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Stability of TiO_2 Nanoparticles in Presence of Fulvic Acids, Importance of pH

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RESEARCH ARTICLE

Manufactured nanoparticles are now present in many daily use commercial products such as cosmetics, paints, food packaging, etc. One of the main consequences regarding the environment is their uncontrolled release and diffusion in the aquatic systems. To explore their environmental behavior in term of stability, coagulation and dissociation, it is important to perform investigation at the laboratory scale as a prerequisite for understanding their environmental behaviors. In this study, the stability of titanium dioxide (TiO_2) nanoparticles as a function of pH and fulvic acid concentration (one of the major organic component found in aquatic systems) is systematically examined by measuring the size and zeta potential variations of TiO_2 nanoparticles, fulvic acids mixtures and aggregates they can form. Experiments are also conducted at three different pH values corresponding to the three possible TiO_2 surface charge states: positive, neutral, and negative. The TiO_2 size and zeta potential evolution is then examined as a function of the concentration of negatively charged fulvic acids (FAs) by increasing successively the fulvic acids concentrations. Our results point out that in absence of fulvic acids, TiO_2 aggregation is achieved for pH values between 5 and 8 i.e., when the nanoparticle surface charge is close to the point of zero charge. At low and high pH values, nanoparticle surface charges result in strong electrostatic repulsions hence preventing aggregation. In presence of fulvic acids fast aggregation is achieved at low pH and with fulvic acids concentration comprised between 4 and 8 mg/L. In such conditions the nanoparticle surface charge neutralization is achieved via the adsorption of the negative fulvic acids on the positively charged nanoparticles. By increasing further the fulvic acids concentration, surface charge inversion is obtained then resulting in the restabilization of the nanoparticle solution via aggregate fragmentation (disaggregation). At high pH, the negatively charged fulvic acids are not found to adsorb significantly on the negatively charged nanoparticles. These results clearly pointed out the role of the pH, electrostatic interactions and FAs concentrations on the stability of NPs such as TiO_2. It is shown that the environmental FAs concentrations are self-important to promote the dispersion of 50 mg/L TiO_2 nanoparticle solutions including aggregates.

Keywords: Titanium Dioxide, Nanoparticles, Fulvic Acids, Nanoparticle Stability, Nanoparticle Aggregation, Nanoparticle Aggregate Disaggregation.

1. INTRODUCTION

With the development of the (bio)nanotechnologies, the world demand in manufactured nanoparticles (NPs) is continuously increasing. Their presence in many products constitutes a fast growing market, especially for titanium dioxide (TiO_2) which represents, with silver, one of the most abundant metal or metal oxide nanoparticles commercially used.[1,2] The percentage of TiO_2 that is produced in the nano range is expected to increase exponentially in the next years. These NPs are nowadays found in various daily use products such as sun creams, paints, cosmetics or cleaning products[3–6] with the potential to revolutionize modern life. They are also considered and

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tested in the improvement of water treatment processes[7] in particular with regards to the removal of micro pollutants. However, an increasing body of scientific evidence suggests that many nanoparticles end up in the environment. Their fate, transport, and transformation processes in soils, waters and the atmosphere are very difficult to evaluate and control[8–10] with regards to the variety of potential mechanisms. NPs have very specific properties which depend on a multitude of parameters and variables such as their chemical composition, size, shape, crystal structure, surface coating, functionalization, medium composition, etc. Additional difficulties also rise from NPs detection and quantification in the environment[11–13] owing to the fact that the natural matrices are heterogeneous, made of various chemical compounds such as particulate, colloidal, dissolved inorganic and organic compounds.[14, 15] Based on these considerations, it is of importance to characterize first, step by step, and in a systematic way, the behavior of NPs in more simple matrices in order to get an insight on the key factors and main interaction mechanisms that will be useful not only for the prediction of the transport and fate of manufactured NPs in the environment, but also improving our understanding of the possible NPs transformation processes and the toxicity of nano-sized objects.[16–18] From an environmental point of view, natural organic matter (NOM) is the major colloidal component in natural waters[14, 19–21] and thus is expected to play determinant roles in the behavior of manufactured nanoparticles in aquatic systems. NOM is mainly composed of humic substances (HSs) which can be separated in three categories: (HAs) which are soluble above pH 2, fulvic acids (FAs) which are soluble at any pH and humin which is insoluble at any pH.[22] In this study, focus is made, in a systematic way, on the interaction of FAs and manufactured TiO_2 NPs by considering realistic environmental FAs concentrations (i.e., in the range 0–10 mg/L). Previous works have been achieved to understand TiO_2 stability as a function of pH. Dunphy et al. observed aggregation of TiO_2 NPs even at pH 1.[23] The size of the aggregates and the amount of aggregation was very limited at low pH values and was found to increase as pH approaches the NPs point of zero charge (PZC). They also observed that the size of the TiO_2 NPs was playing a role on the value of PZC observing that smaller TiO_2 NPs had lower PZC values. They concluded that from pH 1 to 12 about 80% of the TiO_2 aggregates were mobile excepted at the PZC where the aggregates were large enough to sediment. French et al. studied the influence of the ionic strength as well as the ion valency as a function of pH by considering 5 nm TiO_2 NPs.[24] TiO_2 NPs were found to form stable small 50–60 nm aggregates at pH 4.5 and at low NaCl salt concentration (0.0045 M). Increasing the salt concentration to 0.0165 M was found to lead to the formation of micron size aggregates within 15 minutes. Increasing the pH to respectively 5.8 and 8.2 and maintaining the salt concentration constant, the aggregate size (few microns) was found to increase as well as the kinetic of aggregate formation. Then the use of divalent salt ($CaCl_2$) demonstrated that the aggregation rates was increasing in comparison to the monovalent NaCl salt indicating that the ion valence was playing key roles on the aggregation of TiO_2 NPs. Pettibone et al. investigated the influence of the presence of adipic and oxalic acid on 5 and 32 nm TiO_2 NPs.[25] Even if the two NPs seem to exhibit the same chemical reactivity with the organic compounds, their aggregation rates were not similar since the 5 nm NPs had fastest rates. In the two cases the organic compound concentration was found to increase the aggregation rates. Complementary ATR-FTIR measurements indicated that the surface adsorption of the organic compounds was not similar but interestingly these differences were not macroscopically reflected. Tipping et al. investigated the influence of humic substances HSs on the stability of 300 nm hematite particles at different $CaCl_2$ concentrations.[26] They found that, independently of the salt concentration, HSs enhance the stability of hematite particles with calculated kinetic aggregation constants having similar magnitude order, and that salt had no effect on the HSs conformation. They also concluded that the main effect here was related to the nanoparticle steric stabilization by the HSs resulting in the formation of an adsorbed layer with sufficient thickness to avoid aggregation even if the surface charge was found favorable from an electrostatic point of view to promote aggregation. They point out the ability of such small molecules (5000 Da), which are abundant in aquatic systems, to stabilize solutions containing NPs. Such steric stabilizing effects were also observed using guar gum or alginate by considering zero valent iron nanoparticles.[27]

In our study, the systematic effect of pH on the stability of TiO_2 NPs is first investigated with regards to aggregation. Three major "electrostatic" scenarios are then defined by considering the pH dependence of both TiO_2 NPs surface charge values and signs, and structural charge of the FAs. Then the effect of fulvic acids adsorption on the NPs stability is evaluated by increasing systematically the FAs concentrations. Suwannee river fulvic acids are used here owing to the fact that they are well characterized and widely used as reference materials for natural compounds.[28–33] FAs concentrations which are considered here are representative of the FAs concentration found in natural systems. The importance of NPs charge inversion due the FAs adsorption and aggregate disaggregation induced by steric effects and non-covalent interactions is also investigated for a systematic understanding of the physico-chemical parameters, or combination of parameters, that govern the stability of the TiO_2 NPs. Indeed, NPs will occur in the environment either as aggregated or dispersed materials. Aggregated NPs will rapidly settle down and become immobilized, while dispersed NPs will diffuse in aquatic systems and water films, and thus will be more mobile and bioavailable.

2. MATERIALS AND METHODS

2.1. Materials

TiO_2 nanoparticles from NanoAmor (Nano-Structured and Amorphous Material Inc.) with a determined manufacturer X-ray diffraction diameter of 15 nm were used at a nominal concentration of 50 mg/L for all experiences. Fulvic acids (FAs) were provided by the International Humic Substances Society (Suwannee River Fulvic Acid Standard, II, 2S101F) as a dehydrated powder. FAs 100 mg/L stock solutions were prepared at pH 10 to improve solution stability and stirred over 24 h to ensure complete rehydration. The final solution was then protected from light and maintained between 0 and 5 °C. Experiments were conducted in polypropylene beakers; pH was adjusted using HCl and NaOH (1 M, Titrisol®, Merck) at different concentrations (1, 0.1, 0.01 M) and measured with a Hach-Lange multiparameter HQ40.

2.2. Zeta Potential and Size Measurements

Zeta potential (ζ) and Z-average hydrodynamic diameter (the intensity-weighted mean diameter) were determined with a Malvern Zetasizer Nano ZS. The Zetasizer Nano Series uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a patented technique called M3-PALS to measure particle electrophoretic mobility. This allows the measurement of high conductivity samples, plus the ability to accurately measure samples that have low particle mobilities. Non-invasive backscatter (NIBS®) technology was used for particle sizing. For the size determination, three measurements of 10 sub-runs of 10 seconds each with a delay of 5 seconds between each measurement were achieved. For the zeta potential measurement, three measurements of 15 sub-runs with a delay of 5 seconds between each measurement were used. The ionic strength of the solution was adjusted to 10^{-3} M with NaCl.

3. RESULTS AND DISCUSSION

3.1. Nanoparticles and Fulvic Acids Characterization

3.1.1. TiO_2 NPs

Z-average hydrodynamic diameter and zeta potential (ζ) have been calculated using a Malvern Zetasizer Nano ZS with the Smoluchowski's model approximation for the calculation of ζ rom the electrophoretic mobility determination. Smoluchowski's formula, which can be applied when particles are large compared with the double layer thickness, which is mainly the case in this study, was used. Refractive index was set to 2.51 for a wavelength of 633 nm.[34] According to the manufacturer, the NP TiO_2 powder has a nominal size of 15 nm. The Z-average, which corresponds to the intensity weighted mean hydrodynamic diameter of the ensemble distribution of particles, was determined by DLS and found to be equal to 28 ± 4 nm hence denoting the presence in solution of some small aggregates in good agreement with.[24, 35]

To get an insight on the surface charge pH-dependence and resulting stability of the NPs in solution pH titration curves were first determined by measuring versus pH (from pH 2 to 10) the ζ and Z-average variations of two TiO_2 solutions at 50 mg/L. Results are presented in Figure 1(a). TiO_2 NPs in solution exhibit an average stable and positive ζ value of $+42 \pm 3$ mV from pH 2 to 4. By increasing further the pH, ζ decreases until an average negative value equal to -50 ± 4 mV above pH 9. The point of zero charge (PZC) was observed at pH equal to 6.5 ± 0.4 in good agreement with the values (5.2–7.1) reported in the literature.[24, 36, 37] The TiO_2 solution was found stable bellow pH 4, then fast aggregation was observed between pH 5 and 8 with the formation of

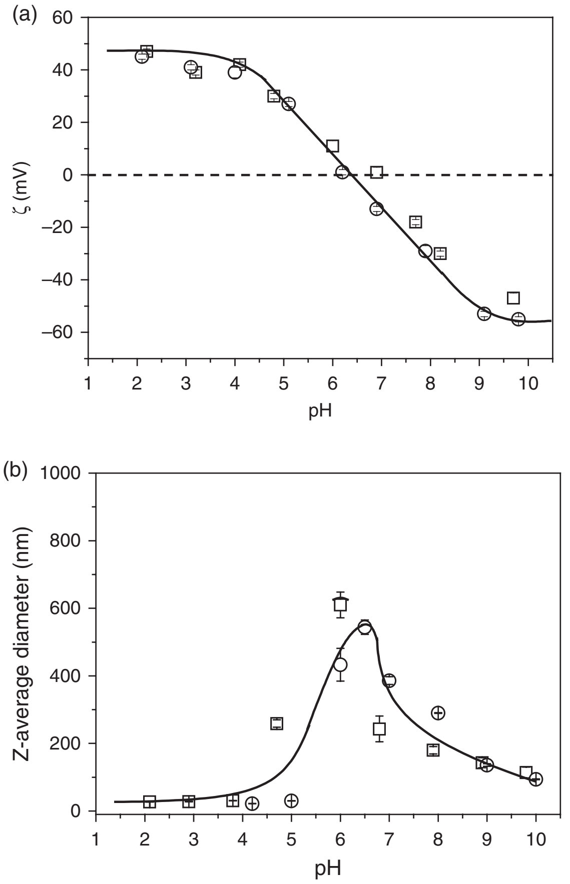

Fig. 1. (a) Zeta potential (ζ) variation as a function of pH for 50 mg/L TiO_2 nanoparticle suspensions for two set of experiments, (□, ○). The nanoparticles are positively charged at low pH and negatively charged at high pH. The Point of Zero Charge (PZC) is observed for a pH equal to 6.5 (b) Z-average hydrodynamic diameter variation as a function of pH. Aggregation is observed between pH 4 and 8 i.e., close to the PZC in good agreement with the zeta potential variation indicating that charge neutralization is the main driving mechanism for aggregate formation. The two curves have been obtained by increasing the solution pH.

large aggregates. Between pH 8 and 12, the TiO_2 solutions rapidly exhibit a stable domain where small aggregates of 150–200 nm are observed (Fig. 1(b)). At low pH the TiO_2 NPs are found stable due to their positive surface charges hence resulting in electro-repulsive interactions between NPs. At high pH values due to their negative surface charge TiO_2 NPs were also found stable but with sizes significantly larger than the sizes found at low pH. Similar behavior was also observed by Dunphy et al.[23] by increasing the pH value. Such result is explained by the fact that, when passing the PZC, aggregates which are formed in the PZC region do not disaggregate immediately by further increasing the pH and thus the electrostatic repulsions. Once aggregates are formed, the surface charging process and charge inversion of the NPs above the PZC is not strong and rapid enough from an electrostatic and kinetic point of view to fully re-disperse again the NPs.

3.1.2. FAs

FAs ζ variations as a function of pH are presented in Figure 2(a). Contrary to TiO_2 NPs no PZC is observable for these compounds; they exhibit a negative surface charge in the investigated pH range in good agreement with.[38, 39] The ζ values decrease rapidly from pH 2 to 6, before stabilization to -57 ± 3 mV. On the other hand, FAs hydrodynamic diameter (Fig. 2(b)) is found comprised between 80 and 150 nm over the entire pH range and found relatively constant with pH. The FAs particle size was not found to vary significantly with FA concentration in the concentration range 10–100 mg/L. At this point it should be noted that intensity-weighted mean diameters are given. Such a measurement, owing to the polydispersity of FAs solutions, certainly overestimates the number and importance of the large FA aggregates over the 5–10 nm small FAs elementary monomer units. Number-weighted size distributions usually denote the presence of a large number of FAs monomer units in presence of few aggregates. It is also admitted that by decreasing the FAs concentration, FAs aggregation is generally reduced. Thus according to these considerations, FAs were represented and considered in this study as small monomer units.

At this point, owing to the pH-dependent TiO_2 surface charge variation and FAs structural charges, three different "electrostatic" scenarios of possible interaction processes between TiO_2 NPs and FAs can be defined:
(a) positively charged NPs in presence of negatively charged FAs which is expected to result in fast FAs adsorption at the NPs surface,
(b) negatively charged FAs in presence of uncharged NPs which is expected to result in FAs adsorption if van der Waals forces are strong enough and thus NPs aggregate formation and
(c) negatively charged NPs in presence of negatively charged FAs, corresponding to the most unfavorable case for FAs adsorption at the TiO_2 NPs surfaces, and hence NPs aggregate formation. The different scenarios are considered and discussed in details by adjusting the FAs concentrations.

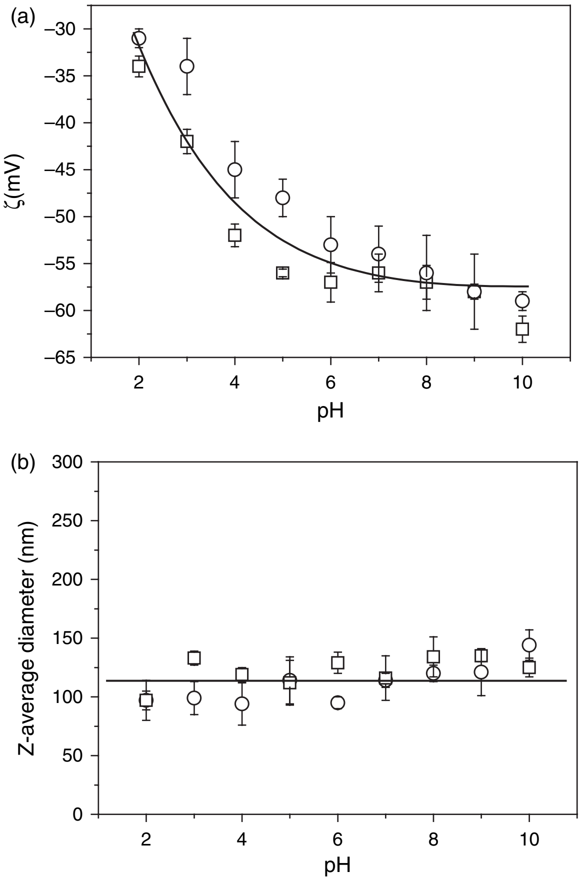

Fig. 2. Zeta potential (a) and Z-average hydrodynamic diameter (b) variations as a function of pH obtained for 50 mg/L FAs solutions for two sets of experiments (□, ○). FAs remain negatively charged at any pH (no PZC) and Z-average values are found stable and comprised between 80 and 150 nm indicating no significant aggregation process between the FAs.

3.2. FAs Concentration Influence on TiO_2 NPs Stability

3.2.1. Positively Charged TiO_2 NPs in Presence of Negatively Charged FAs ($pH = 4.2 < PZC$)

FAs at increasing concentrations were added to a 50 mg/L TiO_2 solution in order to determine the NPs surface charge and mean hydrodynamic diameter evolution as a function of FAs concentration resulting from the adsorption of the negatively charged FAs at the surface of positively charged TiO_2 NPs. As shown in Figure 3(a), by adding successive amount of FAs, the TiO_2 NPs zeta potential is found to rapidly decrease to 0. Surface charge neutralization occurs for a FAs concentration equal to 5 mg/L. By increasing further the FAs concentration, charge inversion is then observed. In Figure 3(b), the corresponding Z-average variations are also reported. Three distinct behaviors are also visible:

(a) at low FAs, i.e., concentrations comprised between 0 to 4 mg/L the Z-average diameter remains relatively small and stable with values less than 200 nm,

(b) then by increasing the FAs concentration a rapid Z-average diameter increase is observed until a maximum value (obtained at 5 mg/L) which is in good agreement with the ζ values observed in Figure 3(a) and with the position of the surface charge neutralization point,

(c) by increasing further the FAs concentration, the sizes decrease rapidly to reach stable Z-average values (from 8 to 12 mg/L) which are found similar to those measured from 0 to 4 mg/L i.e., at low FAs concentration. It is important to note here that charge inversion, due to FAs adsorption, is found to result in a very efficient aggregate disaggregation since similar sizes are found below and above the surface charge neutralization domain. Aggregate disaggregation was found to be less important when pH only was adjusted above the PZC (Fig. 1(b)) in the charge inversion domain. Our results clearly indicate here that steric effects induced by the adsorption of FAs are also playing key roles in the disaggregation of aggregates made of TiO_2 NPs (in addition to the electro-repulsive effects).

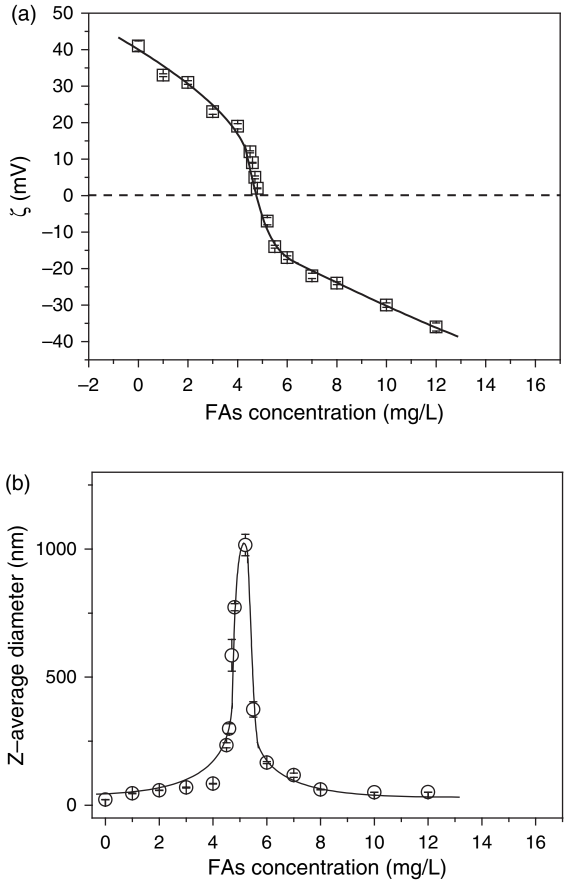

Fig. 3. pH < PZC. Zeta potential (a) and Z-average hydrodynamic diameter (b) variations as a function of FAs concentration. Two domains are observable: one in which the zeta potential is close to zero (corresponding to the charge neutralization of the positively charged nanoparticles by the adsorption of negatively charged FAs) resulting in fast aggregation of TiO_2 ([FAs] between 4–8 mg/L), the second one in which TiO_2 NPs are stable at low FAs concentration or in an excess of FAs ([FAs] between 0–4 and between 8–12 mg/L) hence preventing the NPs aggregation.

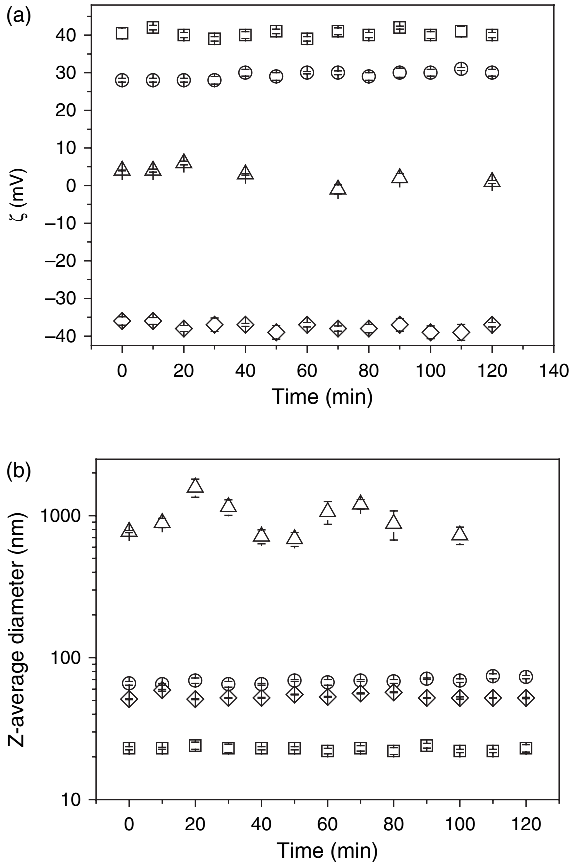

Fig. 4. pH < PZC. Zeta potential (a) and Z-average hydrodynamic diameter (b) evolutions with time for different FAs concentration (□ = 0, ○ = 2, Δ = 4.8, ◇ = 12 mg/L). For [FAs] equal to 4.8 mg/L, fast aggregation is observed and corresponds to the formation of large aggregates. In all conditions, Z-average values are stable with time.

Considering the results presented in Figure 3, four FAs concentration (0, 2, 4.8 and 12 mg/L) were selected to gain an insight into the stability of the TiO_2-FAs solutions over time. ζ and Z-average variations with time (Fig. 4) indicate that the FAs adsorption, surface charge modification, aggregate formation or aggregate disaggregation, and NPs stabilization is a relative fast process when time is expressed in minutes. Indeed no significant mean hydrodynamic diameter or zeta potential variations were found during the measurements. Figure 4 also define clearly three domains with regards to the FAs concentration:

(a) from 0 to 2 mg/L in which the NPs are still positively charged. Mean Z-average hydrodynamic diameter are found equal to 23 ± 2 nm in absence of FAs and 68 ± 3 nm at 2 mg/L,

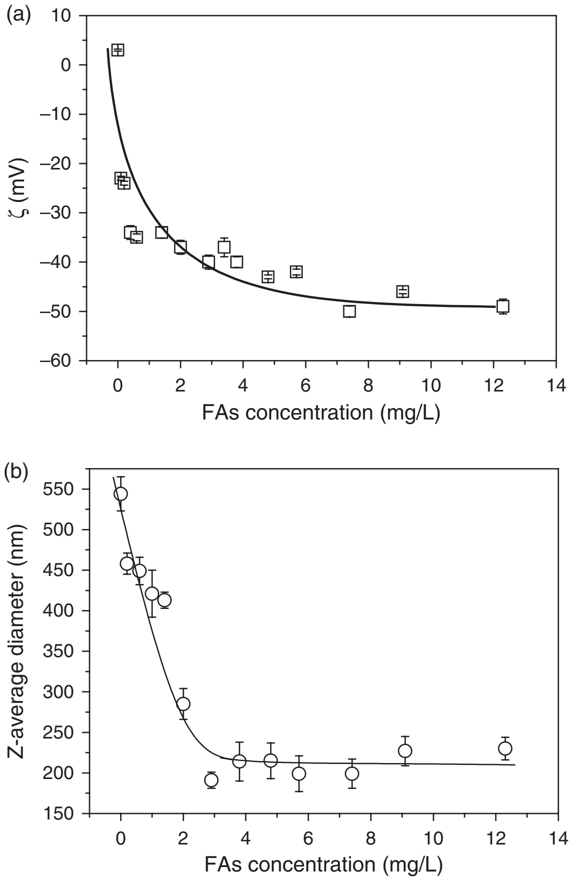

Fig. 5. pH = PZC. Zeta potential (a) and Z-average hydrodynamic diameter (b) variations as a function of FAs concentration. The ζ value increases rapidly as a function of [FAs] to reach an asymptotic value of -46 ± 4 mV. Z-average values are rapidly decreasing to reach a stable value of 200 nm.

(b) a domain in which NPs are forming large aggregates due to surface charge neutralization with Z-average values close to 1000 nm (967 ± 270 nm) at 4.8 mg/L,
(c) a domain in which charge inversion is observed when the FAs concentration is equal to 12 mg/L (−40 mV).

Z-average is found constant and close to 80 nm again.

3.2.2. Uncharged TiO_2 NPs in Presence of Negatively Charged FAs ($pH = 6.2 = PZC$)

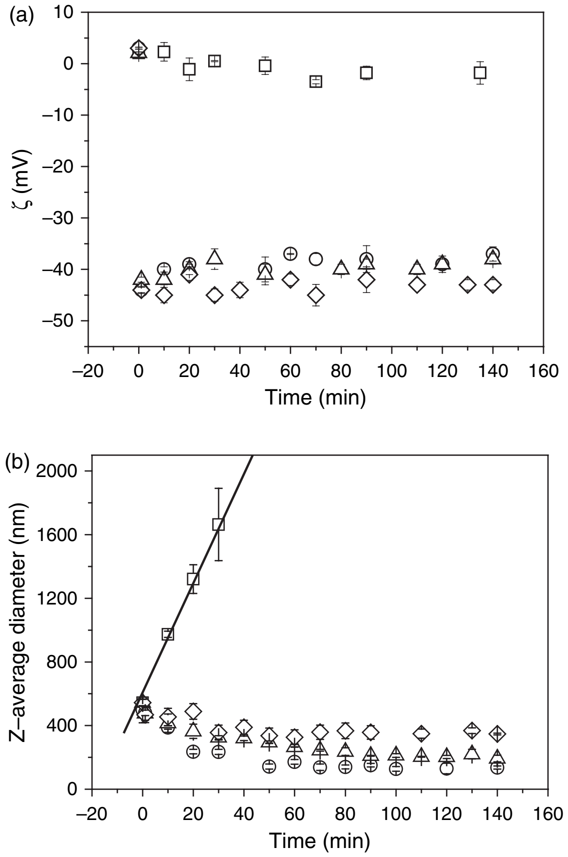

Fig. 6. pH = PZC. Zeta potential (a) and Z-average hydrodynamic diameter (b) variations with time for different [FAs] (□ = 0, ○ = 1.5, Δ = 3, ◇ = 6 mg/L) are plotted. In the absence of FAs aggregation is promoting the formation of large aggregates. The addition of FAs is found to lead to surface coating hence promoting the NPs stabilization and aggregate fragmentation.

At this pH, NPs exhibit a neutral charge in absence of FAs hence resulting in the rapid formation of aggregates. By increasing FAs concentration, Figure 5 indicates a rapid increase of the negative NPs charge to reach an asymptotic value close to -46 ± 4 mV. The corresponding Z-average values are found to decrease in a similar way to reach a plateau value equal to 200 nm. It should be note here that only 3 mg/L of FAs, which is comparable to the FAs concentration range found in freshwaters, result in the stabilization and partial disaggregation of a 50 mg/L TiO_2 solution. Considering the results presented in Figure 5, four FAs concentration (0, 1.5, 3 and 6 mg/L) were chosen to follow the stability of TiO_2-FAs mixtures with time (Fig. 6). In absence of FAs, fast aggregation is observed hence resulting in a quasi linear increase of mean Z-average diameter as a function of time (Fig. 6(b)) and zeta potential values close to zero (Fig. 6(a)). On the other hand, in presence of FAs, TiO_2 NPs solutions are found relatively stable with time. Zeta potential and Z-average values indicate rapid charge inversion and absence of aggregation. A slight decrease of the mean Z-average diameter as a function of time is observed which is explained by the continuous disaggregation with time of the TiO_2 aggregates due to FAs adsorption. This is in good agreement with the work of Amal et al.[40] on iron oxide where it was observed that FAs adsorption effect on disaggregation was still present after a long period of time.

3.2.3. Negatively Charged TiO_2 NPs in Presence of Negatively Charged FAs (When $pH = 9.5 > PZC$)

For a pH value greater than the PZC, FAs and NPs which both exhibit negative ζ potential values are not found to

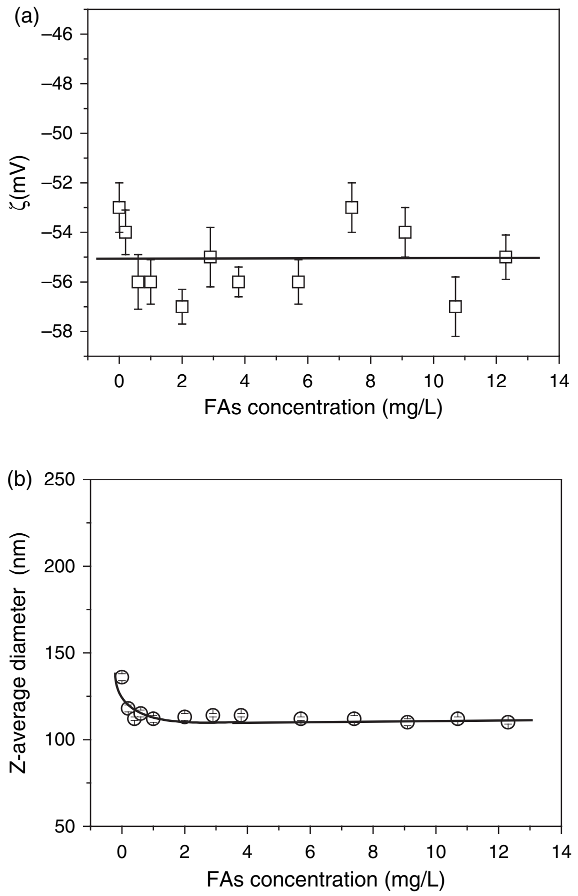

Fig. 7. pH > PZC. Zeta potential (a) and *Z*-average (b) variations as a function of FAs concentration. The ζ values are found stable by increasing the FAs concentration. *Z*-average hydrodynamic diameter values exhibit a small decrease then are stabilized with time.

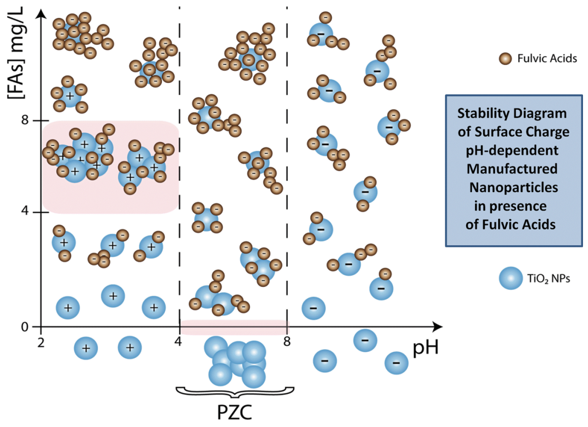

Fig. 8. Stability diagram of TiO_2 NPs as a function of pH and FAs concentration. Aggregation is observed in two cases only (i) in the PZC region in absence of FAs and (ii) when FAs concentrationis comprised between 4 and 8 mg/L i.e., when surface charge neutralization is achieved. In the other cases, NPs stabilization is achieved via charge inversion and aggregate dispersion. The presence of FAs is thus expected to mainly promote the NPs stability.

interact significantly from an electrostatic point of view. Indeed, in Figure 7(a), ζ values indicate no FAs adsorption since the ζ values are similar in absence or presence of FAs. Similar trends on the *Z*-average variation are observed despite the slight decrease of the *Z*-average from 136 to 112 nm. Such a decrease is expected to result from the potential but limited adsorption of FAs via Van der Waals forces owing to the amphiphilic character of the FAs.

4. CONCLUSIONS

The determination of detailed stability diagrams is an important tool and a prerequisite for the analysis of the surface transformation, aggregation, disaggregation behavior and possible dispersion of NPs in various environments in response to change in pH and FAs concentrations. As shown in the TiO_2 stability diagram proposed in Figure 8, there is a complex and non linear interplay between the pH and the FAs concentration. The few colored areas denote the pH-[FAs] regions in which aggregation is observed and clearly indicate that only two aggregation domains are possible; (i) at the NPs pH point of charge neutralization in the absence of FAs and (ii) when NPs charge neutralization is achieved by FAs adsorption in the pH domain where the NPs are positively charged. In all the other cases FAs adsorption and further increases of FAs concentration are expected to promote the TiO_2 NPs stabilization or NPs aggregate disaggregation. This work hence suggests that very low concentrations of fulvic acids (>8 mg/L) are sufficient to rapidly stabilize 50 mg/L TiO_2 nanoparticles, independently of the medium pH, and that fulvic acids play important roles in the dispersion of aggregated NPs. The negatively charged FAs strongly adsorb on positive and neutral NPs respectively. This indicates that the driving force for FAs adsorption is a combination of electrostatic attractive interactions between the FAs and the NPs, electrostatic repulsive interactions between the FAs at the NPs surfaces, and van der Waals interactions. Steric effects at the NPs surface are also playing key roles in the NPs stability indicating that even really small molecules (50–2000 Da) such as FAs can stabilize TiO_2 NPs suspensions due to their amphiphilic characters. Such results clearly reveal also that the release of TiO_2 NPs in natural systems, even if they are aggregated, can rapidly lead to their redispersion and diffusion as individual particles. The present results also suggest that, when studying NPs aggregation processes in presence of FAs, the interaction of FAs with NPs can be considered as instantaneous compared to the nanoparticle aggregation processes. The results and conclusions reported here on the increased NPs stability due to the presence of FAs should be considered as a first step for several reasons due to the fact that the presence of biopolymers in aquatic systems, monovalent and multivalent salt, as well as natural inorganic colloids, may also significantly modify the final stability and transport of manufactured nanoparticles in aquatic systems.

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