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Influences of anion concentration and valence on dispersion and aggregation of titanium dioxide nanoparticles in aqueous solutions

Huijun He[1,2], Yan Cheng[1,2], Chunping Yang[1,2,3,*], Guangming Zeng[1,2], Canyao Zhu[1,2], Zhou Yan[1,2]

1. College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China. E-mail: hehuijun@hnu.edu.cn
2. Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China
3. Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling, College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou, Zhejiang 310018, China

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ABSTRACT

Dispersion and aggregation of nanoparticles in aqueous solutions are important factors for safe application of nanoparticles. In this study, dispersion and aggregation of nano-TiO_2 in aqueous solutions containing various anions were investigated. The influences of anion concentration and valence on the aggregation size, zeta potential and aggregation kinetics were individually investigated. Results showed that the zeta potential decreased from 19.8 to −41.4 mV when PO_4^{3-} concentration was increased from 0 to 50 mg/L, while the corresponding average size of nano-TiO_2 particles decreased from 613.2 to 540.3 nm. Both SO_4^{2-} and NO_3^- enhanced aggregation of nano-TiO_2 in solution. As SO_4^{2-} concentration was increased from 0 to 500 mg/L, the zeta potential decreased from 19.8 to 1.4 mV, and aggregate sizes increased from 613.2 to 961.3 nm. The trend for NO_3^- fluctuation was similar to that for SO_4^{2-} although the range of variation for NO_3^- was relatively narrow. SO_4^{2-} and NO_3^- accelerated the aggregation rapidly, while PO_4^{3-} did so slowly. These findings facilitate the understanding of aggregation and dispersion mechanisms of nano-TiO_2 in aqueous solutions in the presence of anions of interest.

Introduction

In the past decades, nanomaterials were globally applied. The societal impact of nanotechnology has been anticipated to be as drastic as that of the first industrial revolution (Keller et al., 2013). Materials including nano-Fe, nano-Au, nano-TiO_2, and carbon nanoparticles could be prepared at nanoscale and have been widely applied in herbicides, cosmetics, electronics, wastewater treatment, air remediation, *etc.* (Yao et al., 2015; Lv et al., 2012; Puddu et al., 2010). However, production and application of nanomaterials have led to the inevitable introduction of nanoparticles into the environment.

Nano-TiO_2, one of the most utilized nanomaterials, is used in the production of cosmetics, catalysts and groundwater remediation (Robichaud et al., 2009; Yu et al., 2010; Zhang et al., 2015; Lalhriatpuia et al., 2015; Bet-moushoul et al., 2016). Nano-TiO_2 could be hazardous when released into the environment (Jin et al., 2008), causing toxicological risks to the ecosystem and human health due to its large specific surface area, nanoscale size, photocatalysis and chemical structure (Boxall et al., 2007; Chen et al., 2015). When lights were available, nano-TiO_2 would

* *Corresponding author*. E-mail: yangc@hnu.edu.cn (Chunping Yang).

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produce reactive oxygen species that could induce oxidative damage to microorganisms, crustaceans, and so on (Adams et al., 2006; Long et al., 2006). Delay of daphnia magna growth and even death *via* bioaccumulation could also be observed in *Daphnia magna* (Zhu et al., 2010). Neurovirulent damage on mice hippocampal neurons could be caused by nano-TiO_2 *via* induction of cavitation (Wang et al., 2007). Furthermore it was found that the respiratory system was affected, resulting in sublethal affects when nano-TiO_2 coexisted with Na^+ and K^+ in rainbow trouts (Federici et al., 2007). The concentration of 2 mg/L of nano-TiO_2 exacerbated the toxicity of tributyltin to abalone embryos (Zhu et al., 2011). In summary, close attention should be paid to the impact of nanomaterials on human health and the ecosystem.

The stability, toxicity and ultimate fate of nanoparticles in the water environment are affected by the aggregate size and suspension time, which are related to ionic strength, valence of cations, pH, surfactants and natural organic matters (NOMs) (Zhang et al., 2012; Mukherjee and Weaver, 2010). Humic acid, which is one kind of NOMs, would be adsorbed onto nano-TiO_2 which could consequently become more stable and thus more toxic in water (Yang et al., 2013). In general, surfactants could improve the transport of nano-TiO_2 in aqueous solutions. Anionic surfactants led to a smaller aggregate size than non-ionic surfactants (Godinez and Darnault, 2011). Surface potential could be affected by pH, and the aggregate size increased when the zeta potential approach the point-of-zero-charge of the nanoparticles (Dunphy-Guzman et al., 2006). It was also observed that high ionic strength and low total organic carbon (TOC) led to larger aggregate size for nano-TiO_2, while high TOC resulted in more stable nanoparticles in aqueous solutions (Keller et al., 2010). Divalent Ca^{2+} and Mg^{2+} ions led to larger nano-TiO_2 aggregate sizes than monovalent ions such as Na^+, and the coexistence of Ca^{2+} and NOMs increased the particle size due to the presence of specific Ca^{2+}-NOM bridges (Romanello and Cortalezzi, 2013). The observed aggregation could be explained by the Darjaguin–Landau–Verwey–Overbeek (DLVO) theory, which states that the aggregation and stability of colloidal particles is determined by Van der Waals interactions and electrical repulsive forces (Elimelech et al., 1998). When the Van der Waals force is larger than the corresponding electrical repulsive force, aggregation prevails; otherwise, the particles tend to disperse.

Recently, the effects of cations on aggregation and dispersion of nanoparticles have been reported (Romanello and Cortalezzi, 2013; Chen et al., 2006, 2007). However, little information regarding the effects of anions on the aggregation of nano-TiO_2 is available. In this context, the objectives of this study are to investigate the effects of various anions on the aggregation size and zeta potential of nano-TiO_2 in aqueous solutions. Results and conclusions are supposed to lead to a better understanding of the performance and kinetics of nano-TiO_2 aggregation in aqueous solution.

1. Materials and methods

1.1. Preparation of nano-TiO_2 dispersions

TiO_2 (anatase) nanoparticles with an average particle size of 5–10 nm and over 99.8% purity employed were procured from Aladdin Chemistry Co. Ltd.

Stock solutions of anions were prepared with ACS grade reagents and ultrapure water. The three stock solutions prepared were 2500 mg/L NO_3^-, 2500 mg/L SO_4^{2-}, and 100 mg/L PO_4^{3-}. Fifty milligrams per liter nano-TiO_2 particles were dispersed in different solutions containing NO_3^-, SO_4^{2-}, or PO_4^{3-}. Of them, 50 mg/L nano-TiO_2 dispersions were mixed with 1.0, 3.0, 50, 200 and 500 mg/L NO_3^-; 1.0, 3.0, 50, 200 and 500 mg/L SO_4^{2-}; 0.5, 1.0, 3.0, and 50 mg/L PO_4^{3-} by addition of stock solutions. Control experiments were also carried out in parallel.

To evaluate the dispersion characteristics of nano-TiO_2 particles, 50 mL of a dispersion was first filled in a tapered bottle (100 mL). Then, all dispersions were sonicated in a sonicator (Nishang Ultrasonics Company, Shanghai, China) to disperse the solutions. Sonication was performed at a ultrasonic power of 100 W at a frequency of 40 kHz, with a period of 30 min, and at 25°C. After sonication, the zeta potential and size of the dispersions were measured.

All samples were left without adjustment of pH except for experiments in which the pH value of point-of-zero-charge was examined.

1.2. Characterization of particles

Dynamic Light Scattering (DLS) for the measurement of the zeta potential and particle size was carried out using a Nano ZS90 Malvern Zetasizer (Malvern Instrument, Worcestershire, UK) (Li and Sun, 2011; Tkachenko et al., 2006; Badawy et al., 2010). The zeta potential values were calculated from electrophoretic mobility using the Smoluchowski model (Buttner et al., 2010), and particle sizes (average hydrodynamic diameter) was obtained from the diffusion coefficiency using the Stokes–Einstein equation (Hsiao and Huang, 2011). The average of 30 measurements was taken to determine the zeta potential value. Particle size was measured once for every group. The Nano ZS90 Malvern Zetasizer was operated for 60 sec at 25°C to equilibrium. Disposable folded capillary cells and polystyrene cuvettes were employed to measure the zeta potential and size of particles, respectively.

When the effect of anion concentration on the aggregation of nano-TiO_2 was evaluated, measurements of the zeta potential and size of particles were performed within seconds after a dispersion was prepared.

When the effect of dispersion time was examined, the zeta potential and particle size was measured at a set time after a dispersion was completed.

When the aggregation kinetic of a dispersion was studied, particle size was measured immediately after a dispersion was carried out, and each sample was measured 30 times with an interval of 60 sec.

2. Results and discussion

2.1. Initial characterization of particles in suspension

Initial characterization of the particles in a suspension was studied at 50 mg/L of nano-TiO_2. The values of pH of nano-TiO_2 suspensions were adjusted to be 1.0, 3.0, 5.0, 7.0, 9.0, and 11.0, respectively, using 1.0 mol/L NaOH and 1.0 mol/L HCl. Then, the zeta potential was measured immediately after the

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