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Influence of aggregation on nanoscale titanium dioxide ($nTiO_2$) deposition to quartz sand

Zhong Tang, Tao Cheng*, Leanne M. Fisher-Power

Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland and Labrador, A1B 3X5, Canada

HIGHLIGHTS

- $nTiO_2$–clay aggregates formed when $nTiO_2$ & clay colloid carried opposite charges.
- $nTiO_2$ & $nTiO_2$–clay aggregates may deposit onto quartz sand.
- Deposition occurred via electrostatic attraction or secondary minimum.
- Humic acid prevented aggregation & deposition under most conditions.
- Humic acid may facilitate deposition via Mg^{2+} bridging of $nTiO_2$ & metal oxides.

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ABSTRACT

Although extensive research has been conducted to investigate $nTiO_2$ aggregation and deposition, effects of aggregation on concurrent/subsequent deposition of $nTiO_2$, which has important implications to the fate and transport of $nTiO_2$ in groundwater, has received only limited attention. The objective of this study was to investigate how pH, dissolved organic matter (DOM), and valence of background solution cation influence aggregation and concurrent/subsequent deposition of $nTiO_2$. Experiments were performed to examine $nTiO_2$ aggregation and deposition onto quartz sand with co-present illite, kaolinite, and montmorillonite colloids under various geochemical conditions. Results showed that $nTiO_2$ formed hetero-aggregates (i.e., $nTiO_2$-clay aggregates) at low pH when $nTiO_2$ and clay colloids carried opposite charges, and the hetero-aggregates may either deposit or remain suspended depending on their interactions with quartz sand and Fe/Al oxyhydroxide coatings. Deposition of $nTiO_2$ and/or $nTiO_2$-clay aggregates occurred as a result of electrostatic attraction, secondary minimum, and potentially Mg^{2+} bridging. Humic acid prevented $nTiO_2$ aggregation and deposition under most conditions. In $MgCl_2$ solutions, however, it facilitated deposition by adsorbing to $nTiO_2$ and Fe/Al oxyhydroxides, thereby enabling Mg^{2+} bridging. This study demonstrated the important and complex roles of pH, DOM, cation valence, and clay colloids in controlling aggregation and subsequent deposition of $nTiO_2$.

1. Introduction

Nanoscale titanium dioxide particle ($nTiO_2$) is a widely used engineered nano-material and extensive research has been conducted to understand its fate and transport in the environment due to the potential risks $nTiO_2$ may pose to ecosystems and human health (Skocaj et al., 2011). Deposition is a primary process that controls $nTiO_2$ transport in groundwater (Godinez and Darnault, 2011; Cai et al., 2014), by which $nTiO_2$ is attached to sediment grains and removed from water. Aggregation is another important process that influences $nTiO_2$ transport, by which smaller particles are attracted to each other to form larger aggregates that are susceptible to gravity sedimentation and physical straining (Chen et al., 2011).

It is well established that water chemistry and components could have remarkable influence on $nTiO_2$ aggregation and deposition. While neutral pH, high ionic strength, and multivalent cations are found to promote homo-aggregation of $nTiO_2$ (Chen et al., 2011; Loosli et al., 2015; Wu and Cheng, 2016; Tang and Cheng, 2018), dissolved natural organic matter (DOM) normally hinders $nTiO_2$ aggregation via absorbing onto $nTiO_2$ and intensifying the negative charges on particle surfaces (Erhayem and Sohn, 2014; Wu

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* Corresponding author.
E-mail address: tcheng@mun.ca (T. Cheng).

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and Cheng, 2016; Tang and Cheng, 2018). DOM, however, may also promote aggregation by bridging or partially neutralizing nanoparticle surface charge when DOM concentrations are low (Jung et al., 2014; Wu and Cheng, 2016).

$nTiO_2$ deposition in porous media is also affected by water chemistry. High pH, low ionic strength, and DOM generally impede $nTiO_2$ deposition, since when $pH > pH_{pzc,\ nTiO2}$ (point of zero charge, around pH 6.7 for $nTiO_2$ (Wu and Cheng, 2016)), these conditions intensify the negative charges of $nTiO_2$ and therefore increase the repulsive electrostatic forces between $nTiO_2$ and negatively-charged media surfaces. Meanwhile, low pH, high ionic strength, and multivalent cations (e.g., Ca^{2+}, Mg^{2+}) enhance deposition, as these conditions reduce the negative charges or even make $nTiO_2$ positively charged (Chen et al., 2011; Han et al., 2014; Xu et al., 2017).

Water-borne clay colloids, a common groundwater component, could have significant effect on $nTiO_2$ aggregation and deposition. Clay minerals normally carry negative charges in natural groundwater, mainly due to their constant negative structural charges (Sposito, 1984). $nTiO_2$, in contrast, have a point of zero charge near neutral pH (Tang and Cheng, 2018; Wu and Cheng, 2016), and may carry positive charges in low pH water. Under conditions where $nTiO_2$ and clay are oppositely charged, hetero-aggregates between $nTiO_2$ and water-borne clay colloids may form (Zhou et al., 2012; Valera-Zaragoza et al., 2014; Tang and Cheng, 2018). Particle surface charge is influenced by pH, ionic strength, cation valence, and DOM, therefore the formation of $nTiO_2$-clay aggregates is affected by all the above factors. It is reported that low pH, high ionic strength, and multivalent cations (e.g., Ca^{2+} and Mg^{2+}) promote the formation of $nTiO_2$-clay aggregates, whereas high pH, low ionic strength, and DOM hinders such aggregation (Tang and Cheng, 2018).

Although much work has been conducted to investigate $nTiO_2$ aggregation and deposition, most of the studies focus on a single process (i.e., either aggregation or deposition), and how $nTiO_2$ aggregation influences concurrent/subsequent deposition has only been examined in a few studies. In porous media, nanoparticles may form aggregates during transport, and the formation of aggregates could further alter nanoparticle deposition and transport (Wiesner and Bottero, 2007). Solovitch et al. (2010) found that the rate of $nTiO_2$ homo-aggregation in pore water may be comparable to that of deposition, and the formation of aggregates enhanced $nTiO_2$ deposition. However, aggregates that were not deposited sampled a smaller fraction of the pore space (i.e., size exclusion effect) and passed through the column within a shorter period of time compared to the smaller $nTiO_2$ (Solovitch et al., 2010). Cai et al. (2014) reported that in dilute NaCl solutions, the mobility of $nTiO_2$ in quartz sand column was enhanced in the co-presence of suspended bentonite and kaolinite colloids, attributed to the formation of $nTiO_2$-bentonite and $nTiO_2$-kaolinite hetero-aggregates, which have lower deposition rates and therefore higher mobility compared to $nTiO_2$. In contrast, the mobility of $nTiO_2$ in dilute $CaCl_2$ solutions with co-present suspended kaolinite colloids was lower than $nTiO_2$ alone, which was attributable to straining of the larger but less negatively charged $nTiO_2$-kaolinite aggregates (Cai et al., 2014). The aforementioned studies have shown the important implications of the aggregation process to particle deposition and transport, and provided valuable insights into the mechanisms involved in such processes; however, a number of critical issues have not been addressed. pH and DOM are two key factors that control $nTiO_2$ hetero-aggregation in the presence of clay colloids (Tang and Cheng, 2018), yet, their influence on concurrent aggregation and deposition has not been examined. In addition, valence of the background solution cations (e.g., Ca^{2+} vs. Na^+) is expected to have distinct effects at different pH, and in the absence and presence of DOM. Yet, the combined effects of cation valence, pH, and DOM on concurrent aggregation and deposition have not been investigated. Furthermore, Fe and Al oxyhydroxide coatings are common constituents of sediment grains and may substantially alter nanoparticle deposition (Liu et al., 2012). However, deposition of $nTiO_2$ homo- and hetero-aggregates has not been studied using media other than pure quartz sand.

In a previous study, we found that cation valence, humic acid, and illite colloids could remarkably affect $nTiO_2$ aggregation (Tang and Cheng, 2018). In this current work, our objective was to examine the influence of $nTiO_2$ aggregation on its subsequent deposition. Batch experiments were performed to study $nTiO_2$ aggregation and deposition onto quartz sand using dilute NaCl or $MgCl_2$ solutions as background electrolytes at different pH, with or without added DOM and clay colloids. Illite, kaolinite, and montmorillonite colloids were chosen as representative clay colloids due to their abundance in natural groundwater and the disparity in their surface charge density (Wainipee et al., 2013). In batch systems, contribution to deposition from straining (which could be important in column systems) is largely eliminated (Treumann et al., 2014), therefore, results obtained from such systems help to demonstrate how deposition is controlled by physiochemical forces. Based on experimental measurements and interaction energies calculated using DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, we proposed the mechanisms of how aggregation influenced $nTiO_2$ deposition under different geochemical conditions.

2. Materials and methods

2.1. Experiments

$nTiO_2$ aggregation and deposition. Preparation of the $nTiO_2$ suspension, HA stock solution, and clay stock suspensions, as well as pre-cleaning and characterization of the quartz sand are described in the Supporting Information (SI). Batch experiments were conducted to study $nTiO_2$ aggregation and deposition. The components ($nTiO_2$, clay particles, and HA) and their concentrations in the experiments are shown in Table 1 (Suspension type 1–8). In each experiment, clay stock suspension and HA stock solution were mixed with freshly prepared $nTiO_2$ suspension to achieve the desired concentrations. The clay and HA concentrations used in the experiments (10 and 3 mg/L respectively) were within the range of their typical concentrations in natural groundwater water. The $nTiO_2$ concentration (50 mg/L) was higher than the expected $nTiO_2$ concentrations in natural water. This higher concentration was required to facilitate sample analysis, and comparable to the $nTiO_2$ concentrations used in similar studies (Solovitch et al., 2010; Cai et al., 2014). Mixed suspensions were sonicated for 30 min with 120 W power to disperse the particles, and pH was adjusted by adding small volumes of 0.1 M NaOH and 0.1 M HCl solution.

After pH adjustment, 100 mL of suspension was immediately mixed with 75 g pre-cleaned quartz sand in 125 mL high-density polyethylene bottles, and pH was adjusted again to 5 or 9. Then the bottles were shaken at a speed of 120 rpm for 4 h on a standard analog shaker (VWR International). All the experiments were performed in duplicate. The absorbance of particle suspensions was measured at $t = 0$, 30, 60, 120, 180, and 240 min using a UV–Vis spectrophotometer (Genesys 10S UV–Vis, Thermo Scientific). During the experiment, small volumes of 0.1 M NaOH or HCl were added when necessary to maintain pH at 5 or 9. For each measurement, the bottle was removed from the shaker and let stand for 30 s to allow the sand grains to settle before a supernatant sample was taken for absorbance measurement. A wavelength of 600 nm was used for measuring the absorbance, since at this wavelength,