



# Transport and aggregation of rutile titanium dioxide nanoparticles in saturated porous media in the presence of ammonium



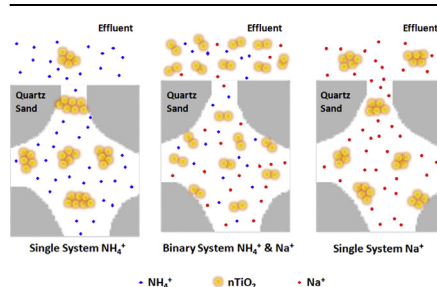
Xiaoting Xu, Nan Xu<sup>\*</sup>, Xueying Cheng, Peng Guo, Zhigang Chen, Dongtian Wang

Jiangsu Key Laboratory of Environmental Functional Materials, School of Chemistry Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

## HIGHLIGHTS

- The aggregation/retention of nTiO<sub>2</sub> is stronger in single NH<sub>4</sub><sup>+</sup> than that in Na<sup>+</sup>.
- The enhanced transportability of nTiO<sub>2</sub> in binary system of Na<sup>+</sup>+NH<sub>4</sub><sup>+</sup>.
- Two-site kinetic retention model provides good simulation for transport in NH<sub>4</sub><sup>+</sup>.
- The reversible retention of nTiO<sub>2</sub> in NH<sub>4</sub><sup>+</sup> is related to K<sub>2</sub> on Site 2 from model.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The widely used artificial nanoparticles (NPs) and the excess of ammonium (NH<sub>4</sub><sup>+</sup>) fertilizers are easily released into the natural environment. So, clarifying the mobility of NPs in the presence of NH<sub>4</sub><sup>+</sup> is therefore of great urgency and high priority. Currently, few studies focus on the transport and deposition of nanoparticle titanium dioxide (nTiO<sub>2</sub>) in single and binary systems containing NH<sub>4</sub><sup>+</sup>, especially describing this process by a mathematical model. In this work, the comparison between the transport and retention of rutile nTiO<sub>2</sub> in single and binary electrolyte solutions of NH<sub>4</sub>Cl and/or NaCl (0.5–50 mM) were conducted at pH 6.0 and 8.0 through running the column experiments. Experimental results show that the aggregation and retention of nTiO<sub>2</sub> in solution containing mono-valence cations obeys the order as follows: NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup> > Na<sup>+</sup> + NH<sub>4</sub><sup>+</sup> at the same ion strength (IS). It is attributed to the lower critical coagulation concentration (CCC) of rutile nTiO<sub>2</sub> in NH<sub>4</sub><sup>+</sup> than that in Na<sup>+</sup> solution. In particular, the simultaneous presence of NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> favors the transportability of nTiO<sub>2</sub> due to the strong competitive adsorption on the surface of NPs. The two-site kinetic retention model provides the good simulation for their transport behavior. The likely mechanism is that the secondary energy minimum of nTiO<sub>2</sub> in NH<sub>4</sub><sup>+</sup> system associated with the greater K<sub>2</sub> at surface Site 2 (from model) on sand can be explained for the more reversible deposition. Ammonium leachate associated with NPs can thus be considered a serious concern.

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## 1. Introduction

Engineered nanoparticles (NPs) are large-scale production for commercial purposes such as fillers, semiconductors, opacifiers, catalysts, and drug carriers (Nel et al., 2006). It is estimated that NPs

<sup>\*</sup> Corresponding author.

E-mail address: [nanxu@mail.usts.edu.cn](mailto:nanxu@mail.usts.edu.cn) (N. Xu).

industry will be a trillion dollar market (Auffan et al., 2009; Wiesner et al., 2006). However, it is known that lots of NPs have been released into the natural aquatic environment (Brar et al., 2010; Kiser et al., 2009; Robichaud et al., 2009; Westerhoff et al., 2011). NPs whose pH of isoelectric point ( $\text{pH}_{\text{iep}}$ ) is closer to the pH of environment are less likely to remain suspended and transport over the large distances (Mukherjee and Weaver, 2010). Rutile titanium dioxide ( $\text{nTiO}_2$ ) without surface modification has such behavior which the limited transport was observed in clean porous media at solution pH approaching to  $\text{pH}_{\text{iep}}$  of  $\text{nTiO}_2$  particles (Chen et al., 2011; Godinez and Darnault, 2011). Currently, some researchers have found that  $\text{nTiO}_2$  has the potential effects on biology in nature. For instance, the damage of unicellular green alga was observed in the presence of  $\text{nTiO}_2$  by inhibiting its growth in first 2–3 days of cultivation (Wang et al., 2008). The threat of  $\text{nTiO}_2$  to the environment and public health is related to their ability of remaining dispersed or to the formation of submicron aggregates in water (Godinez and Darnault, 2011). So, it is essential to investigate the transportability of rutile  $\text{nTiO}_2$ .

The aggregation of  $\text{nTiO}_2$  may be impacted by the ionic strength and pH of solution, surfactants, organic matter and components. As the ionic strength increased and the valence charge of cations (such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) diminished the magnitude of the electrostatic repulsion, the aggregation of NPs could be intensified (Fang et al., 2009; French et al., 2009; Saleh et al., 2008). The stability and mobility of  $\text{nTiO}_2$  were markedly enhanced at high pH (Snoswell et al., 2005). With the addition of surfactants, the elimination of electrostatic interaction results in the improvement of  $\text{nTiO}_2$  stability in solution (Chen and Elimelech, 2007). Thus,  $\text{nTiO}_2$  commonly remain dispersed by coated with nonionic and ionic surfactants (Chowdhury et al., 2012). In addition, humic acid is reported for effectively stabilizing the suspension of NPs due to improve the steric repulsion effect (Horst et al., 2010). Moreover, bacteria (i.e. *Escherichia coli*) resulted in the much less deposition of  $\text{nTiO}_2$  than natural organic matter (Horst et al., 2010). As known, excess of ammonium ( $\text{NH}_4^+$ ) fertilizer has contaminated soil and water environments. However, limited information is available about the effect of  $\text{NH}_4^+$  on the mobility of  $\text{nTiO}_2$ . To the best of our knowledge, two-site kinetic retention model has not been used for the simulation of transport behavior of  $\text{nTiO}_2$  in the presence of  $\text{NH}_4^+$  with/without  $\text{Na}^+$ .

The objective of this study is to explore the transport and retention of rutile  $\text{nTiO}_2$  in  $\text{NH}_4^+$  solution. The possible mechanisms will be investigated by changing the solution pH, flow velocity and ion strength in single and binary electrolyte systems containing cations:  $\text{NH}_4^+$  and/or  $\text{Na}^+$ . Meanwhile, the applicability of classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory will be used to calculate the  $\text{nTiO}_2$ -sand interaction energy in the presence of  $\text{NH}_4^+$ . Finally, a one-dimensional form of two-site kinetic retention model will be employed to simulate their breakthrough curves.

## 2. Materials and methods

### 2.1. Preparation of $\text{nTiO}_2$ suspension

$\text{TiO}_2$  used in this study were purchased from Gaosida Nano-material Company (Gilin Province, China) with purity of 99.9%. The  $\text{nTiO}_2$  samples are characterized as rutile by taking a Powder X-ray diffractometer (XRD, D8-Focus, Bruker AXS Co., Ltd., Germany) with a Cu K $\alpha$  radiation. The average particle size of  $5 \times 20$  nm was based on measurements from Transmission Electron Microscopy (TEM, FEI Tecnai G2 F20 S-Twin) images. Its specific surface area was  $156.2 \text{ m}^2 \text{ g}^{-1}$  measured by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method. Prior to being used in each transport experiment,  $\text{nTiO}_2$  suspension was

prepared by adding 0.20 g of  $\text{nTiO}_2$  powder to 200 mL electrolyte solution. The ion concentrations (ICs) of electrolytes were chosen by sodium chloride (NaCl) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) solution (0.5–50 mM) in single and/or binary system. All the transport experimental pHs were adjusted to  $6.0 \pm 0.1$  or  $\text{pH } 8.0 \pm 0.1$  by using HCl or NaOH solutions. And then the  $\text{nTiO}_2$  suspension was homogenized by stirring on a magnetic plate for 1 min and sonicated for 30 min at room temperature. The experimental details are similar as our previous experiments (Chen et al., 2015).

### 2.2. Determination of $\text{nTiO}_2$ aggregation kinetics

The initial growth rate of nanoparticles (NPs) hydrodynamic radius  $a_h(t)$  with time ( $t$ ) indicates their aggregation kinetics. The rate is measured by dynamic light scattering and mainly determined at various salt concentrations. Assuming that all primary particles within an aggregate are independent and scatter identically, the aggregation rate constant,  $K_{11}$ , is determined from the initial relative rate of change of the hydrodynamic radius as well as  $N_0$ :

$$\left(\frac{da_h(t)}{dt}\right)_{t \rightarrow 0} \propto K_{11}N_0 \quad (1)$$

$$\alpha = \frac{1}{W} = \frac{K_{11}}{(K_{11})_{\text{fast}}} = \frac{\frac{1}{N_0} \left(\frac{da_h(t)}{dt}\right)_{t \rightarrow 0}}{\frac{1}{(N_0)} \left(\frac{da_h(t)}{dt}\right)_{t \rightarrow 0, \text{fast}}} \quad (2)$$

Here, the terms with subscript “fast” refer to diffusion-limited aggregation where all collisions result in aggregation, and  $K_{11}$  is the slow aggregation rate constant where only a fraction of collisions results in aggregation. The attachment efficiency  $\alpha$  (ranging from 0 to 1) is the probability of an irreversible attachment resulting from the collision of two colloidal particles (Chen et al., 2006; Mylon et al., 2004). It serves to quantify the initial aggregation kinetics of  $\text{nTiO}_2$  in different electrolyte concentrations.

### 2.3. Column transport experiments

The column transport experiments were performed in glass columns with a length of 20 cm, inner diameter of 2.5 cm and both ends with 80  $\mu\text{m}$  nylon net films. The porous media in all experiments were prepared with the average diameter of 600  $\mu\text{m}$  quartz sand and the corresponding porosity was 0.55. Initially, the quartz sands need to be washed by using NaOH and HCl solution before packing column. The procedures were similar as our previous study (Chen et al., 2015), which are included in Supporting Information (SI). After that, columns were saturated by DI water flushing upward with a peristaltic pump for at least 24 h. The transport experiments were run as following three procedures. At beginning, 4 pore volumes (PVs) of background electrolyte were pumped upward to sand columns. Then, a pulse of  $\text{nTiO}_2$  ( $1.0 \text{ g L}^{-1}$ ) suspended in the same electrolyte was introduced. At the same time, the outflow from columns was collected into 10 mL glass tubes at 10 min intervals by a fraction collector (BS-100A, Huxi Analytical Instrument Factory Co., Ltd., Shanghai, China). Thirdly, another 4 PVs background electrolyte injection followed and ended by DI water finally until no  $\text{nTiO}_2$  in the effluent. All experiments were conducted at 25  $^\circ\text{C}$  room temperature. The transport behavior of  $\text{TiO}_2$  can be investigated by studying the breakthrough curves (BTCs), which is obtained by analyzing the concentration ratio  $C/C_0$  of  $\text{nTiO}_2$  in influent ( $C_0$ ) and effluent ( $C$ ) of columns as a function of pore volumes (PVs). The additional physical conditions for column experiments are summarized in Table S1 in SI and DLVO theory

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