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The effect of humic acid on the aggregation of titanium dioxide nanoparticles under different pH and ionic strengths

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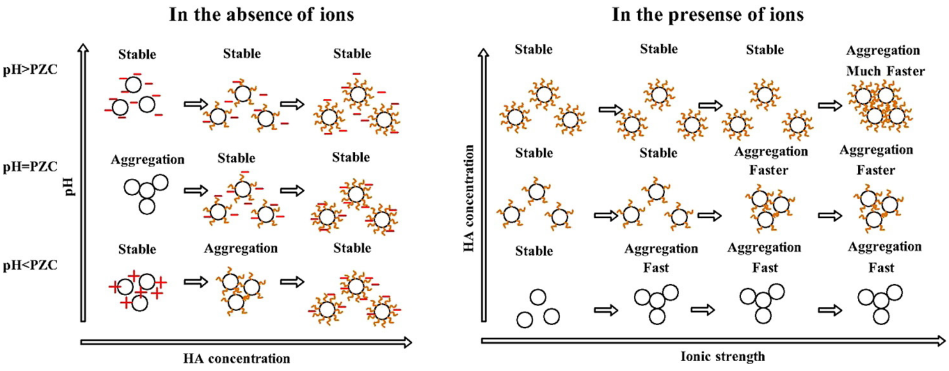
HIGHLIGHTS

- Charge neutralization was observed when pH = 4 and ionic strength is very low.
- Steric hindrance only occurs when ionic strength is lower than CCC.
- Humic acid plays a bridging effect when ionic strength is higher than CCC.

GRAPHICAL ABSTRACT



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ABSTRACT

With the increasingly widespread use of titanium dioxide nanoparticles (TiO_2 NPs), the particles' environmental impacts have attracted concern, making it necessary to understand the fate and transport of TiO_2 NPs in aqueous media. In this study, we investigated TiO_2 NP aggregation caused by the effects of humic acid (HA), ionic strength (IS) and different pH using dynamic light scattering (DLS) to monitor the size distribution of the TiO_2 NPs continuously. It was determined that HA can influence the stability of TiO_2 NPs through charge neutralization, steric hindrance and bridging effects. In the absence of IS, aggregation was promoted by adding HA only when the pH (pH = 4) is less than the point of zero charge for the TiO_2 NPs ($pH_{PZC} \approx 6$) because HA reduces the zeta potential of the TiO_2 NPs via charge neutralization. At pH = 4 and when the concentration of HA is 94.5 μg/L, the zeta potential of TiO_2 NPs is close to zero, and they reach an aggregation maximum. A higher concentration of HA results in more negatively charged TiO_2 NP surfaces, which hinder their aggregation. When the pH is 5.8, HA enhances the negative zeta potential of the TiO_2 NPs and increases their stability via electrostatic repulsion and steric hindrance. When the pH (pH = 8) is greater than pH_{pzc}, the zeta potential of the TiO_2 NPs is high (~40 mV), and it barely changes with increasing HA concentration. Thus, the TiO_2 NPs are notably stable, and their size does not grow at pH 8. The increase in the critical coagulation concentration (CCC) of TiO_2 NPs indicated that there is steric hindrance after the addition of HA. HA can enhance the coagulation of TiO_2 NPs, primarily due to bridging effect. These findings are useful in understanding the size change of TiO_2 NPs, as well as the removal of TiO_2 NPs and HA from aqueous media.

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1. Introduction

The application of nanotechnology in consumer and industrial products has increased exponentially over the past several years. Nanomaterials are widely used in herbicides, cosmetics, printers, electronics, groundwater remediation, waste water treatment, and many other applications (Keller et al., 2013; Theron et al., 2008). The toxicity of nanomaterials is determined by their size, shape, chemical structure and surface properties. It is imperative to evaluate the potential risks that these novel materials pose to the environment and human health, and the first step is to assess their mobility in the environment (Wiesner et al., 2006).

During the recent years, the potential risks of nanoparticles have raised concerns. The cytotoxicity of TiO_2 NPs has been discussed (Jin et al., 2008). It has been reported that TiO_2 NPs can cause respiratory toxicity and disturbances in metabolism (Federici et al., 2007). A single intratracheal injection of 0.1 mg nanoTiO_2 can induce severe pulmonary inflammation and emphysema (Chen et al., 2006). TiO_2 NPs can induce clastogenicity, genotoxicity, oxidative DNA damage, and inflammation (Trouiller et al., 2009). In addition, under low intensity UVR, ROS in seawater increases with increasing nano-TiO_2 concentration, which leads to increased overall oxidative stress in seawater, and causes decreased resiliency of marine ecosystems (Miller et al., 2012). Nano-TiO_2 had positive effects on root elongation in some species (Song et al., 2013). TiO_2 NPs have cytotoxic, genotoxic and hemolytic effects on human erythrocyte and lymphocyte cells in vitro and can induce a significant reduction in mitochondrial dehydrogenase activity in human lymphocyte cells (Ghosh et al., 2013). Nanoparticles can be transported in the human body, deposited in organs, transferred across cell membranes and accumulated in mitochondria, causing damage to humans (Colvin, 2003).

To some extent, the size range of nanoparticles in natural water determines their stability, toxicity, transport and ultimate fate (Zhang et al., 2008, 2012). As reported, the size of nanoparticles is related to solution chemistry, typically including natural organic matter (NOM), ions and pH, and it was also found that three nanoparticles (TiO_2, ZnO, CeO_2) can aggregate easily when the IS is high and the total organic carbon (TOC) is low; conversely, their stability is high when the TOC is high for a wide range of IS, but not at very high IS (Keller et al., 2010). NOM in aquatic systems has a significant effect on the transport and transformation of the nanoparticles, and the nanoparticles' adsorption capacity toward hydrophobic organic compounds (HOCs) will change their stability and toxicity (Adegboyega et al., 2013; Baalousha et al., 2013; Louie et al., 2013; Wirth et al., 2012; Yang et al., 2009; Zhang et al., 2013). NOM is also commonly present in ground water and surface water, although at different concentrations (Wang et al., 2010, 2011). These macromolecules can be adsorbed onto the surfaces of the nanoparticles, enhancing their stability and mobility in flowing waters (Chappell et al., 2009; Hyung et al., 2007). The adsorption capacity of the nanoparticles is related to the pH, and NOM is absorbed by the nanoparticles' surface via electrostatic adsorption and ligand exchange (mainly hydroxyl and carboxyl groups). The adsorption of NOM reduces the surface zeta potential and changes the electrostatic repulsion, which affects the nanoparticle stability (Yang et al., 2009).

Humic substances (HS) represent an active and important fraction of natural organic matter (NOM), and they play important roles in the fate and transport of pollutants (Aiken, 1985; Buffle et al., 1998; Zheng et al., 2008). HS can be categorized into three groups: fulvic acids (FAs), which are the major component and the smallest structures of HS, and are soluble at any pH; HA, which represents bigger structures that are insoluble at pH <2; and humin, which is insoluble at any pH (Jones and Bryan, 1998; Piccolo, 2001). The role of HA in nanoparticle transport is of particular interest. The fate of fullerenes (nC_{60}) and their toxic implications in natural freshwaters are affected by humic acid (Meng et al., 2013; Pakarinen et al., 2013), and humic acid is more effective than fulvic acid at stabilizing nC_{60} nanoparticles (Zhang et al., 2013). Humic acid affects the adsorption of other pollutants on the surface of multiwalled carbon nanotubes (MWCNTs) (Hou et al., 2013). Humic acid also reduces the removal of TiO_2 NPs via coagulation (Wang et al., 2013).

TiO_2 NPs are some of the most widely used nanoparticles. Most TiO_2 NPs are used for coatings, paints, and pigments as well as cosmetics (Keller et al., 2013). In 2010, over 34,000 t of TiO_2 NPs were used in coatings, paints, and pigments, and TiO_2 is by far the most significant engineered nanoparticle materials in terms of exposure, based on the estimated releases and use in the dominant applications (Keller and Lazareva, 2013). At the nanoscale, the refractive index of TiO_2 NPs is even higher; therefore, it is also used in sunscreens and cosmetics as well as paints, varnishes, and coatings (Hendren et al., 2011). The adsorption of HA increased TiO_2 NP stability in suspension, and TiO_2 NPs were more toxic in the presence of HA (Yang et al., 2013). It was demonstrated that the aggregation of TiO_2 NPs is dependent on the presence and copresence of NOM (0.2–41.1 mg/L DOC), the pH of the solution, as well as other properties, such as the IS of the solution and the presence of relevant monovalent and divalent ions (Ottofuelling et al., 2011). Zhang et al. tested the stability of TiO_2 at various DOC concentrations (1–10 mg/L NOM, equivalent to 0.406–4.06 mg/L DOC) and observed the stability in the presence of 0.4 mg/L DOC (Zhang et al., 2009). However, it is not clear if a very low concentration of NOM (e.g., <0.2 mg/L DOC) has the same effect on the stability of TiO_2 NPs; a low concentration of DOC is possible in some industrial wastewater.

The goal of this study was to study the effect of HA on the aggregation or stabilization of TiO_2 NPs under different pH and ISs. We chose three typical pH: $pH = 4$ ($pH < pH_{pzc}$); $pH = 5.8$ ($pH = pH_{pzc}$); and $pH = 8$ ($pH > pH_{pzc}$). Because TiO_2 NPs are very stable at $pH = 8$, we also measured the critical coagulation concentration (CCC) to further investigate the role of HA in the stabilization of TiO_2 NPs at high pH. Finally, to compare the different CCCs at $pH = 4$ and $pH = 8$, we studied the aggregation and sedimentation performances under high IS (>CCC).

2. Materials and methods

2.1. Titanium dioxide nanoparticles

NanoTiO_2 (rutile) was purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). As reported by the manufacturer, these nanoparticles have a diameter × length of 10 nm × 40 nm; specific surface area = 130–190 m^2/g; purity = 99.5%; and may contain up to 5 wt.% silicon dioxide as a surface coating. In our recent publication (Qi et al., 2013), we used scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images to characterize the size and shape of the TiO_2 NPs. The primary size of the TiO_2 NPs is within the reported range. The pH_{PZC} of the TiO_2 NPs was measured using a Malvern Zetasizer (Nano ZS 90, UK). It was found that the pH_{PZC} of the TiO_2 NPs is ~6 (Fig. S1). A 1-g/L TiO_2 NP stock suspension was prepared by weighing an appropriate amount of dry powder, mixing it with deionized water, and sonicating the suspension for 20 min (Qi et al., 2013). The TiO_2 NP suspension was added into a small glass bottle and dispersed using a Nishang Ultrasonics SY-180 (power, 180 W, nominal frequency, 40 kHz, Shanghai, China). In order to control water temperature inside the sonicator, circulating cooling water was used, which maintained the water temperature at 19 °C. Each ultrasound time was 60 s, and interval time was 5 s. Our previous experiments indicated that this method is able to disperse the TiO_2 NPs to meet the requirement for the following tests. A fresh stock suspension was prepared daily.

2.2. Humic acid

The humic acid was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. An HA stock solution was prepared by dissolving a certain amount of HA powder into deionized water, adjusting the pH to 11 by adding 0.1 M NaOH, and then stirring the solution at 600 rpm