly dependent on surface functional groups. They are able to complex large amount of poorly ordered iron (hydr)oxides in soil as a function of pH and other environmental conditions. Accordingly, with the present study we intend to assess the colloidal properties of Fe(II) coprecipitated with humic acids (HA) and their effect on Fe hydroxide crystallinity under abiotic oxidation and order of addition of both Fe(II) and HA. TEM, XRD and DRS experiments showed that Fe–HA consisted of Ferrihydrite with important structural variations. DLS data of Fe–HA at acidic pH showed a bimodal size distribution, while at very low pH a slow aggregation process was observed. Electrophoretic zeta-potential measurements revealed a negative surface charge for Fe–HA macromolecules, providing a strong electrostatic barrier against aggregation. Under alkaline conditions HA chains swelled, which resulted in an enhanced stabilization of the colloid particles. The increasing of zeta potential and size of the Fe–HA macromolecules, reflects a linear dependence of both with pH. The increase in the size and negative charge of the Fe–HA precipitate seems to be more affected by the ionization of the phenolic acid groups, than by the carboxylic acid groups. The main cause of negative charge generation of Fe/HA is due to increased dissociation of phenolic groups in more expanded structure. The increased net negative surface potential induced by coprecipitation with Ferrihydrite and the correspondent changes in configuration of the HA could trigger the inter-particle aggregation with the formation of new negative surface. The Fe–HA coprecipitation can reduce electrosteric repulsive forces, which in turn may inhibit the aggregation process at different pH. Therefore, coprecipitation of Ferrihydrite would be expected to play an important role in the carbon stabilization and persistence not only in organic soils, but also in waters containing dissolved organic matter.

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## 1. Introduction

The importance of clay minerals for Organic Matter (OM) stabilization in soil environment has been recently demonstrated to show slower decomposition rates of OM associated with different

mineral compounds (Kaiser et al., 2002; Dignac and Rumpel, 2012). In specific soils (Andosol, Spodosols, Histosols etc.) the long-term OM stabilization were correlated with poorly ordered Fe and Al mineral contents (Kaiser et al., 2007). Mineral reactive surfaces were mainly provided by nanophases of iron and Al oxides that may accumulate in the clay fraction and were consider responsible of high amount of OC accumulation in the top soil. Recently, Lalonde et al., 2012 proposed that the associations

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between OM and iron were formed primarily through coprecipitation and/or direct chelation, promoting the preservation of organic carbon in marine sediments. In marine sediments, OM–iron association was found in form of nanospheres of goethite 10 nm in size (van der Zee et al., 2003). In addition Ferrihydrite nanoparticles have been found in aquatic environment associated with OM in sediment material (Tipping, 1981). The extent of Ferrihydrite–humic acid interactions was ascribed to a large variety of sizes and molecular organization, depending on solution pH and ionic strength as well as the chemical properties of both HA and iron phases (Cheng, 2002; Schwertmann et al., 2005). Aggregation of humic substances occurred in presence of iron at low pH and included charge neutralization whereas solubilization phenomena occurred only at high pH (Alvarez-Puebla and Garrido, 2005; Siéliéchi et al., 2008). Many soluble organic compounds have been found to inhibit crystallization of Ferrihydrite (Cornell and Schwertmann, 1979). Models of iron binding to OM have been investigated with extended X-ray absorption fine structure (EXAFS) spectroscopy. It was found that the major fraction of the organically complexed iron was hydrolyzed most likely in a mixture of dimeric and trimeric complexes, showing higher solubility ( $\log K_s = 5.6$ ) than insoluble Ferrihydrite (Tiphaine et al., 2006; Gustafsson et al., 2007). The effect of DOM on the reactivity of poorly crystalline iron (hydr)oxides under reducing conditions has been recently reported by Henneberry et al. (2012). Most of the studies used low-molecular weight organic compounds such as oxalic, citric and hydroxybenzoic acids (Mikutta, 2011) rather than more complex, naturally occurring HA. As HA is composed of a diverse range of organic components, there is a need to determine the effect on Fe colloidal reactivity of its coprecipitation with natural and structurally heterogeneous HA. Such knowledge is important in order to assess the reactivity of poorly crystalline iron (hydr)oxides with organic carbon in soil environments and has high relevance on the potential stability of HA (Mikutta et al., 2004). Specifically, the main interest was focused in the Fe(II) state as source of Ferrihydrite likewise most of the natural processes occurring with periodically fluctuating redox conditions in poorly drained soil and in aquatic environment. The purpose of this paper was to investigate the microstructure of synthetic iron coprecipitates in solid state through Transmission electron Microscopy (TEM), X-ray Diffraction (DRX) and Diffuse Reflectance Spectroscopy (DRS) and their colloidal behavior as a function of pH, in aqueous dispersions through Photon Correlation Spectroscopy and Laser Doppler electrophoresis.

## 2. Materials and methods

Total iron, after dissolution with a mixture of 1 M HCl and 1 M HNO<sub>3</sub>, was determined by atomic absorption on a Perkin Elmer 3130 spectrophotometer. Fe<sup>2+</sup> concentration was determined by measuring the absorbance at 562 nm on a spectrophotometer according to the ferrozine method after 0.5 M HCl extraction.

### 2.1. Sample preparations

Humic acid (HA) was extracted from a commercial liquid mixture of Humic Substances (Leonardite, CIFO, Italy) using a mixture of 0.5 M NaOH and 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> under a N<sub>2</sub> atmosphere for 24 h at 25 °C, and precipitated by bringing the alkaline extract to pH 2.0 with 12 M HCl. The extracted was centrifuged at 8000g for 20 min and dispersed again with NaOH 0.1 M at pH 10 with vigorous shaking. The elemental composition of the HA determined with C,H,N,S

analyzer was C, 53.96%; H, 4.38%; N, 1.31%; S, 1.87% O, 37.3%; and ash, 1.18%.

Pure Fe(II) and Fe(III) precipitates were obtained by neutralizing 3 mmol solutions of, respectively, Fe(SO<sub>4</sub>)·7H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub> in 70 mL of pure water, which were potentiometrically titrated to pH 7.0 by adding NaOH 0.5 N at a feed rate of 0.5 mL min<sup>-1</sup> (Cornell and Schwertmann, 2003). Then, pH was adjusted to neutral value in a final volume of 100 mL.

Ferrihydrite–HA coprecipitates were synthesized according to the methods described by Colombo et al. (2012a,b) through coprecipitation of a 3 mmol Fe(II) stock solution of Fe(SO<sub>4</sub>)·7H<sub>2</sub>O with 1 g of HA at room temperature at pH 7. Here, the sequence of addition of Fe(II) and HA was reversed in the two types of examined Ferrihydrite–HA coprecipitates. The resulting final Fe/HA precipitates contained 92.3% of HA, 7.7% Fe in total and 11% of Fe<sup>2+</sup>/Fe<sup>3+</sup>. All chemicals used in this study were ACS reagent grade; ultrapure water (Milli-Q, Millipore, 18.2 MΩ cm) was used. A Metrohm Herisau E536 automatic titrator coupled with an automatic syringe burette 655 Dosimat was used for all automated titration. All stock solutions were dialyzed (dialysis tube cut off <10 kDa), then all suspensions, held in polypropylene containers, were kept at 20 °C in the dark. Opportune aliquots of both the Fe(II/III) (hydr)oxide precipitate, HA standards and Fe/HA precipitate suspensions were freeze-dried for mineralogical and chemical analysis (see Methods information in S.I).

### 2.2. Dynamic light scattering: Particle Size (PS) and Electrophoretic Mobility (EM)

Both PS and EM measurements were performed at 25 ± 0.1 °C with a Zetasizer Nano-ZS (Malvern, Instruments), consisting of an Avalanche photodiode (APD) detector and a 4 mW He–Ne laser ( $\lambda = 633$  nm). This instrument was widely used for a large variety of colloidal dispersions.  $\zeta$  potential data were calculated from EM by the Henry equation (Hunter, 1981; Angelico et al., 2013):

$$EM = \frac{2\varepsilon\zeta}{3\eta} f(\kappa R) \quad (1)$$

where  $\varepsilon$  is the dielectric constant,  $\eta$  the viscosity,  $R$  the particle hydrodynamic radius and  $\kappa R$  the ratio of  $R$  to Debye length. To convert EM into  $\zeta$  the Smoluchowski factor  $f(\kappa R) = 1.5$  was used (valid for  $\kappa R \gg 1$ ). Effective voltage gradient was in the range 40–140 mV mm<sup>-1</sup>.

PS distributions and PolyDispersity Index (PDI) were obtained from the intensity autocorrelation function by the cumulant and CONTIN methods, respectively, using the Malvern software (DTS Version 6.01). The apparent hydrodynamic diameter  $D_{app}$  was calculated from the Z-average translation diffusion coefficient  $\bar{D}$  through the Stokes–Einstein equation assuming spherical particles:

$$D_{app} = \frac{k_B T}{3\pi\eta\bar{D}} \quad (2)$$

where  $k_B$  is the Boltzmann constant and  $T$  is temperature.

PS and  $\zeta$  data of Fe–HA (HA) aqueous dispersions were monitored in the pH range of 2–10. Diluted mother solutions were prepared by dissolving 0.36 mL of the Fe–HA (HA) dialyzed suspensions in 0.5 L of 0.015 M NaCl stock solution and stirred for 6 h. Final concentration was 20 mg L<sup>-1</sup> for both the systems.

### 2.3. X-ray diffraction (XRD)

X-ray powder diffractograms (XRD) of random specimens were obtained using a PANalytical X'Pert PRO MPD X-ray diffraction system (PANalytical, Almelo, The Netherlands) equipped with a

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