



# Stability studies for titanium dioxide nanoparticles upon adsorption of Suwannee River humic and fulvic acids and natural organic matter



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## HIGHLIGHTS

- NOOM type (HA, FA, NOM) affects the extent of adsorption onto nano-TiO<sub>2</sub>.
- Type and concentration of ions and pH affect NOOM removal onto nano-TiO<sub>2</sub>.
- Fate and transport of nano-TiO<sub>2</sub> depend on NOOM type and concentration.

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## ABSTRACT

In many studies humic acid, fulvic acid, or natural organic matter is used interchangeably to model the effect of naturally derived organic matter on geochemical processes in the environment. In this study, the term NOOM (naturally occurring organic matter) is used to include both humic and fulvic acids as well as natural organic matter and compares the effect of NOOM type on NOOM removal onto nano-TiO<sub>2</sub>. In general, regardless of variations in solution chemistry, the order of the percentage of removal of NOOM onto nano-TiO<sub>2</sub> was humic acid > natural organic matter > fulvic acid. The order of adsorption constant values of NOOM onto nano-TiO<sub>2</sub> was also found to be humic acid > natural organic matter > fulvic acid under all conditions studied. The extent of NOOM removal by nano-TiO<sub>2</sub> was enhanced in the presence of the divalent ions, magnesium and calcium, at pH 7.8 when compared to the presence of the monovalent ions, sodium and potassium. Also, lower NOOM removal by nano-TiO<sub>2</sub> in the presence of sodium salts of dihydrogen phosphate, bicarbonate and nitrate relative to chloride was observed and was likely due to the competition between polyatomic anions and NOOM adsorption onto the surface of nano-TiO<sub>2</sub> indicating an anionic effect. Low concentrations of NOOM (10–20 mg L<sup>-1</sup>) destabilized nano-TiO<sub>2</sub> in solution, however, the stability of nano-TiO<sub>2</sub> increased as the amount of NOOM adsorbed onto nano-TiO<sub>2</sub> increased at higher dissolved NOOM concentrations and significant stabilization was seen at 25 mg L<sup>-1</sup> NOOM. Thus, the three fractions of NOOM, humic and fulvic acids and natural organic matter and their concentrations were found to affect nano-TiO<sub>2</sub> stability to different degrees although pH dependent trends in cation and anion effects had similar patterns. While the effects of adsorption of these three commonly used types of NOOM onto nanoparticles are similar, there are important differences that can be related to structural differences.

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## 1. Introduction

Among the various nanoparticles, titanium dioxide nanoparticles (nano-TiO<sub>2</sub>) are one of the most extensively used nanoscale materials to date, and are utilized as additives to commercial products such as cosmetics, pharmaceuticals, and food colorants (Joo et al., 2009; Robichaud et al., 2009). Because of the widespread production and use of nano-TiO<sub>2</sub>, especially in paints, nano-TiO<sub>2</sub> is rapidly accumulating in the environment with expected rapid increases during the next decade (Farre et al., 2009). Nano-TiO<sub>2</sub> has been found in waste water, sewage, and runoff (Lee et al., 2001; Nowack and Bucheli, 2007; Kaegi et al., 2008).

Several studies have reported the toxicity of nano-TiO<sub>2</sub> to plants and animals (Aruoja et al., 2009; Okuda-Shimazaki et al., 2010; Gao et al., 2012). The toxicity of nano-TiO<sub>2</sub> to developing zebrafish, *Danio rerio*, was found to be enhanced in the presence of natural organic matter (Yang et al., 2013).

Because adsorption modifies the surface properties of nanomaterials, it is an important factor in the fate and transport of NPs (Paria and Khilar, 2004). Several studies have successfully investigated the fate and transport of NPs under different environmental factors including the presence of naturally occurring organic matter (NOOM), pH, ionic strength, and specific electrolytes (Hyung and Kim, 2008; Bui and Choi, 2010; Chen et al., 2011; Thio et al., 2011; Li and Sun, 2011). NOOM, as a natural non-living organic material, is the result of the microbial decomposition of animal and plant residues and is widely

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distributed on the planet in soils, sediments, and natural waters (Fu et al., 2005; Rezacova and Gryndler, 2006; Pospisilova and Fasurova, 2009). NOOM consists of heterogeneous organic mixtures, containing aromatic and aliphatic based functional groups (Rezacova and Gryndler, 2006). The variability of NOOM in structure and elemental composition is based on its type and source and environmental history. Humic substances (HSs) and natural organic matter (NOM) constitute the two main types of NOOM used in laboratory studies. Many researchers use NOM, HA (humic acid) or FA (fulvic acid) to model NOOM, which can be purchased as such from the International Humic Substances Society (IHSS). Natural organic matter contains both high and low molecular weight substances. The high molecular weight fractions include humic substances while the non-humic fraction includes low molecular weight compounds such as carbohydrates, proteins, and sugars (Kickuth, and Scheffer, 1976; Xie et al., 2008; Badis et al., 2009).

Many studies have documented the adsorption of NOOM onto NPs and the effects of monovalent and divalent ions on adsorption and on NP stability (Chen and Elimelech, 2007; French et al., 2009; Zhang et al., 2009; Bui and Choi, 2010; Akaighe et al., 2012). In our previous work, the effect of HA source on the adsorption of HA onto nano-TiO<sub>2</sub> was studied (Erhayem, 2011) and a significant effect was found. This study focuses on the effect of NOOM type (HA, FA and NOM) from the same source on NOOM adsorption onto nano-TiO<sub>2</sub> and on the consequent effects on nano-TiO<sub>2</sub> stability in the presence of environmentally relevant cations and anions.

## 2. Experimental methods

### 2.1. Materials

Titanium dioxide nanoparticles (nano-TiO<sub>2</sub>-P25; CAS-Reg No: 13463-67-7) were purchased from Degussa and used as received. Suwannee River 1S101H humic acid (SRHA), Suwannee River 1S101F fulvic acid (SRFA) and Suwannee River 1R101N natural organic matter (SRNOM) were purchased from the International Humic Substances Society (IHSS, St. Paul, MN). The samples were stored in a desiccator until used. All other chemicals were purchased from Sigma-Aldrich or Fischer Scientific and used without further purification. Solutions were prepared using distilled water passed through an 18.2 MΩ Milli-Q purification system or in moderately hard reconstituted water (MHRW) containing calcium, magnesium, sodium, potassium, chloride, bicarbonate, and sulfate ions (EPA, 1993; Akaighe et al., 2012). The pH of stock solutions was adjusted by adding NaOH or HCl and determined by using an Orion pH/ISE meter (model 710A, Thermo Fisher Scientific). The ionic strength was adjusted by adding solid NaCl. All the experiments were performed at room temperature (22 ± 1 °C).

### 2.2. Preparation of NOOM stock solutions

NOOM stock solutions were prepared by dissolving solid NOOM (80 to 100 mg) in either Milli-Q water (without adjusting the pH or ionic strength) or in MHRW at a pH and ionic strength of 7.9 ± 0.2 and 4.6 mmol L<sup>-1</sup>, respectively. The NOOM suspensions were stirred overnight at room temperature and then filtered through 0.45 μm filters (MF Membrane Filter, Cat No.: HAWP04700). The final NOOM concentrations were then adjusted to 10–50 mg L<sup>-1</sup> and the pH of these stock solutions was adjusted to the final desired pH with NaOH or HCl. The ionic strength of the NOOM solutions was adjusted with solid NaCl. All salts were purchased from Sigma Aldrich and used without further purification.

### 2.3. Instruments

UV–vis absorbance measurements were performed by using a 1 cm optical path length quartz cuvette with an Agilent Technology 8453 spectrophotometer. TEM images for selected NOOM-coated and

uncoated nano-TiO<sub>2</sub> were captured using a (0.5 nm) Zeiss EM-900 instrument with an accelerating voltage of 80 kV using 400-mesh Carbon/Formvar TEM grids (Electron Microscopy Sciences).

### 2.4. Adsorption constant studies

In order to obtain adsorption isotherms, the NOOM solutions were adjusted to the desired pH (4.8 ± 0.2 and 7.8 ± 0.2) and ionic strength (10, 50 and 100 mmol L<sup>-1</sup> NaCl) before addition of nano-TiO<sub>2</sub>. The NOOM solutions were also prepared in MHRW, at a pH of 7.9 ± 0.2 and ionic strength of 4.6 mmol L<sup>-1</sup> NaCl. Various amounts of nano-TiO<sub>2</sub> (5, 10, 15, 20 and 25 mg) were then added to 10 mL of 10 mg L<sup>-1</sup> of the various NOOM solutions. The NOOM–nano-TiO<sub>2</sub> suspensions were stirred for 48 h (based on time study) to allow the suspensions to equilibrate. The suspensions were then allowed to settle for 4 h before filtering using 0.45 μm syringe filters. The spectra were collected before addition of nano-TiO<sub>2</sub> and after equilibration with nano-TiO<sub>2</sub>. The amount of adsorbed NOOM onto nano-TiO<sub>2</sub> was determined from the difference in the UV–vis absorbance at 254 nm.

### 2.5. NOOM removal by nano-TiO<sub>2</sub>

In order to evaluate the effect of pH on NOOM removal by nano-TiO<sub>2</sub>, NaOH and HCl were used to set the pH of the stock NOOM solution at various values from 4.8 ± 0.2 to 10 ± 0.2 while maintaining a constant ionic strength of 100 mmol L<sup>-1</sup> NaCl. Then 5 mg of nano-TiO<sub>2</sub> was added to 10 mL of 10 mg L<sup>-1</sup> NOOM solution and after continuous stirring for 48 h and filtering (0.45 μm syringe filter), the percentage removal of NOOM was calculated from UV–vis measurements at 254 nm. In order to evaluate the effect of solution ionic strength on NOOM removal by nano-TiO<sub>2</sub>, the ionic strength of NOOM solutions was varied from 10 to 40 mmol L<sup>-1</sup> by adding solid NaCl at a constant pH of 4.8 ± 0.2. In order to study the effect of cations, the chloride salts of sodium, potassium, magnesium and calcium were chosen while a possible anion effect was evaluated by comparing results obtained in sodium nitrate and sodium chloride solutions using the same procedure and pH (4.8–10.0) as described above. The effect of electrolyte concentration on NOOM removal by nano-TiO<sub>2</sub> was further investigated using 10 mg L<sup>-1</sup> NOOM solutions containing 10, 20 and 40 mmol L<sup>-1</sup> of monovalent and divalent ions such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or HCO<sub>3</sub><sup>-</sup> at a constant pH of 7.4 ± 0.2. Due to the alteration of pH by the polyatomic anions, sodium acetate buffer was used to control the solution pH. Upon addition of 5 mg of nano-TiO<sub>2</sub>, the same procedure as described above was used to calculate the percentage of NOOM removal by nano-TiO<sub>2</sub>.

### 2.6. Sedimentation studies

Nano-TiO<sub>2</sub> sedimentation was studied by monitoring suspended nano-TiO<sub>2</sub> concentrations via time resolved optical absorbance measurements at different pH and ionic strength values in order to evaluate the effect of NOOM type on fate and transport of nano-TiO<sub>2</sub>. The experimental setup was identical to that described for adsorption studies. Suspensions were stirred for 48 h after which 2.5 mL of the suspension was placed in a 3 mL quartz UV–vis cuvette and was then analyzed for optical absorbance at 378 nm using time intervals of 150 s over a 2 h period. Calibration curves of nano-TiO<sub>2</sub> concentration versus absorbance at 378 nm proved to be reliable regardless of degree of aggregation.

## 3. Results and discussion

### 3.1. Adsorption constant studies

The adsorption of SRHA, SRNOM, and SRFA onto nano-TiO<sub>2</sub> showed similar trends with time, but the extent of adsorption differed (Fig. S-1).

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