An investigation on the aggregation phenomena of Titanium dioxide nanoparticles in natural waters: role of ionic strength, and organic matter

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ABSTRACT

The aggregation of TiO_2 nanoparticles under different aqueous matrixes representative of natural waters was experimentally investigated. Conditions included indiferent electrolytes (NaCl) and specifically adsorbing cations ($CaCl_2$ and $MgCl_2$), in the presence and absence of natural organic matter. The nanoparticles of 21 nm primary particle size, formed stable aggregates of aproximately 250 nm under conditions unfavorable for aggregation, while size increased significantly at pHs near or at the pzc of the material (pzc TiO_2 6.3). The pH for favorable aggregation was affected by the presence of divalent cations and natural organic matter, turning the nanoparticles mobile at conditions were otherwise limited mobility should be expected. DLVO calculations confirmed the experimental observations, if the stable aggregate size was applied as the primary size of the particles. Aggregate morphology observed by SEM was in agreement with proposed mechanisms.

Keywords: TiO_2 nanoparticles, aggregation, kinetics, DLVO theory.

1 INTRODUCTION

With the continuing growth of nanotechnology and nanomaterials being applied in consumer products, the scenario where these materials reach the natural environment is a high probable one for the near future. In order to asses the risk involved in the application of nanotechnology [1], a thorough understanding of the behavior of nanoparticles in natural waters is needed, but much lacking.

TiO_2 nanoparticles are within the most common nanomaterials, finding applications in cosmetics, paints, catalyst, and many other fields. However, a comprehensive study of the aggregation of these nanomaterials under a variety of conditions that could elucidate the mechanisms governing its behavior, including aggregation rates, aggregate size and morphology is still unavailable.

The objective of this work is to provide a complete characterization of the aggregation process of TiO_2 nanoparticles under environmentally relevant conditions, investigating size, kinetics and morphology, and to model this measurements in order to obtain a predictive tool for their behavior. Due to length constrains, only partial results are presented here.

2 METHODS AND MATERIALS

Titanium dioxide nanoparticles (Aeroxide P25) were provided by the manufacturer (Evonik Degussa Corporation, Parsippany, NJ). P25 is a hydrophilic fumed TiO_2, a mixture of the rutile and anatase forms with an average primary particle size of 21 nm, as reported by the manufacturer.

Particle suspensions were prepared in different solvent chemistries. First, electrolyte solutions were prepared, keeping ionic strength constant at 0.9 mM under inert electrolytes (NaCl, Sigma-Aldrich), divalent cations (Sigma-Aldrich $MgCl_2$, and Anedra $CaCl_2$) and all the previous under different organic matter concentrations. Tannic Acid (Carlo Erba reagents) (TA) and Humic Acid (humic acid sodium salt, Aldrich) (HA) were used as models for naturally occurring organic matter. The conditions assessed were: NaCl; $CaCl_2$; $MgCl_2$; $CaCl_2$+1ppm AT; $CaCl_2$ + 0,5ppm AT; $MgCl_2$ + 1ppm TA; $MgCl_2$ + 0,5ppm TA; NaCl + HA 1ppm TOC; CaCl2 + HA 1ppm TOC. For every solution, ultrapure type I water (resistivity 18 MΩ) was used. All containers were previously washed and rinsed carefully to prevent dust particle interference. Aliquots (100 ml) were taken at a time and their pH was adjusted, using NaOH (Anedra) or HCl (Anedra) solutions previously filtered through 0.22 μm Millipore filters. Once the pH stabilized, 2.5mg TiO_2 was added to the solution and gently stirred to assure a homogeneous suspension. Final pH was recorded and aliquots taken for size and ζ potential measurement.

2.1 Aggregation kinetics

Kinetic size measurements were carried out using Dynamic light scattering (DLS, Malvern Zetasizer Nano ZS). Immediately once the suspensions were prepared, samples for size measurement were taken in disposable polystyrene cuvettes. Size measurements were taken

continuously until stabilization of the aggregation process was observed.

2.2 Zeta Potential Measuremet

Laser Doppler velocimetry (Malvern Zetasizer Nano ZS) was used to characterize the electrophoretic mobility (EPM) of the TiO_2 NPs in the various electrolyte solutions. Measured EPMs were converted to ζ-potential using the Smoluchowski equation. Disposable folded capillary cells were employed. The samples were taken from the freshly prepared suspensions, but measured after reaching equilibrium.

2.3 Image Analysis

Two TiO_2 suspensions were prepared, as explained previously, for each of the following conditions: NaCl, NaCl + TA, $CaCl_2$. One of the suspensions was adjusted to a pH where the particles were stabilized, and the other to a pH at which they showed aggregation. A drop of each suspension was placed over a glass support that has been previously gold coated to create a conductive surface. The sample drop was immediately dried to minimize the reorganization of the aggregated particles. Images were taken with SEM Zeiss Supra 40 microscope.

2.4 DLVO Calculations

Interactions potentials were calculated for the conditions investigated based on classical DLVO theory of colloidal stability, where only Van der Waals attraction forces and electrostatic repulsion were considered. Although other non-DLVO forces are likely to play a role in the aggregation process [2], they were not included in the analysis presented here.

3 RESULTS AND DISCUSSION

3.1 Size Measurements

Given the high polydispersity of the samples, number measurements were considered more representative of the real size distribution than Z-average or intensity values given by the instrument. The particle size at the peak was graphed as a function of measurement number. The first measurements of that graph were adjusted to linearity (the number of measurements considered was such that the highest R^2 value was obtained). The slope of the first part of such graph was considered to be an indirect measure of particle aggregation velocity. Final average size was also determined.

3.2 Effect of electrolyte

Average particle size was determined for a constant ionic strength of 0.9 mM, given by NaCl, $CaCl_2$, and $MgCl_2$. Specific interactions were expected for divalent ions, as reported previously in the literature.

The average particle size of the aggregates is shown in Figure 1 for each electrolyte in a pH range between 3 to 9, as well as the determined zeta potential under the same conditions. In the presence of NaCl, the nanoparticles formed stable aggregates of average size 250 nm, except in the neighborhood of the pzc of the material, in good agreement with previously reported values. Z-potential measurements located the pzc of P25 NPs at a pH=6.3. However, when divalet cations were present, a specific interaction was manifested in the form of surface adsorption and therefore the z-potential measurements were highly modified, showing positive surface charges while otherwise a negative or less positive value would be expected. In comparison with the determinations made under the indiferent electrolyte conditions, $CaCl_2$ solutions exhibited adsorption effects begginig at pH 6, prevented the particles from adopting a negative charge and even produced a charge reversal at pHs above 10, where a net positive charge could be detected. In contrast, $MgCl_2$ produced a steady shift of the z-potential vs pH curve to the left, with a detectable pzc of pH 8 and no observed charge reversal effect under the pHs investigated.

3.3 Effect of NOM

The effect of the presence of NOM was investigated under all previously considered conditions [3]. Two model organic compounds were considered: tannic acid and humic acid. Only tannic acid data is presented in this article.

The average aggregate size and surface charge measured by z-potential determinations for a ionic strength of 0.9 mM given by NaCl, $CaCl_2$, and $MgCl_2$, in the presence of 1 ppm tannic acid is shown in Figure 2. Surface charge measurements suggested that tannic acid readily adsorbs onto the particle surface, resulting in a more negative charge, and a shift towards more acidic pHs of the corresponding pzc. The net effect of the presence and consequent adsorption of tannic acid on the surface of the nanoparticle aggregates was the stabilization of the suspension at an average particle size of 250 nm in all the range of pHs of environmental interest. When divalent cations were present, their tendency to adsorb was tempered by the competing adsorbant, and although the absolute value of the charge was reduced, a moderate -20 mV was measured for Ca and Mg solutions, still resulting in a stablization effect.

3.4 Image analysis

SEM images were obtained at both a stable and aggregated pH for each chemical condition investigated, in order to characterize the morphology of the aggregates formed. Figure 3 shows aggregates formed in 0.9mM NaCl at pH 4, and Figure 4 at pH 6.7.
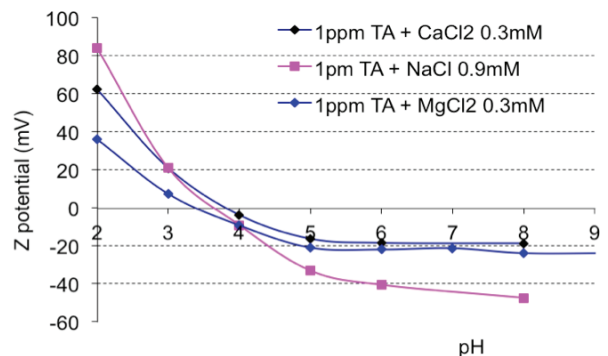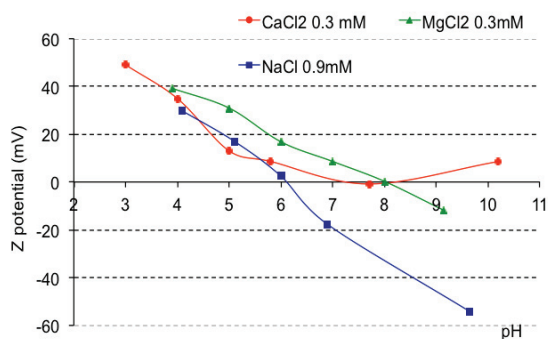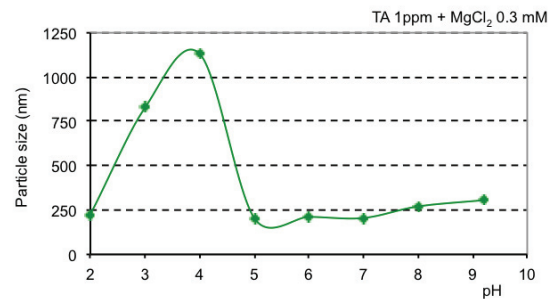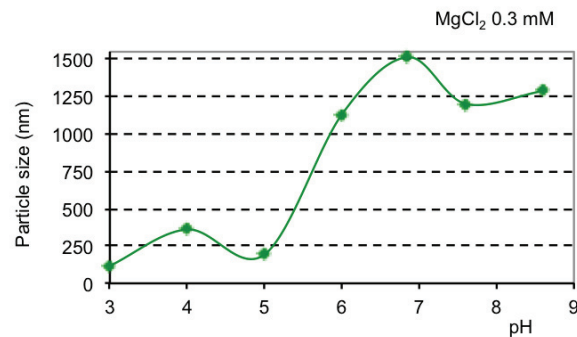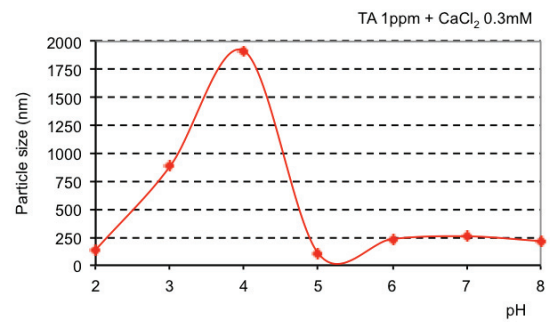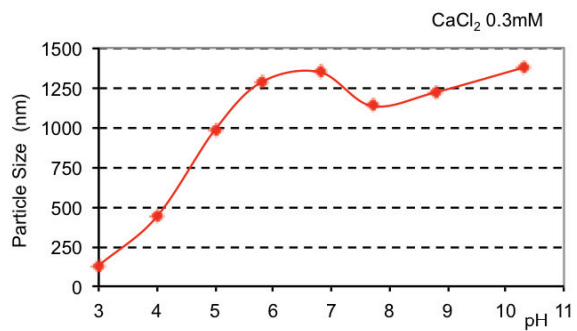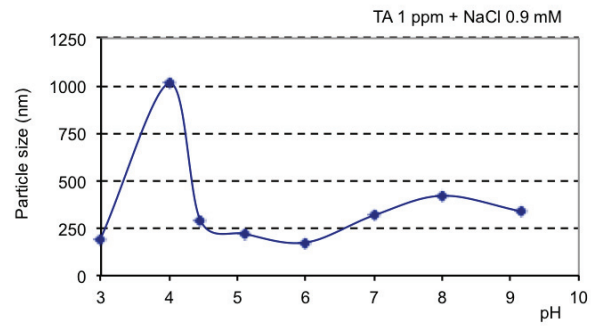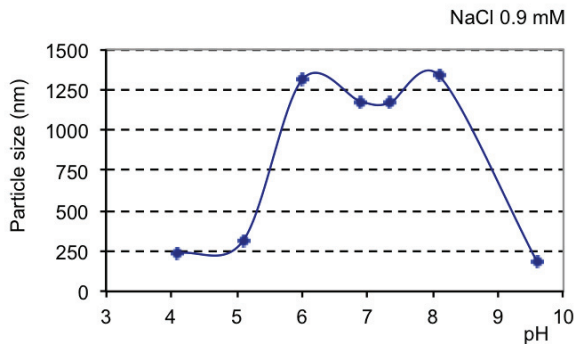
Figure 1: Effect of electrolyte type on size and surface charge (z-potential) of TiO₂ aggregates: (a) 0.9 mM NaCl; (b) 0.3 mM CaCl₂; (c) 0.3 mM MgCl₂; (d) Z-potential for the above mentioned conditions.

Figure 2. Effect of electrolyte type in the presence of NOM on size and surface charge (z-potential) of TiO2 aggregates: (a) 0.9 mM NaCl + 1 ppm Tannic acid; (b) 0.3 mM CaCl2 + 1 ppm Tannic acid; (c) 0.3 mM MgCl2 + 1 ppm Tannic acid; (d) Z-potential for the above mentioned conditions.

The aggregates formed at pH 4, under relatively unfavorable conditions showed a size in good agreement with DLS measurents, and as a consequence of the low sticking probability for collisions between particles [4], were generally rounded and compact. In contrast, the aggregates formed at pH 6.7, showed an open, fractal-type morphology, and even the substrate could be seen at a point through its structure, resulting from the high attachment efficiency that occured near the pzc of a material. The observations can also be explained by the aggregation rates detemined in the aggregation kinetic investigations (not shown here).
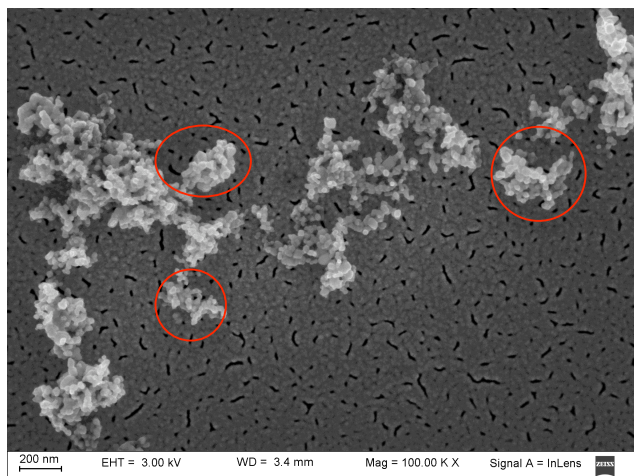

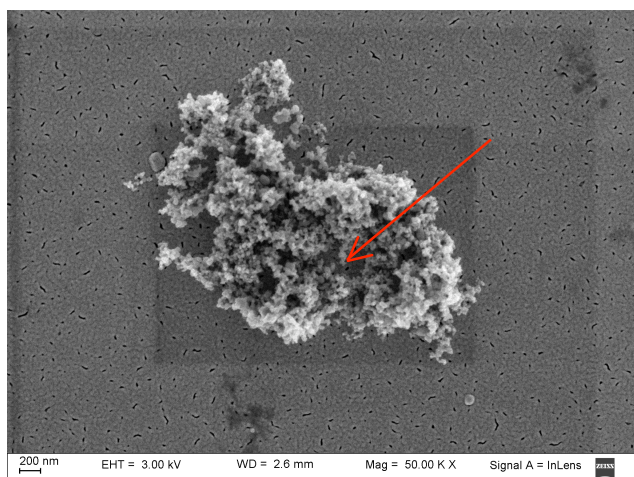Figure 3. TiO$_2$ nanoparticle aggregates under 0.9 mM NaCl, pH 4. Individual aggregates are marked.

Figure 4. TiO$_2$ nanoparticle aggregates under 0.9 mM NaCl, pH 6.7. The oppening through the structure is marked, where the substrate can be seen.

3.5   DLVO calculations

The experimental results were modeled by classic DLVO colloidal theory and good agreement was observed when the stable aggregate size (250 nm) was taken as the primary particle size.

4   CONCLUSIONS

Changes in pH exhibit an important effect on the aggregation behavior given the amphoteric property of the metal oxides. TiO2 nanoparticles aggregate rapidly at pHs near the point of zero charge of the material, in good agreement with values reported in the literature. The presence of adsorbing divalent cations shift the point of zero charge of the surface to lower pH values, making the particles stable under conditions that otherwise aggregation would have been observed. The presence of organic compounds, with a strong tendency for adsorption on the TiO$_2$, also has a stabilization effect. The experiments conducted demonstrated that although nanomaterials are unstable and expected to form large particles even in low to moderate ionic strength conditions, the presence of adsorbent species can render them stable and therefore mobile in the natural environment. In summary, the behavior of nanomaterials in natural waters is a complex phenomenon and a thorough experimental and modeling effort is needed to elucidate the transformations that the particles undergo and the potential risks posed to human health and the environment. All the observed effects could be explained in the light of the DLVO theory, and no specific or steric interactions were evidenced.

5   ACKNOLEDGEMENTS

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