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A case study of aggregation behaviors of titanium dioxide nanoparticles in the presence of dodecylbenzene sulfonate in natural water

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ABSTRACT

The present work aims to ascertain the mechanisms of surfactant (dodecylbenzene sulfonate; DBS) effects on the aggregation behaviors of TiO_2 nanoparticles (TiO_2-NPs) in natural water samples. Aggregation experiments were conducted at a TiO_2-NPs concentration of 10 mg/L in deionized water and in natural water samples *via* dynamic light scattering and Zeta potential determination. Average attachment efficiency was calculated to compare the aggregation behaviors of nanoparticles in the two aqueous media. Results showed that the effects of DBS on aggregation could be interpreted by both Derjaguin–Landau–Verwey–Overbeek (DLVO) and non-DLVO mechanisms. In natural water samples, aggregation did not occur rapidly and was able to develop slowly under all conditions, and the roles of DBS were obvious at high DBS concentration owing to the impacts of inherent components of natural water samples, such as colloids and natural organic compounds. Future aggregation studies should concentrate on multi-factor, multi-colloidal and dynamic aspects under similar environmental conditions.

Introduction

Recently, nanomaterials have attracted growing attention for a wide range of applications such as electronic devices, pharmaceuticals, cosmetics, energy and environmental technologies (Suresh et al., 2013) due to several unique advantages such as quantum effects, surface effects, and small-size effects (Anil Kumar and Khan, 2010). It has been estimated that nanomaterial production for sliver and titanium dioxide is 500 and 50,000 ton per year, respectively (Kunhikrishnan et al., 2015). Inevitably, there will be an ever increasing amount of nanoparticles entering into environment, both intentionally and incidentally. For example, the concentration of nanomaterials was predicted to range from 4 ng/L (fullerenes) to 4 μg/L (titanium dioxide nanoparticles, TiO_2-NPs) in sewage treatment effluents (Kunhikrishnan et al., 2015), and these nanoparticles would be eventually discharged into surface water. Since the toxicity of nanoparticles is generally dependent on the size, structure and surface properties thereof (Aruoja et al., 2009; Suresh et al., 2013; Choi and Choy, 2014), the environmental transport and transformation of these nanomaterials will be of concern, especially in aqueous environments.

Although the physiochemical properties of nanoparticles differ widely, they may behave in similar manners in aqueous solutions in terms of aggregation, deposition, and dissolution, as well as interactions with biomacromolecules, natural organic

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matters (NOMs) and biological organisms (Lowry et al., 2012). In aqueous environments, the particle–particle interactions can lead to nanoparticle dispersion or aggregation, which may change their physicochemical properties. The aggregation of nanoparticles depends on a number of factors such as pH, ionic strength, organic matter, particle concentration, and microorganisms (Petosa et al., 2010; Batley et al., 2013). When the pH of a nanoparticle suspension approaches the point of zero charge (PZC), the nanoparticles tend to aggregate rapidly due to low surface charge and low electrostatic repulsion (Zhu et al., 2014). The incorporation of counterion species can cause the shift of zeta potential toward a lower value, hence promoting the aggregation process greatly (Shih et al., 2012; Anderson et al., 2014). Basically, the aquatic organic matters in natural water include NOMs and anthropogenic organic compounds categorized by their sources. Several studies addressed the effects of NOMs on the aggregation behaviors of nanoparticles (Thio et al., 2011; Zhu et al., 2014; Li et al., 2015), yet little attention has been paid to the latter case due to the complexities of their sources, compositions and properties.

Surfactants are commonly used to disperse nanoparticles in water solutions (Imae et al., 1991; Raja et al., 2015), and may be a kind of ubiquitous anthropogenic organic pollutant in water environments. The influence of surfactants on the aggregation and transport of a variety of nanoparticles has been investigated in previous studies (Godinez et al., 2013; Godinez and Darnault, 2011; Bai et al., 2010; Wang et al., 2012; Liu et al., 2013; Topuz et al., 2014). Godinez et al. (2013) and Godinez and Darnault (2011) examined the aggregation, transport and deposition kinetics of TiO_2-NPs in the presence of anionic (dodecylbenzene sulfonate, DBS) and non-ionic (Triton X-100) surfactants. They found that the surfactants could enhance the transport of TiO_2-NPs in saturated porous media due to electrostatic and steric repulsion forces. Bai et al. (2010) found that Triton X-series surfactants could enhance the stabilization of carbon nanotubes in water through their adsorption, thus affecting the environmental behaviors of carbon nanotubes. Wang et al. (2012) explored the enhanced stability of fullerene in the presence of Tween 80 (nonionic surfactant). On the other hand, surfactants may also induce the aggregation of nanoparticles. For instance, silica nanoparticles can be aggregated by the cationic surfactant cetyltrimethylammonium bromide through depletion flocculation or volume-restriction and the hydrophobic effect (Liu et al., 2013). However, these studies solely concentrated on the effects of surfactants in deionized water (DI-water) or synthetic natural water. To the best of our knowledge, few studies (Adeleye and Keller, 2014; Doyle et al., 2014; Chekli et al., 2015) have reported on the actual aggregation behaviors of nanoparticles in natural water environments, particularly in the presence of surfactant-like substances. Furthermore, these studies showed that the effects of surfactants on the environmental behaviors of nanoparticles depended on the surfactant type, among which anionic surfactants are the most commonly found surface-active species in natural water and chosen as the sole surfactant standard in the Chinese Environmental Quality Standards for Surface Water (NEPA, 2002). DBS is selected as the standard anionic surfactant for the detection of surface water anionic surfactants according to the Chinese NEPA (the National Environmental Policy Act) Standard Methods (NEPA, 1987), indicating their significance in natural water. Therefore, we employed DBS as the target surfactant in this study.

The present study aims to explore the influence of the anionic surfactant DBS on the aggregation behaviors of TiO_2-NPs, particularly in natural water. The aggregation of TiO_2-NPs was examined in detail at different DBS concentrations and pH in natural water samples. Furthermore, the aggregation behaviors of TiO_2-NPs in DI-water were also investigated to determine the differences in the aggregation behaviors of nanoparticles and the effects of DBS in these two aqueous media.

1. Materials and methods

1.1. Materials and chemicals

Areoxide TiO_2 P25 was supplied by Evonik Degussa Corporation (Evonik Degussa Corporation, Essen, Germany) with a purity of 99.5% (wt.%) and an average particle size of 21 nm. Sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR) and DBS (CP) were obtained from Tianjin Benchmark Chemical Reagent Co., Ltd. (Tianjin Benchmark Chemical Reagent Co., Ltd, Tianjin, China).

1.2. Characterization of TiO_2-NPs and dodecylbenzene sulfonate (DBS)

An X-ray diffractometer (D8 ADVANCE, Bruker Corporation, Karlsruhe, Baden-Württemberg, Germany), was employed to analyze the TiO_2-NPs powder, with monochromatic Cu $K\alpha$ radiation (λ = 0.15418 nm) operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ angular range of 10–90° with step sizes of 0.02° and dwell time of 0.02 sec.

The critical micelle concentration (CMC) of DBS was determined by the conductometric method (Hait et al., 2003) at 20°C in DI-water. Briefly, 1.74 g DBS powder was added into 500 mL DI-water to obtain a 10 mmol/L DBS stock solution. Then the stock solution was diluted to a series of DBS concentrations of 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, and 3.50 mmol/L. All solutions were kept in a 20°C thermostatted water bath for 20 min, then the conductivities of these solutions were measured with a conductivity meter (sension378, HACH, Loveland, Colorado, USA) immediately. The CMC of DBS is the corresponding DBS concentration of the inflection point in the conductivity–concentration curve.

1.3. Characteristics of natural water samples

Natural surface water samples were collected from the Songhua River in Harbin, China. A pH meter (FE20, Mettler Toledo, Zurich, Switzerland) and a Zeta potential tester (Zetasizer Nano Z, Malvern, Malvern Instruments, UK) were employed to measure the pH and Zeta potential of the natural water samples, respectively. An inductively coupled plasma atomic emission spectrometer (Optima 5300DV, Perkin Elmer, Waltham, Massachusetts, USA) was used to determine the contents of the main cations in the Songhua River samples. The concentrations of the main anions were detected by ion