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.
- ζ-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 colloidal 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.

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
between OM and iron were formed primarily through cocrystallization and 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 Ks = 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 HNO3, was determined by atomic absorption on a Perkin Elmer 3130 spectrophotometer. Fe2+ 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 Na2P2O7 under a N2 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(SO4)2·7H2O and Fe(NO3)3 in 70 mL of pure water, which were potentiometrically tilted to pH 7.0 by adding NaOH 0.5 N at a feed rate of 0.5 mL min−1 (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(SO4)2·7H2O 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 Fe2+/Fe3+. 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 (λ = 633 nm). This instrument was widely used for a large variety of colloidal dispersions. ζ potential data were calculated from EM by the Henry equation (Hunter, 1981; Angelico et al., 2013):

$$\zeta = \frac{2\pi c}{3\eta} \left( \frac{kR}{\lambda} \right)$$

(1)

where c is the dielectric constant, η the viscosity, R the particle hydrodynamic radius and kR the ratio of R to Debye length. To convert EM into ζ, the Smoluchowski factor f(R/kR) = 1.5 was used (valid for kR ≫ 1). Effective voltage gradient was in the range 40–140 mV mm−1.

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 Dapp was calculated from the Z-average translation diffusion coefficient D through the Stokes–Einstein equation assuming spherical particles:

$$D_{app} = k_B T \frac{3\pi\eta D}{T}$$

(2)

where kB is the Boltzmann constant and T is temperature.

PS and ζ 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−1 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
PW3050/60 θ goniometer and a Co kα X-ray tube operated at 40 KeV and 35 mA (see Fig. S2 in S.I).

The diffraction patterns were collected from 3° to 80° 2θ at 0.05° steps with 60 s measurement time per step. The data were analyzed with the X’Pert High Score Plus software package (PANalytical, Almelo, The Netherlands), the 100 reflection of quartz that was used as a measure of the instrumental broadening.

2.4. Diffuse Reflectance Spectroscopy (DRS)

Diffuse Reflectance spectra were recorded from 250 to 900 nm in 0.5 nm steps at a scan speed rate of 30 nm min⁻¹ using a JASCO spectrophotometer equipped with a BaSO₄-coated integrating sphere 73 mm in diameter. The reflectance spectra were transformed into the Kubelka–Munk (K–M) function \[\left(1-R^2\right)/2R\]; where \(R\) is the reflectance and then the second derivative curves of these functions were calculated. Spectral filtering (Savitzky–Golay filtering) and second derivative calculation of Kubelka–Munk spectral curves were performed using the JASCO specific software of analysis (Sellitto et al., 2009; see Fig. S2 in S.I).

2.5. TEM observation

Samples for TEM were prepared by evaporating a dilute suspension on carbon-coated Formvar films supported by copper grids and subsequently coated with C to enhance conductivity. Microscope observations were conducted with a Philips CM12 electron microscope operating at 120 kV.

Fig. 1. Transmission Electron Microscopy micrographs (TEM) of the Fe–HA complexes dispersed in 50% alcohol and 50% water and quickly dried at 40 °C; (a–d) subangular particles with sponge-like structure of about 1000–1000 nm; (e) small rounded globular particles of about 20–30 nm and (f) subangular rounded particle of about 100–150 nm.
3. Results and discussion

3.1. TEM observation, X-ray diffractograms and diffuse reflectance spectra of Fe(II) coprecipitated with HA vs synthetic Fe(hydr)oxides

TEM micrographs of Fe–HA and HA–Fe samples showed different class of subangular particles with sponge-like structure ranging from 100 to 1000 nm in size (Fig. 1a and b). Size measurement showed a particle distribution centered at 200 nm (pseudo Gaussian curve, see Fig. S1 in S.I.), where more than 40% of particle were of 100–150 nm and very few particles around 800–1000 nm. TEM micrographs also revealed the presence of small rounded globular particles ranging from 5- to 20 nm assembled into a micelle-like structure (Fig. 1e). Indeed, most of the subangular rounded particles with 100–150 nm sizes were also observed as discrete particle association of large aggregate and small globular particles of about 5–20 nm (Fig. 1e). This was consistent with the following results obtained with DRX, where clearly appears that the Fe–HA and HA–Fe precipitates contain a large amount of poorly ordered crystalline material as Ferrihydrite.

The X-ray diffraction pattern of the Fe standards obtained by neutralizing Fe(II) and Fe(III) with NaOH alone and in presence of HA yielded poorly resolved X-ray reflections (Fig. 2). Fe(II) precipitate standard showed more resolved reflections at \(d = 0.418, 0.330\) and 0.252 nm indicating the presence of Goethite (0.418 nm) and very small reflection of Lepidocrocite (0.330 nm) (Cornell and Schwertmann, 2003). Fe(II) and Fe(III) precipitate standard showed a characteristic two-line Ferrihydrite pattern with a typical broad reflection with diffuse shoulder extending at 0.252, 0.152 nm (Fig. 2). X-ray diffraction patterns recorded for both Fe–HA and HA–Fe coprecipitates were very similar, independently of the order of addition of the components. Both the coprecipitates revealed lower degree of crystallinity similar to Fe(III) precipitate standards with a broad reflections at 0.252 nm. Differences in X-ray diffraction patterns between the coprecipitates Fe/HA and both Fe(II) and Fe(III) synthetic (hydr)oxides, highlighted the important role of HA as inhibitor in the formation of both Goethite and Lepidocrocite against the formation of Ferrihydrite. Lepidocrocite and

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Fig. 2. Powder X-ray diffractograms recorded with Co Kα radiation. In the colored version of the paper: green and purple profiles refer to, respectively, Fe(II) and Fe(III) precipitates, while black and red to Fe–HA and HA–Fe coprecipitates, respectively. G = goethite; F = Ferrihydrite; Q = quartz. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 3. Diffuse reflectance spectra (K/M curve) expressed in terms of second derivative, for Fe(II) Fe(III) precipitates (a) and (b) and in presence of HA, respectively, for Fe–HA (c) and HA–Fe precipitates (d). G = goethite; F = Ferrihydrite.

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Fig. 4. (A) Particle surface charge at 25 °C expressed as \(\zeta\) potential (mV) and (B) hydrodynamic particle diameter (\(D_{app}\)) in nm as a function of pH of pure HA (diamonds) and Fe–HA (red circles) aqueous suspensions in 0.015 M NaCl background electrolyte. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Goethite represent the most common species formed upon oxidative transformation of Fe(II) in absence of HA while Ferrihydrite came from hydrolysis of Fe(III) \cite{Cornell2003}. The degree of crystallization of Ferrihydrite was largely affected by the presence and composition of HA \cite{Schwertmann2005, Mikutta2011, Eusterhues2008, Eusterhues2011}.

The diffuse reflectance spectra of the samples are illustrated in Fig. 3 in form of their second derivative. Three specific bands appeared in the range between 300 and 800 nm due to the typical absorption of iron oxides. These bands are due to electronic pair transitions (EPT) within the 3d5 shell of Fe(III) ion in the crystalline structure. According to the ligand field theory, Sherman and

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

**Fig. 5.** (A) Pure HA aqueous suspension at pH 2 and NaCl 0.015 M. Upper panel (closed circles): time-evolution of the apparent particle diameter ($D_{app}$) showing a size growth scaling almost linearly with time. Solid line is a linear fit: intercept 782 ± 17 nm, slope 7.9 ± 0.4 nm min$^{-1}$, $r^2$ 0.95. Lower panel (closed squares): the polydispersity index (PDI) fluctuates in the range 0.3–0.4 indicating broad size distributions. (B) HA aqueous suspension at pH 3 and NaCl 0.015 M. Upper panel (open circles): time-evolution of $D_{app}$ showing size fluctuation in the range 120–140 nm. Lower panel (open squares): the polydispersity index (PDI) fluctuates in the range 0.4–0.6 indicating broad size distributions. (C) Particle size number (%) distributions for pure HA aqueous suspensions in NaCl 0.015 M. Main histogram: bimodal size distribution at pH 2 (recorded after 1 h from the pH adjustment) characterized by a narrow peak at 300 nm and a broad one around 1500 nm. Inset: monomodal size distribution at pH 8 showing a maximum centered at 83 nm.
Waite (1985) assigned the first ETP band to Ferrihydrite at 380–430 nm in terms of double exciton processes ($^{4}A_{1}$ → $^{6}A_{1}$). Fe(III) precipitate standard showed the most intense ETP band at 370 nm that was related to the presence of face-sharing octahedral of the structure of Ferrihydrite (Fig. 3b). The second ETP band was the characteristic bands assigned for Goethite with minimums around 430 nm and a maximum at 450 nm and (Fig. 3a). The positions of those bands were successfully used to predict the Goethite content in soils (Scheinost et al., 1998; Sellitto et al., 2009). The second EPT band at 480–500 nm in the Fe(III) precipitate (i.e. Ferrihydrite standard) was a perceptible shoulder (Fig. 3b). A third EPT band at 710–750 nm was assigned for the $^{4}T_{2}$ → $^{6}A_{1}$ transition specific only for Ferrihydrite. In comparison to the second derivative spectrum of the Ferrihydrite, spectra acquired for both types of Fe–HA and HA–Fe precipitates were mainly characterized by the EPT band at 370 nm, assigned to Ferrihydrite, and an third poorly-resolved band at 700 nm, both were totally absent in the goethite. According to DRS data, one can argue the presence of Ferrihydrite arranged in poorly ordered octahedral structure, which in turn may be strictly associated with HA in the Fe/HA coprecipitates.

3.2. Zeta-potential vs pH

Fig. 4A shows the pH-dependence of the particle surface charge measured in both HA and Fe–HA coprecipitate aqueous dispersions. Overall, zeta ($\zeta$)-potential data were found prevalently negative in the investigated pH range and increased (in absolute value) with increasing pH, although with substantial differences between untreated HA and Fe–HA coprecipitate.

3.2.1. Zeta-potential of HA aqueous suspensions

Fig. 4A (diamond symbols) illustrates zeta ($\zeta$)-potential data of HA suspensions at various pH values in the range 2–10. Apart a flat behavior observed in the interval of pH $<\approx 7$, they became more negative with increasing pH, ranging from $-16$ mV (pH 2) to $-36$ mV (pH 10). The initial flat step could be due to a continuous distribution of equilibrium dissociation processes, which is typical of carboxylic groups in acidic–circumneutral pH (Gustafsson et al., 2007) whereas at alkaline pH the phenolic groups can be found in ionized state. The enhanced colloidal stability of HA aqueous suspensions reached at high pH values (no floculation phenomena), can be ascribable to the intra-chained electrostatic repulsion and reconformation of humic network, in accordance with literature (Alvarez-Puebla and Garrido, 2005; Siéliéchi et al., 2008).

3.2.2. Zeta-potential of Fe–HA coprecipitate aqueous suspensions

A deeper influence of pH on the surface electrical zeta ($\zeta$)-potential was observed for aqueous dispersions of Fe–HA coprecipitate (Fig. 4A, circle symbols). In particular, $\zeta$ decreased monotonically with increasing pH, first sharply from pH 2 ($-2.8$ mV) to 4 ($-32.2$ mV) and then more slowly from pH 5 to 10. Despite the very slow floculation phenomena observed in the low-pH interval (pH = 2–3), it was still possible to measure the particle electrophoretic mobility, although with a modest accuracy. The Fe–HA coprecipitate aqueous suspensions presented the most negative $\zeta$ values compared to the bare HA solutions. The maximum difference was observed in pH range 4–8, where normally Fe oxides and (hydr)oxides are positively charged as observed e.g. in hematite nanoparticles (Colombo et al., 2012a,b).

At pH 3–4 below the p$K_a$ for the carboxylic groups (pH $<\approx 6$), the $\zeta$ potential observed for Fe–HA coprecipitate was more negative compared with HA indicated a moderate charge neutralization of the Ferrihydrite coprecipitate particles. Whereas at pH 4–8 we observe a significant increase of $\zeta$ potential in correspondence of the ionization of phenolic groups (p$K_a$ – $<\approx 7$), the sharp $\zeta$ rise observed for Fe–HA coprecipitate towards less negative values indicated a more efficient charge neutraliza-

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**Fig. 6.** (A) Fe–HA aqueous suspension at pH 2 in NaCl 0.015 M. Upper panel (closed circles): time-evolution of the apparent particle diameter ($D_{app}$) showing a size growth scaling almost linearly with time. Solid line is a linear fit: intercept 796 ± 20 nm, slope 1.9 ± 0.2 nm min$^{-1}$, $r^2$ 0.70. Lower panel (closed squares): the polydispersity index (PDI) fluctuates in the range 0.5–0.8, indicating very broad size distributions. (B) Fe–HA aqueous suspension at pH 3 in NaCl 0.015 M. Upper panel (open circles): $D_{app}$ increases linearly with time. Solid line is a linear fit: intercept 290 ± 5 nm, slope 5.6 ± 0.1 nm min$^{-1}$, $r^2$ 0.99. Lower panel (open squares): PDI increases systematically from 0.2 up to about 0.6.
tion. As acidic groups are ionized with increasing pH, charge, as well as intra- and intermolecular electrostatic repulsion increase, restricting aggregation phenomena, in agreement with results obtained using molecular modeling proposed by Alvarez-Puebla and Garrido, 2005. In this model, the ionization of carboxylic acid groups has a smaller effect on colloidal size than ionization of phenolic acid groups. This authors explained this result in term of lower ionization of phenolic groups. The formation of H-bonds is not completely inhibited and the structure remains folded over onto itself due to the formation of H-bonds, in spite of the fact that carboxylic groups are ionized.

At pH very acidic pH (2–3) charge neutralization and bridging flocculation leaded to destabilization of the colloidal system. Shift to pH between 4–8 and with ε toward more negative values could provide favorable binding sites for stabilization of OM; namely, precipitation of ferricydrite on HA that would be expected to play an important role in the stabilization and persistence not only in organic-rich settings, but also in waters containing dissolved OM (Henneberry et al., 2012).

3.3. Particle size distributions vs pH

Fig. 4B reports the apparent hydrodynamic particle diameter \( D_{\text{app}} \) measured with DLS technique, at various pH in the range 2–10, for both the systems in the same solutions used for the measurement of zeta \( \zeta \)-potential. It is worth to remark that depending on pH and ionic strength, variation of particle surface charge (i.e. \( \zeta \)) can modify the self-assembling properties of heterogeneous macromolecules, which in turn would give rise either to a shrinking (intra-chain electrostatic attractions predominate) or swelling (electrostatic repulsive forces predominate) effect. Thus, the combined effect of steric stabilization and charge stabilization can affect the final average sizes of both HA and Fe–HA colloidal particles in water solutions.

3.3.1. Hydrodynamic particle diameters of HA aqueous suspensions vs pH

Fig. 4B (diamond symbols) shows the particle sizes of bare HA solutions. According to literature, a monotonic increment of \( D_{\text{app}} \) occurred for pH \( \geq 3 \), increasing from 130 (pH 3) up to 160 nm (pH 10). As a matter of fact, a flocculation (aggregation) kinetic process was detected at pH 2 with the apparent diameter \( D_{\text{app}} \) increasing linearly with time from 800 to 1300 nm (Fig. 5A), whereas at pH 3 no aggregation phenomena was observed (Fig. 5B) with \( D_{\text{app}} \) fluctuating statistically around 129 nm (±10) and characterized by monodisperse particle distributions. At pH 2, the rate of particle size increment (~8 nm min\(^{-1} \)) from the slope of linear correlation in 5A) was sufficiently slow to allow for stable DLS measurements within the time windows of each experiments (~1–2 min), with intercept at 782 ± 17 nm, slope 7.9 ± 0.4 nm min\(^{-1} \). The polydispersity index (PDI) fluctuated in the range 0.3–0.4 indicating broad size distributions. At pH 2 the particle distribution was bi-modal, characterized by narrow peak at 300 nm and a broad one around 1500 nm (Fig. 5C). The reduction in the intermolecular electrostatic repulsion at acid pH can be responsible for the observed HA slow flocculation process, according to previous observations on similar HS systems (Cheng, 2002). However, increasing pH from 6 to 10 may induce sufficient

Fig. 7. Particle size number (%) distributions of Fe–HA aqueous suspensions at various pH in NaCl 0.015 M: (A) pH 3, bimodal with a narrow peak at 142 nm and a second very broad peak around 800–900 nm; (B) pH 4, with a narrow peak at 121 nm; (C) pH 6.3, with a narrow peak centered at 124 nm and (D) pH 8, with a narrow peak at 91 nm.
electrostatic repulsive interactions between HA molecular segments, giving rise to an apparent increment of the average diameters observed at higher pH (Fig. 4B).

3.3.2. Hydrodynamic particle diameters of Fe–HA coprecipitate vs pH

Particle sizes for Fe–HA coprecipitate were found almost unaffected by varying pH in the range 4–10 (Fig. 4B, circle symbols), with $D_{\text{app}}$ fluctuating in the range 202–210 nm, well above the highest size recorded for bare HA aggregates (Fig. 4B, diamond symbols). However, the colloidal stability was worsened few minutes after HCl aq had been added to decrease the pH below 4. Indeed, flocculation phenomena was observed although with different aggregation rates: particle growth at pH 2 was slower than what observed at pH 3 (see the slope of linear fits ~2 and 6 nm min$^{-1}$ in Fig. 6A and B, respectively). Moreover, the size distributions were also different; with very large particles at pH 2 compared to pH 3 (see the evolution of PDI as a function of time displayed in the lower panels of Fig. 6B). This behavior can be interpreted in terms of an enhanced charge neutralization process and subsequent flocculation occurring at acid pH due to the fraction of carboxylic groups not involved in direct coordination with ferrihydrite (Siéliéchi et al., 2008).

Above pH 3, size distributions of Fe–HA were found narrower and mono-dispersed, without showing any aggregation phenomena similarly to what recorded for pure HA suspensions. Fig. 7 illustrates typical numeric size distributions obtained, respectively, at pH = 3, 4, 6.3 and 8. Those characteristics correspond to high stable colloidal particles owing to the deprotonation of acidic groups, which prevents any flocculation mechanism.

4. Conclusion

The samples obtained through coprecipitation of Fe(II) and HA in diverse order of addition revealed through DRX and DRAS analyses the presence of Ferrihydride with low structural order. Coprecipitation of Ferrihydride on the HA molecules induced net negative surface potential changing macromolecular conformation. The aggregation was fast in acidic pH for both pure HA and Fe–HA when hydrophilic surfaces were involved and electrostatic repulsion was practically absent. At neutral or alkaline pH negative charges of the Fe–HA macromolecules increased and the surfaces generated an increasing electrostatic barrier against aggregation. At pH below the $pK_a$ for the phenolic groups ($pH<7$), the sharp $\zeta$ rise observed for Fe–HA precipitate towards less negative values (in comparison to HA), indicated a more efficient charge neutralization. As negative charge increases, hydrodynamic particle diameter ($D_{\text{app}}$) of Fe–HA precipitate raises as well. In correspondence of neutral-alkaline pH, the negative surface charge decreases, thereby enhancing colloidal stability. The favored opening of deprotonated Fe–HA network at alkaline pH would also support the experimental evidence of the more negative charge surface. HA contains both functional groups (carboxylic, phenolic, and carbonyl groups) and hydrophobic moieties. In the precipitation Fe(II) process the HA negative phenolic groups seems mainly involved in electrostatic interaction with the Fe hydroxyl surface groups, whereas the HA insoluble part (hydrophobic moiety) allows the macromolecule to accumulate on the inorganic surface. Modeling of the HA with sphere shape and charge located at the surface is thus unlikely, while a network of linear macromolecules that hold for low to moderate electrostatic potentials and large colloids is more consistent. These results confirm that structural variations of HA and their conformational variation strongly affect the colloidal stability of Ferrihydrite–HA association at pH ranging 5–7 and new negative surfaces were formed. Sterically stabilized oxide Fe/HA produced from coating by low polar and high molecular weight HA like leonardite may increase the mobility of Ferrihydrite in soil, and they may act as a carrier of Fe in the aquatic environment. Thus, coating of Fe nanoparticle with structurally different HAs may have a significant impact in terms of iron mobility implications and carbon stabilization. Since the OM stabilization occurred preferentially when HA macromolecules were aggregated with small micropore ($<10$ nm) of iron and aluminum oxides nanoparticle, the presence of Ferrihydrite coprecipitated with HA would be expected to play an important role in the stabilization and persistence not only in organic-rich settings, but also in waters containing dissolved OM. Development of sterically stabilized Fe/HA complexes, with low polar, high molecular weight leonardite could be useful for soil and groundwater remediation.

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Appendix A. Supplementary material

Preparation of Fe(II), Fe(III), Ferrihydrite–HA precipitate suspensions; description of methodology applied to the Fe/HA complexes analyses with Transmission Electron Microscopy (TEM), Fig. S1; X-ray Diffraction (XRD), Fig. S2; Diffuse Reflectance Spectroscopy (UV–VIS) and Fig. S3; Dynamic Light Scattering (DLS). Supplemental data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.10.092.

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