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The effect of inorganic ions on the aggregation kinetics of lab-made TiO_2 nanoparticles in water

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ABSTRACT

Metal oxide nanoparticles released from nanotechnology-based industries have attracted more attention recently because of their potentially hazardous effect to humans and the ecosystem. The aggregation of nanoparticles has a great influence on their fate in the environment and is relevant to their potential toxicities. In this study, we synthesized stable TiO_2 nanoparticle suspension and investigated their distinct aggregation kinetics in the presence of various inorganic ions. Different concentrations of salts (NaCl, $CaCl_2$ and Na_2SO_4) were chosen to represent various environmental solutions. The particle size of TiO_2 nanoparticles increased when ionic concentrations went up. The stability of TiO_2 nanoparticles in water is also affected by combinations of salts and ionic strength. For our lab-made TiO_2 nanoparticles, it was easier to form aggregates in the presence of anions than in the presence of cations. Furthermore, divalent ions were better than monovalent ions in promoting aggregation formation. The attachment efficiencies of TiO_2 aggregates were constructed based upon the aggregation kinetics. The critical coagulation concentration values for our lab-made TiO_2 nanoparticles were higher than previously reported. The aggregation kinetics fit the Derjaguin–Landau–Verwey–Overbeek theory well; that is, divalent anions neutralized the nanoparticle surface charge and promoted aggregate formation more efficiently than the monovalent ones did. Our results indicated that the ionic concentration and ionic type required for the aggregation of TiO_2 NPs are critical. These factors should be taken into account for interpreting the behavior of NPs and for developing strategies to remove NPs from the aquatic environment.

1. Introduction

Nanoparticles (NPs) have been used in many consumer goods due to their lower cost and higher efficiency. The total revenue from products incorporating nanotechnology was estimated to be around US$1 to 2.5 trillion in 2015 (Lux Research, 2009; Roco, 2011). The rapid increase in the production and usage of engineered NPs leads to a high risk of human exposure to these materials in the natural environment (Mueller and Nowack, 2008). NPs may cause various toxic effects due to the interaction of NPs at biological interfaces and the penetration of NPs into organisms (Kahru et al., 2008; Navarro et al., 2008; Oberdörster, 2004; Wiesner et al., 2006). Recent studies are intended to understand the properties, fates and transformations of engineered NPs in environments. The type and concentration of NPs, as well as geographic properties, such as chemical compositions and concentration at specific locations, could affect the stability, transportation and distribution of NPs (Domingos et al., 2009a; Keller et al., 2010; Nowack and Bucheli, 2007). The fate of NPs in the environment is relevant to its effects on human health and the ecosystem (Gao et al., 2009).

TiO_2 NPs are the most prevalently manufactured nanomaterials. They have been widely used in consumer goods, such as antibiotic agents, ultraviolet blockers, and cosmetics as well as in various applications, such as solar cells, memory devices, and environmental catalysts. From 1980 to 2008, there were over 12 thousand studies related to this material, far more than other types of NPs (Kahru et al., 2008). Based upon the substance flow analysis, the concentration of several engineering NPs in the environment of Switzerland was calculated and TiO_2 NP was the highest in water and soils among these commonly used NPs (Mueller and Nowack, 2008). The pH_{pzc} of TiO_2 is between pH 4–7 (Ishikawa et al., 2005; Machesky et al., 1998; Ridley et al., 2006; Yang et al., 2009). Therefore, it is easy to aggregate in natural water bodies, in which the pH value is about pH 6–8. Such characteristics make TiO_2 NPs easy to deposit with short transport distance (Lecoanet et al., 2004; Solovitch et al., 2010). For dry commercial TiO_2 NP powders, aggregates formed once they entered into water. Only around 200 nm TiO_2 NP particles can be obtained by using ultrasonic method to disaggregate large aggregates (Tso et al., 2010; Zhang et al., 2008a). Alternatively, with organic acids (Baalousha, 2009; Domingos et al., 2009b; Ghosh et al., 2008; Johnson et al., 2007; Mudunkotuwa

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and Grassian, 2010; Yang et al., 2009), polymers (Wang et al., 2006), surfactants (Veronovski et al., 2009) or natural organic matter (Keller et al., 2010) in solutions, TiO_2 NPs could be stabilized. Right now, many commercial stabilized NP suspensions are produced. Furthermore, for the industrial wastewater or the effluent from the NP manufacturing factories, the pH could be different from neutral. TiO_2 NPs could keep their nanoscale in that wastewater or effluent in their synthesized pH conditions. Therefore, it is important to understand the stability and transport efficiency of the stabilized TiO_2 NPs in their effluent, which is relative to its environmental toxicity.

Ionic composition and ionic strength are two other important factors that affect the stability of TiO_2 NPs (French et al., 2009; Mukherjee and Weaver, 2010), as well as other NP materials, such as fullerene, zero-valent iron, or ZnO (Chen and Elimelech, 2006; Saleh et al., 2008a; Zhang et al., 2008a, 2008b). Higher concentrations of NaCl or higher valence of ions (calcium ion rather than sodium ion) promoted the aggregation of TiO_2 NPs due to the increase in ionic strength (French et al., 2009; Mukherjee and Weaver, 2010). If the ionic strength was the same, counter ions (potassium ion vs sodium ion) in smaller hydrated radius more effectively neutralize the negative surface charge of NPs allowing them into aggregates (Mukherjee and Weaver, 2010). Although the influence of ions on the aggregation of TiO_2 have been discussed in the above reports, the effect of anions on the aggregation of positively charged TiO_2 NPs has not yet been identified. Theoretical statements for the colloidal forces which govern NP deposition and aggregation have been proposed; quantitative approaches to evaluate the behaviors of NPs have also been summarized (Petosa et al., 2010). However, we still know little about the exact fate of stabilized TiO_2 NPs in their effluent under environmental conditions.

In this study, the effect of common electrolytes on the aggregation of lab-made TiO_2 NPs at their original pH conditions was investigated. The aggregation kinetics of TiO_2 NPs was analyzed in aqueous solutions containing various concentrations of electrolytes. Combining experimental measurements and theoretical calculations, the critical coagulation concentrations for the aggregation and interaction energy between particles were determined. These findings enable us to understand more about the stability and aggregation of the stabilized TiO_2 NPs. These results facilitate the predictions about their fate and toxicity in the environment and the design of NPs removal strategy.

2. Materials and methods

2.1. Synthesis process and the characteristic of stable TiO_2 NP suspensions

The stable TiO_2 NP suspensions were prepared using titanium tetrachloride and benzyl alcohol as described previously (Niederberger et al., 2002). 0.75 mL titanium tetrachloride was slowly added into 15 mL anhydrous benzyl alcohol under magnetic stirring for 10 min at room temperature. The mixed solution was poured into a 3-trifluoromethyl-4-nitrophenol microwave reactor and then heated to 100 °C within 15 min by 200 W microwave and kept at 100 °C for 2 h by 120 W microwave. The obtained TiO_2 NP suspensions were washed twice with ethanol and acetone and then dispersed in water. Pure water used in this study was double distilled and deionized with a Milli-Q water purification system (Millipore). All suspension samples were used only once.

The distribution of TiO_2 particle size in solution was measured by Zetasizer Nano ZS (Malvern, MA) dynamic light scattering (DLS) at 25 °C with the laser beam at 633 nm. The autocorrelation function was used to measure the intensity of scattered light, which was fluctuated because of the Brownian motions of particles. The average hydrodynamic diameter size and the particle distribution were calculated from the autocorrelation function. The surface area of the TiO_2 particle was measured by a surface area analyzer (ASAP 2020, Micromeritics Corp., USA). Images of the NPs were captured digitally by transmission electron microscopy (TEM, JEM-200CX, JEOL Corp., Japan). X-ray diffraction (XRD) was carried out using an X-ray diffractometer (MXP18, MAC science). The crystalline phase of NP was presented and the crystalline size was calculated by the Debye–Scherrer equation. The electrophoresis mobility of NPs was also measured by Zetasizer Nano. The zeta potential was obtained from the measured electrophoresis mobility according to the Helmholz–Smoluchowski equation.

2.2. Aggregation experiments under various salt solutions

The aggregation experiments were conducted under around pH 3 and 25 °C in which the TiO_2 concentration was 1 g/L. This pH value is optimal for TiO_2 NP suspension. Three electrolytes including NaCl, $CaCl_2$ and Na_2SO_4 were obtained from Acros Chemical. The concentrations of electrolytes were within the following range: NaCl, 0 to 1000 mmol/L, $CaCl_2$, 0 to 200 mmol/L, and Na_2SO_4, 0 to 250 mmol/L. After the electrolyte solutions were added into TiO_2 solutions, the mixtures were vortexed for 1 min and DLS analysis was performed at different time points.

2.3. Determination of NP aggregation kinetics

Based on the aggregation kinetic experiments, the aggregation rates were estimated. The attachment efficiency, α, of TiO_2 NP aggregates at different ion strengths was estimated from the aggregation rate and can be described by the following equation (Chen et al., 2006).

$$\alpha = \frac{k}{k_{fast}} \tag{1}$$

The k value indicated the aggregation rate constants at different salt strengths and the k_{fast} value indicated the fastest aggregation rate constant observed at a specified salt concentration. The attachment efficiency, ranging from 0 to 1, stood for the degree of NP aggregation at different electrolyte concentrations. Based on the aggregation kinetics regimes in the plot of the attachment efficiencies versus salt concentrations, the crossover of the slope of attachment efficiencies dependent on ion concentrations ($\alpha<1$) and the plateau independent of ionic concentrations ($\alpha \sim 1$) were determined. The ion concentration of the crossover represented the critical coagulation concentration (CCC).

2.4. Net NP interaction energy

The attractive forces and electrostatic interaction energies between NPs were estimated by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Guzman et al., 2006). The van der Waals interaction (V_{VDW}) was calculated by Eq. (2) (Elimelech et al., 1995; Hiemenz and Rajagopalan, 1997):

$$V_{VDW} = \frac{-A}{6}\left[\frac{2a^2}{s(4a+s)} + \frac{2a^2}{(2a+s)^2} + \ln s\frac{(4a+s)}{(2a+s)^2}\right] \tag{2}$$

where a is the particle radius, A is the Hamaker constant, and s is distance between the surface of two interacting NPs. Repulsive electrostatic interaction (V_{ES}) was calculated by Eq. (3):

$$V_{ES}(J) = 2\pi\varepsilon_r\varepsilon_0 a\zeta^2 \ln\left(1+e^{-ks}\right) \tag{3}$$

where ε_r is the relative dielectric constant of the liquid, ε_0 is the permittivity of the vacuum, a is the particle radius, ζ is the zeta potential, and k_s is the inverse Debye length.