Fine particle attachment to quartz sand in the presence of multiple interacting dissolved components

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HIGHLIGHTS

- At pH < pH_{pzc}, phosphate has a notable impact on $nTiO_2$ attachment to sand.
- At pH > pH_{pzc}, Ca^{2+} is a key factor in $nTiO_2$ attachment to sand.
- Phosphate adsorption to $nTiO_2$ in $CaCl_2$ solution elevates with increasing pH.
- Combined effect of phosphate and Ca^{2+} is different from their individual impacts.
- Illite colloid attachment to sand is negligible and insensitive to water chemistry.

GRAPHICAL ABSTRACT
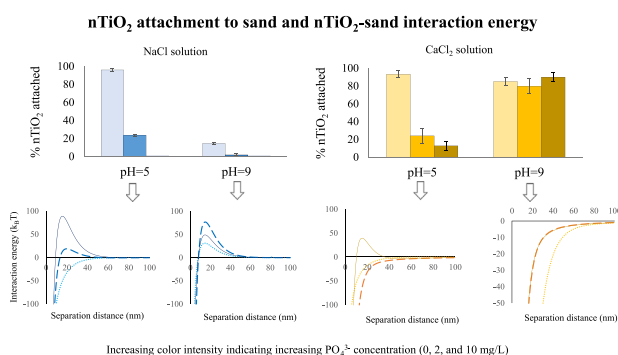
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ABSTRACT

In natural aquatic systems water chemistry is complicated and fine particles encounter multiple water components simultaneously, yet the combined effects of some multiple components on the fate and transport of these particles have not been elucidated. In this study $nTiO_2$ and illite colloid attachment to quartz sand was investigated in 1 mM NaCl and 0.5 mM $CaCl_2$ background solutions using a range of phosphate concentrations (0 to 10 mg/L) at pH 5 and 9. The results obtained from the batch experiments indicated that without using phosphate, $nTiO_2$ aggregation and attachment was strongly influenced by pH and Ca^{2+}, both of which modified $nTiO_2$ surface charges. $nTiO_2$ attachment was high in $CaCl_2$ solution at pH 9 due to attractive forces between $nTiO_2$ and sand, as well as ripening. Furthermore, phosphate adsorption to $nTiO_2$ was higher in $CaCl_2$ solution at pH 9 than that at pH 5 due to attractive forces between $nTiO_2$ and phosphate anions, and also potential surface precipitation of Ca-P minerals at pH 9. Phosphate adsorption to illite was low owing to strong repulsive forces between illite and phosphate. The effect of phosphate on $nTiO_2$ and illite attachment to sand was influenced by pH and cation valency. A decreasing trend in $nTiO_2$ attachment with phosphate addition was observed in NaCl solution at pH 5 and 9, and in $CaCl_2$ solution at pH 5; however, in $CaCl_2$ solution at pH 9, the surface charge of $nTiO_2$ reversed from negative to positive and a substantial amount of $nTiO_2$ attached to sand. Moreover, illite attachment to sand was much lower than that of $nTiO_2$ under all the conditions tested in this study. These findings are important for understanding of the fate and transport of $nTiO_2$ and illite colloids in natural aquatic systems where various anions and cations co-exist.

1. Introduction

Engineered nanoscale titanium dioxide ($nTiO_2$) has become an important functional substance that can be commonly found in many commercial products, including paints, skin care products, foods,

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pharmaceuticals, rubbers, papers, plastics, etc. (Loosli et al., 2013). It is estimated that by 2025, 2.5 million tons of nTiO$_2$ will be manufactured annually (Godinez et al., 2013; Robichaud et al., 2009). Once released to the environment, nTiO$_2$ may migrate through aquatic systems, posing a potential risk to human health and the environment (Chen et al., 2015; Du et al., 2011). nTiO$_2$, as well as clay colloids, may also attach to viruses and bacteria and influence their transport in porous media (Chowdhury et al., 2012; Gentile and Fidalgo de Cortalezzi, 2016; Syngouna and Chrysikopoulos, 2013; Syngouna et al., 2017). To predict the fate and transport of nTiO$_2$ and evaluate the consequences of nTiO$_2$ discharge into subsurface environments, it is important to comprehend the mechanisms governing nTiO$_2$ aggregation and attachment to sediment grains, since aggregation and attachment are the most important processes that immobilizes fine particles in groundwater. Previous studies have shown that water chemistry and components such as pH (Chowdhury et al., 2011), ionic strength (Godinez et al., 2013), major cations (e.g., Na$^+$, Ca^{2+}) (French et al., 2009; Akaighe et al., 2012) and anions (e.g., phosphate) (Chen et al., 2015), dissolved organic matter (DOM) (Wu and Cheng, 2016), as well as clay colloids (Cai et al., 2014) all influence the stability and attachment of engineered nanoparticles.

Clay particles including kaolinite, montmorillonite, and illite colloids are also common in soil and groundwater (Wilson et al., 2014). Among different kinds of clay minerals, illite is demonstrated to have a great capacity as an adsorbent (Xie et al., 2013), due to small particle size and good binding ability (Dror et al., 2012). Stability and aggregation of clay colloids (Jiang et al., 2012; Novich and Ring, 1984) and the impacts of clay colloids on the transport of contaminants have been extensively studied (Cai et al., 2014; Tang and Cheng, 2018; Zhou et al., 2012). However, most of the studies are conducted under simple water chemistry conditions that do not adequately represent typical groundwater in which various cations and anions commonly co-exist.

Phosphate is not one of the major anions commonly found in pristine natural water. However, due to the use of phosphorous fertilizers in agriculture, phosphate is discharged into the aquatic environment. Most of the metal oxides interact with phosphate, adsorb these anions, and control the behaviour and fate of the phosphate in aquatic systems (Connor and McQuillan, 1999; Lv et al., 2012). In groundwater, phosphate may encounter different fine particles such as nTiO$_2$ and clay colloids. It has been reported that phosphate can adsorb to the surface of nTiO$_2$ and alter its size and surface charge (He et al., 2017). Whether phosphate facilitates or inhibits fine particle transport depends on water chemistry. For example, with increasing pH, phosphate adsorption to TiO$_2$ declines, whereas with increasing ionic strength, phosphate adsorption to nTiO$_2$ increases (Kang et al., 2011). Enhanced nTiO$_2$ transport in the presence of phosphate was observed at pH 7.5 compared to that at pH 6.5 due to the more negative charges on nTiO$_2$ surface at higher pH (Chen et al., 2015).

The valency and concentration of background solution also affected the stability and transport of fine particles (Akaighe et al., 2012; Torkzaban et al., 2012; Baalousha et al., 2013). Higher retention of colloidal particles occurred in the presence of divalent cations compared to that in solutions with monovalent cations at the same ionic strength, due to the stronger screening effect of the divalent cations (McCarthy and McKay, 2004). Chen et al. (2011) highlighted that nTiO$_2$ retention in a sand column was higher when CaCl$_2$ instead of NaCl background solution was used, even though the Ca^{2+} concentration was lower than that of Na$^+$. It has been reported that at high pH, strong adsorption of divalent cations converts the surface charge of nTiO$_2$ from negative to positive. The mechanism resulting in nTiO$_2$ surface charge reversal is Ca^{2+} adsorption at the rutile-water interface (Jang and Fuerstenau, 1986). Therefore, it can be anticipated that nTiO$_2$ particles in solutions with divalent cations at high pH might attract negatively charged phosphate ions. For clay particles, it has been demonstrated that there are many sites with a charge imbalance (due to isomorphic substitution) on particle surface, resulting in an excessive amount of negative

charges. Hence, multivalent cations like Ca^{2+} can strongly bind to the clay particles (Sposito, 2008; Torkzaban et al., 2012).

Although many studies have evaluated the various factors (e.g. pH, ionic strength, anions, cations) affecting the aggregation and attachment of fine particles, the behaviours of these particles in natural water is difficult to predict, since chemistry of natural water is far more complicated due to the co-presence of multi-components and their combined effects on water-borne particles. For example, the stability and attachment of nTiO$_2$ in groundwater are influenced not only by the presence of cations or anions, but also by concentration of the ions and their co-existence. While phosphate may increase the stability of nTiO$_2$ (Chen et al., 2011), Ca^{2+} decreases stability by promoting the formation of nTiO$_2$ aggregates (Loosli et al., 2015). Furthermore, due to the low solubility of Ca-phosphate minerals at high pH, Ca-phosphate precipitates may form (Ronson and McQuillan, 2002) and this in turn may affect nTiO$_2$ properties (e.g. zeta potential and size), and eventually its stability and transport. Phosphate concentration was also shown to have considerable impacts on the aggregation and dispersion of nTiO$_2$ via changing the particles' surface charge (He et al., 2017). Several studies have been conducted to understand the aggregation and attachment of nTiO$_2$ particles (Cai et al., 2015; Chen et al., 2015; Chowdhury et al., 2011; Fang et al., 2013; French et al., 2009; Godinez et al., 2013; Tang and Cheng, 2018; Wu and Cheng, 2016); however, no study has investigated the influence of simultaneous presence of phosphate anions and Ca^{2+} cations at different pH on nTiO$_2$ attachment. Such studies will allow us to produce results applicable to aquatic environments contaminated by phosphate and where Ca^{2+} is present.

This paper aims at investigating the combined effects of phosphate and major cations' valency on nTiO$_2$ and illite colloid attachment to quartz sand, a representing aquifer material. The mechanisms involved in the attachment process were studied by conducting systematic laboratory batch experiments using dilute NaCl and CaCl$_2$ background solutions, with different concentrations of phosphate at pH 5 and 9. Zeta potentials and hydrodynamic diameter (HDD) of nTiO$_2$ and illite colloids were measured and used in Derjaguin–Landau–Verwey–Overbeek (DLVO) calculations. The resulting DLVO interaction energy profiles between particles and between particle and sand were compared to the experimental measurements to explore both the applicability and limitations of the DLVO theory.

2. Materials and methods

2.1. Preparation of nTiO$_2$ and illite colloid suspensions, stock solutions, and quartz sand

The reagents used throughout the experiments were certified ACS grade. All the solutions and suspensions were prepared using nano-pure water generated by a Barnstead Nanopure Infinity ultrapure water system (with resistivity >18.2 MΩ × cm and dissolved organic carbon (DOC) concentration < 0.02 mg/L).

Aeroxide® TiO$_2$ P25 powder was purchased (Fisher Scientific) with a reported 99.5% purity, specific surface area of 50 ± 15 m^2/g, and an average particle size of 21 nm. The term nTiO$_2$ is used throughout this paper to refer to nanoscale titanium dioxide particles. Rutile and anatase are two mineral forms of TiO$_2$ and they may have substantially different behaviours (Sygouni and Chrysikopoulos, 2015). X-ray diffraction (XRD) results showed that the Aeroxide® TiO$_2$ P25 used in this study consists of 90% anatase (particles size = 23 nm) and 10% rutile (particle size = 40 nm) (Wu and Cheng, 2016). 500 mg/L nTiO$_2$ stock suspension was prepared by mixing an appropriate amount of dry powder and nano-pure water and sonicating the suspension for 30 min by a Branson Digital Sonifier (Crystal Electronics) with 200 W power to obtain a homogeneous stock suspension.

The illite stock was prepared by suspending 4.0 g of illite powder (IMt-2 Illite Cambrianshale, The Clay Mineral Society) in 1000 mL of nano-pure water in a glass beaker. The suspension was first vigorously