Stability of nano-sized titanium dioxide in an aqueous environment: effects of pH, dissolved organic matter and divalent cations
X. N. Yang and F. Y. Cui

ABSTRACT
Nano-sized titanium dioxide in the aquatic environment has a potential impact on the environment and human health. In this study, the impact of pH value, dissolved organic matter (DOM) and divalent cations (Ca$^{2+}$) on the stability of titanium dioxide nanoparticles (nano-TiO$_2$) in an aqueous environment was investigated in batch tests. The results showed that the particle size of nano-TiO$_2$ was not sensitive to pH value but was inversely proportional to zeta potential. The nano-TiO$_2$ becomes more stable with surface zeta potential, accompanied by small particle size and high dispersion. In the presence of DOM, the particle size was smaller and the stability of nano-TiO$_2$ could be enhanced. This might be a synergistic effect of the ligand exchange and electrostatic force. Particle size increased with the addition of Ca$^{2+}$ and the stability decreased.

Key words | aqueous environment, calcium ions, dissolved organic matter, nano-sized titanium dioxide, stability

INTRODUCTION
The applications of nano-sized titanium dioxide (nano-TiO$_2$) are now leading to the rapid development of several industries. The processes of the production, use and disposal, will inevitably lead to its contamination of air, water, soils and organisms (Benn & Westerhoff 2008; Köhler et al. 2008). The environmental and health consequences of this material and the life-cycle implications merit attention. Due to the specific size, larger surface-to-volume ratio and high reactivity potential, nano-TiO$_2$ easily aggregates, which results in deposition or adsorption onto the surface of an organism. Additionally, toxicity is aggravated through interaction with other pollution. Subsequently, the organism might be subject to different levels of toxicity either through water uptake or adhering to algae that has been exposed to nano-TiO$_2$ (Nel et al. 2006; Wang et al. 2008, 2009). Recent studies have confirmed that nano-TiO$_2$ can be lethal to Daphnia (Zhu et al. 2010) and rainbow trout, and have adverse effects on the aquatic environment and human health through bioaccumulation in the aquatic food chain (Sun et al. 2007).

In aquatic environments, the stability of nanoparticles (NPs) may be affected by many factors, including the properties of organic matter, pH, ionic strength and divalent cations. Dissolved organic matter (DOM) is a ubiquitous colloid, and plays a critical role in the mobility of colloidal particles in aquatic environments (Karlsson et al. 2006; Hakala et al. 2007). Studies have confirmed the significance of DOM in controlling the aggregation of colloids, and the stability of particles in water could also be enhanced by DOM (Tiller & O’Melia 1995). Divalent cations are also considered to be an important factor affecting the stability of particles. The stability of a natural nanoparticle, hematite, is reduced by both monovalent electrolytes and polyelectrolytes (Amal et al. 1990; Zhang & Buffle 1995). On the other hand, the pH value of a solution has a significant impact on both surface charge and aggregation kinetics of nano-TiO$_2$ (Guzman et al. 2006; French et al. 2009). Due to the aggregation and distribution characteristics, there is an urgent need to address the stability of nano-TiO$_2$ under different typical conditions.

In this study, the surface characteristics and particle size distribution under different pH and aquatic conditions was evaluated to examine the aggregation behavior of nano-TiO$_2$ in an aqueous environment. The results provide fundamental information for understanding the specific behavior.
of nano-TiO₂ under different conditions in natural watercourses.

MATERIALS AND METHODS

Nano-TiO₂ and suspension preparation

Rutile titanium oxide in water was purchased from Nanostructured & Amorphous Materials, Inc. (CAS: 1317-80-2, 15 wt% Titanium Oxide in water, APS: 5-30 nm). The stock suspension of 500 mg/L NPs was prepared by pipetting 3.33 g nano-TiO₂ water solution into 1 L of ultrapure water (18.2 MΩ/cm Millipore, Billerica, MA, USA). Before use, the nano-TiO₂ was sonicated (Branson Sonifier W-250D, 25 W at 10% energy input) for 5 min to ensure the homogenous dispersal of the solution, and a further 15 min of sonication was conducted before each experiment.

Preparation of DOM and suspensions with different pH, ionic strength and cation valence

Humic acid sodium salt (CAS: 68131-04-4) was purchased from Sigma-Aldrich. The salt was suspended in water to get a final dissolved organic carbon concentration of 10 C/L. The standard solution of CaCl₂, NaNO₃, NaH₂PO₄ and Na₂HPO₄ was national criteria solution. By addition of the nano-TiO₂ stock suspension (10 mg L⁻¹ nano-TiO₂ for NaNO₃ and CaCl₂ experiments), the suspensions were adjusted to pH 7.0 ± 0.2 with PBS (phosphate buffered saline) buffer and to 1 mmol L⁻¹ ionic strength with 0.1 mol L⁻¹ NaNO₃ and CaCl₂. Then, these were filtered through a 0.45-μm filter to remove large aggregates. A series of concentrations was created with different suspensions: 0 mmol L⁻¹, 0.1 mmol L⁻¹, 0.01 mol L⁻¹ and 0.001 mol L⁻¹. For the CaCl₂ experiment, six different concentrations were used 0, 1, 2, 4, 6 and 8 mmol L⁻¹. In all cases, the suspension was vortexed for 1 min when the salt solutions were added. By titrating with 0.1 mol L⁻¹ HCl and NaOH, the nano-TiO₂ suspensions (10 mg L⁻¹) prepared in buffer solutions were adjusted to pHs in the range of approximately 5-9.

Analysis

The morphology, structure and particle sizes of nano-TiO₂ in water were determined by transmission electron microscopy (TEM) on a JEOL (JEOL, Tokyo, Japan) operating at 100 KV. TEM samples were prepared by dropping 5 μL of the nano-TiO₂ suspension onto the 200 mesh copper grids (a continuous carbon film coating) and air-dried at room temperature. Particle size distributions and the hydrodynamic radius of nano-TiO₂ were determined by dynamic light scattering (DLS) at a 90° angle using a Zetasizer Nano ZS (Malvern Instruments, UK). To ensure a representative sample for the aliquot subjected to DLS analysis, suspensions were agitated vigorously using a vortex mixer, for ~10 s, 2 min prior to removing an aliquot for DLS analysis. Suspensions were stored at room temperature between DLS measurements. The point of zero charge (PZC) was determined by electrophoretic mobility measurements. Quantifications of nano-TiO₂ were carried out using an inductive coupling plasma emission spectrophotograph (5300DV, Plasma1000). To determine the apparent characteristics, image analysis was carried out using an atomic force microscope (AFM) (BioScope, Veeco). The particle size distribution was determined according to DLS with particle size and potential analysis apparatus (PALS/90P, Brookhaven) (Zhang et al. 2008), and the test temperature was controlled at 23 ± 2 °C. The electrophoresis mobility was determined using the nanoSizer (Malven, ZETASIZE).

Batch test

Batch tests to evaluate the aggregation stability under different conditions were performed using nano-TiO₂ solution with a concentration of 10 mg L⁻¹. The pH was adjusted with HCl and NaOH to the required value. To test the effects of DOM, nano-TiO₂ (10 mg L⁻¹) was added to DOM solution of concentrations of 0, 1, 2, 4, 6, 8 and 10 mg L⁻¹, and the stability was expressed through the variation of particle size distribution and zeta potential. The solution was adjusted with NaNO₃ to maintain the ionic strength of 1 mmol L⁻¹. The pH was stabilized at 7.0 ± 0.2 with HCl and NaOH. The effect of Ca²⁺ was carried out in a constant temperature oscillator at 25 °C for 24 h to reach adsorption equilibrium. After the adsorption reaction, the particle size distribution and the apparent characteristics were analyzed (Zhang et al. 2008).

RESULTS AND DISCUSSION

Effects of pH on the stability of nano-sized titanium dioxide

Variation of zeta potential with pH value is presented in Figure 1. It was found that the zeta potential of the surface of nano-TiO₂ particles varied with pH. Under low pH...
conditions, the adsorption of protons by hydroxyl on the surface of nano-TiO₂ mainly contributed to the positive charge on nano-TiO₂. On the other hand, negatively charged particles were observed due to proton loss at high pH values. The relationship between the protons and pH is expressed in Equations (1) and (2), in which the Ti-OH is the surface hydroxyl of nano-TiO₂. The zero potential point location was between pH 6 and 7, and the absolute value of potential increased as the pH deviated from the isoelectric point.

\[
\text{Ti-OH} + H^+ \rightleftharpoons \text{Ti-OH}_2^+ \quad (1)
\]

\[
\text{Ti-OH} - H^+ \rightleftharpoons \text{Ti-}\text{O}^- \quad (2)
\]

Figure 2 shows the variation in the diameter of nano-TiO₂ at different pH values. The average diameter of nano-TiO₂ varied between 147.9 and 231.4 nm at pH values from 5 to 9. The average diameter was greatest at pH 6.0, and the absolute zeta potential value was lowest. At other pH values, the diameter decreased as absolute zeta potential value increased, suggesting that the diameter varied inversely with the absolute zeta potential value. This result indicated that aggregation stability was increased with the charge at the surface of nano-TiO₂. Figure 3 shows AFM scanning images of nano-TiO₂ under different pH values (scanning range: 1 μm × 1 μm). The image analysis was in accordance with the above results. At pH 6, the distribution of nano-TiO₂ particles was relatively intensive and the diameter of the aggregated particles was relatively large. In contrast, the diameter was smaller at pH values of 8 and 9, and a medium diameter could be found in the low pH condition. The distribution of nano-TiO₂ aggregates was most intense as a result of a low zeta potential value and electrostatic repulsion.

**Effect of DOM on stability of nano-TiO₂**

It is well known that DOM is a common organic pollutant in the aquatic environment, and could influence the stability of nano-TiO₂. Figure 4 presents the variation of zeta potential under different DOM concentrations. The addition of DOM to nano-TiO₂ suspensions induced enhanced colloidal stability. The zeta potential of nano-TiO₂ (10 mg L⁻¹) was −16 and −37.5 mV under no and 1 mg L⁻¹ DOM, respectively, but no obvious variation was found under other conditions. This may be due to the DOM with a negative charge being adsorbed onto nano-TiO₂ surfaces and imparting negative charges to them (Zhang et al. 2008).

The hydraulic radius of the nano-TiO₂ did not exhibit variation but showed similarity at around 190 nm, as shown in Figure 5, and AFM images can also verify the DLS results (Figure 6). At pH 7, the suspension was most stable. The reason for this is likely that when pH is greater than the PZC (pH 6.2), the surface of nano-TiO₂ has a net negative charge due to the increasing fraction of total surface sites present as −TiO−. DOM contains many organic functional groups such as carboxyl, phenol, hydroxyl, amine and quinine groups, which provide a number of different potential binding sites. The hydroxyl groups on the surface of nano-TiO₂ may undergo a ligand exchange reaction with the functional group on the outside of DOM. As illustrated in Equations (3) and (4), the hydroxyl groups on the surface of nano-TiO₂ form Ti-OH,
and the L- forms the weak acid group of DOM. L- as the basis ligand can exchange with the hydroxyl groups of nano-TiO₂, thereby the aggregation of particles occurs.

\[
\text{Ti-OH} + \text{L}^- \rightleftharpoons \text{Ti-L}^+ + \text{OH}^- \tag{3}
\]

\[
2\text{Ti-OH} + \text{L}^- \rightleftharpoons \text{Ti}_2\text{-L}^+ + 2\text{OH}^- \tag{4}
\]

Figure 3 shows the AFM image (1 μm × 1 μm) of DOM, nano-TiO₂ and the reaction products. The aggregation phenomenon of particles could be seen after the dosage of DOM, which resulted in an increase in the degree of aggregation and a decrease in density of aggregates. The image analysis confirmed the integrated function of static repellant and ligand exchange.
Effect of Ca\textsuperscript{2+} on stability of nano-TiO\textsubscript{2}

The effect of divalent cations was investigated in a CaCl\textsubscript{2} suspension by adjusting a series Ca\textsuperscript{2+} concentration to 1, 2, 4, 6, 8 mmol L\textsuperscript{-1}. The observed influence of Ca\textsuperscript{2+} on the stability of nano-TiO\textsubscript{2} was obvious. The absolute value of zeta of nano-TiO\textsubscript{2} with DOM (10 mg/L) suspension decreased significantly (Figure 7). The explanation is that the Ca\textsuperscript{2+} neutralized the negative charge of the overall suspension. More Ca\textsuperscript{2+} neutralized more negative charges, resulting in a less negative charge and lower absolute values of zeta potential. Thus, aggregation occurred with the incremental addition of Ca\textsuperscript{2+}, from 190 nm (0 mmol L\textsuperscript{-1}) to the micron level, 3.40 μm (1 mmol L\textsuperscript{-1}), 5.21 μm (2 mmol L\textsuperscript{-1}), 6.32 μm (4 mmol L\textsuperscript{-1}), 8.78 μm (6 mmol L\textsuperscript{-1}) and 11.44 μm (8 mmol L\textsuperscript{-1}) (Figure 8(a), (b)).

The reason for this might be that the positive charge of the Ca\textsuperscript{2+} neutralized the electronegativity of nano-TiO\textsubscript{2} and DOM, and the zeta potential was negatively correlated to the concentration of Ca\textsuperscript{2+}. The diameter distribution of the reaction products between nano-TiO\textsubscript{2} and DOM under different Ca\textsuperscript{2+} concentrations showed this (Figure 8); the diameter of DOM and nano-TiO\textsubscript{2} aggregates increased obviously with the concentration of Ca\textsuperscript{2+}, and the diameter was at the micrometer level when the Ca\textsuperscript{2+} concentration was over 2 mmol L\textsuperscript{-1}. The diameter increased from 190 nm for the initial product to 1,144 nm at a Ca\textsuperscript{2+} concentration of 8 mmol L\textsuperscript{-1}.

The image analysis of the reaction products of DOM and nano-TiO\textsubscript{2} under different Ca\textsuperscript{2+} concentrations by AFM within the range of 2 μm × 2 μm is shown in Figure 9.
An increase in the diameter of aggregates was found after the reaction of TiO$_2$ and DOM, and the dosage of Ca$^{2+}$ promoted the adsorption and aggregation of TiO$_2$ and DOM. The neutralizing function of Ca$^{2+}$ accelerated the integration of TiO$_2$ and DOM, which reduces the stability of the particles.

**CONCLUSION**

Zeta potential varied obviously with pH value, and the zero potential point was between the pH values of 6 and 7; the variation of nano-TiO$_2$ aggregates diameter was insensitive to pH and was in negative relation to the absolute zeta potential. The aggregation stability was determined by the particle size and the charge of nano-TiO$_2$.

The zeta potential of nano-TiO$_2$ was reduced in the presence of DOM. The variation of TiO$_2$ aggregates was not obvious for both the integrated function of static repellant and the ligand exchange.

The increase in the diameter of aggregates of the reaction product of TiO$_2$ and DOM was obvious in the presence of Ca$^{2+}$. The neutralizing function of Ca$^{2+}$ accelerated the integration of TiO$_2$ and DOM, which will reduce the stability of the particles.

**ACKNOWLEDGEMENT**

This work was financially supported by the National Natural Science Foundation (51078102).

**REFERENCES**


First received 10 November 2012; accepted in revised form 11 February 2013