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Modeling the transport of TiO₂ nanoparticle aggregates in saturated and unsaturated granular media: Effects of ionic strength and pH

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ABSTRACT

This study aims to explore the mechanisms governing the transport and retention kinetics of TiO₂ nanoparticle aggregates (NPAs) in flow-through columns of packed sand, particularly under unsaturated conditions. The study was carried out at different pHs (2.6, 7.1, and 9.6) and ionic strengths (ISs) (1.0, 10, and 50 mM). A two-site kinetic attachment model was used to describe transport behaviors of TiO₂ NPs. At low ISs (i.e., 1.0 and 10 mM) and in neutral/alkaline conditions, high mobility of TiO₂ NPs was observed in both saturated and unsaturated conditions. However, the retention of TiO₂ NPs was substantially enhanced at the high IS (50 mM) and in extremely acidity condition (pH = 2.6), because of increased aggregation and straining of TiO₂ NPs during their transport course. The breakthrough curves (BTCs) of TiO₂ NPs under unsaturated and saturated conditions almost overlapped, suggesting that decreasing the water saturation did not enhance the retention of TiO₂ NPs in sand columns. This was probably due to the repulsive interactions existed between negatively charged air–water and TiO₂ NPs systems that resulted in unfavorable attachment conditions. The two-site kinetic attachment model provided a good description for the BTCs of TiO₂ NPs both in saturated and unsaturated conditions. The fitted parameters could successfully explain the transport behaviors of TiO₂ NPs under various solution chemistries.

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1. Introduction

TiO₂ nanoparticles (NPs) are one group of the most widely used nanomaterials in consumer products including sunscreens, cosmetics, paints, and solar cell energy. Recently, they were increasingly applied for the photocatalytic degradation of pollutants in water, air, and soil matrices (Nowack

and Bucheli, 2007). With the rapid growth of the production, consumption and disposal of nanomaterials, they will inevitably and ultimately enter the environment (Wiesner et al., 2006). Accidental and/or deliberate introduction of TiO₂ NPs into subsurface environments may lead to contamination of drinking water. Moreover, TiO₂ NPs can act as colloidal carriers for the sorption of contaminants and then facilitate

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transport of these contaminants into subsurface and groundwater environments, which was regarded as “colloid-facilitated transport of contaminants” (Fang et al., 2011; Wang et al., 2011). Previous studies have shown the adverse effect of TiO₂ NPs to aquatic organism, soil bacterium, plants, animals, and even human cells (Bang et al., 2011; Chen et al., 2004; Rehn et al., 2003; Wilson et al., 2008; Zhang et al., 2007). Consequently, the fate and transport of TiO₂ NPs in subsurface draw greater attention now.

In general, NPs can pass both unsaturated zone (e.g., vadose zone) and saturated media (e.g., aquifers). During the past decades, most researches on the transport of TiO₂ NPs have been devoted to its transport and retention in saturated granular media (Ben-Moshe et al., 2010; Lecoanet et al., 2004; Nowack and Bucheli, 2007; Tian et al., 2011; Wiesner et al., 2006). The influence of solution chemistries, surfactants, and flow rate on the mobility of TiO₂ NPs in saturated porous media has been properly documented (Chowdhury et al., 2011; Godinez and Darnault, 2011; Lecoanet and Wiesner, 2004; Li et al., 2011). For example, their transport properties are largely dependent on the size, surface charge, agglomeration rate as well as the clay content in soil packed columns (Darlington et al., 2009; Fang et al., 2009; Guzman et al., 2006). Two major mechanisms controlling the retention of NPs in saturated media were solid–water interface deposition and straining (Bradford et al., 2003; Jaisi et al., 2008).

However, little if any is known about the transport and retention of TiO₂ NPs in unsaturated granular media. Compared with saturated conditions, the fate and transport of NPs in unsaturated conditions are more complicated due to the presence of the air–water interface. NPs can be attached to solid–water interface, be attached to the air–water interface, be strained in water films that are enveloping the solid phase, and also be retained at the solid–air–water triple points (Bradford and Torkzaban, 2008; Gao et al., 2008; Lazouskaya and Jin, 2008). In particular, water film that surrounds the solid grains is as thin as tens of nanometers, which is comparable to the size of NPs when they are exposed into water (Nowack and Bucheli, 2007; Torkzaban et al., 2008). Straining is demonstrated to play an important role in retaining colloids including NPs in unsaturated conditions (Bradford et al., 2006). Therefore, the retention of NPs is expected to be more significant in unsaturated conditions than that in saturated ones. Results of Chen et al. (2008) indicated that the retention of TiO₂ NPs in packed glass beads columns was likely to be more pronounced when the water saturation is lower. The same trend was observed by Zhang et al. (2012) for fullerene NPs retention in unsaturated media. While Tian et al. (2011) found that the reduction in moisture content showed little effect on the retention of carbon nanotubes in unsaturated conditions. They pointed out that the hydrophobic air–water interface was not favorable for carbon nanotubes deposition by bubble column experiments. The air–water interface was generally reported to be negatively charged, which is unfavorable for the deposition of negatively charged colloids due to the repulsion interaction between air bubbles and colloids (Chen and Flury, 2005). Through microscopic observations in a glass micromodel containing suspended air bubbles, however, Chen and Flury (2005) found that colloids did not adhere to the liquid–gas interface.

Gamerding and Kaplan (2001) reported that IS and water content had an interactive influence on colloids deposition whereby synergism effect was generally observed. The controversy in the above literature indicated that the transport especially retention behaviors of NPs in unsaturated porous media are still poorly understood.

Many researchers pointed out that taking into consideration of model-fitted parameters is vital to gain insight in understanding colloid deposition mechanisms (Wang et al., 2012; Chen et al., 2005; Gamerding and Kaplan, 2001; van Genuchten and Wagenet, 1989). They demonstrated that the breakthrough curves (BTCs) of colloids can be adequately fitted using a variety of models. For example, an attachment and detachment model as well as a two-site kinetic attachment model (an attachment and straining model) was successfully used to fit the BTCs of colloids in unsaturated granular media (Gargiulo et al., 2007).

Although many nanomaterials are produced with a small targeted size that is less than 100 nm, nanoparticles are likely to form much larger colloidal aggregates in water due to their high surface area and surface potential (Wiesner et al., 2006). Once the nanoparticles entered natural environment, they always existed in aggregate form (Fang et al., 2009; Nowack and Bucheli, 2007). The transport of engineered nanoparticles in porous media is generally referred to the transport of nanoparticle aggregates (Lecoanet et al., 2004; Ben-Moshe et al., 2010). Therefore, the objective of this work was to explore the mechanisms governing the transport and retention kinetics of TiO₂ nanoparticle aggregates (NPAs) through granular media, especially in unsaturated conditions. The effects of solution chemistries, i.e., ISs (1.0, 10, and 50 mM) and pHs (2.6, 7.1, and 9.6) on the transport of TiO₂ NPAs were systematically investigated. Particularly, breakthrough data were simulated using the two-site kinetic attachment model that accounted for time-depth dependent deposition processes. Fitted model parameters were used to gain insight into the mechanisms controlling TiO₂ NPAs transport in granular media.

2. Theory and modeling

2.1. DLVO energy

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to calculate the interaction energies between TiO₂ NPAs and grain (sand) system, as well as the TiO₂ NPAs and air–water system (Bradford and Torkzaban, 2008; Chowdhury et al., 2011; Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Interaction profiles for the TiO₂–sand–air systems were developed assuming sphere-plate geometry and using the following equations (Chowdhury et al., 2011):

$$\phi_{\text{total}}(h) = \phi_{\text{el}}(h) + \phi_{\text{vdw}}(h) \quad (1)$$

$$\phi_{\text{el}}(h) = \pi \epsilon_0 \epsilon_r \left\{ 2\psi_p \psi_c \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\psi_p^2 + \psi_c^2) \ln[1 - \exp(-2\kappa h)] \right\} \quad (2)$$

$$\phi_{\text{vdw}}(h) = -\frac{A_r p}{6h} \left[1 + \frac{14h}{\lambda} \right]^{-1} \quad (3)$$

where ϕ_{total} , ϕ_{el} , and ϕ_{vdw} are the total, electrostatic, and van der Waals interaction energies, respectively, and h is the separation distance between the TiO_2 NPAs and the interface of interest. ϕ_{total} , ϕ_{el} , and ϕ_{vdw} are commonly made dimensionless by dividing by the product of the Boltzmann constant ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$) and the absolute temperature (T). ϵ is the dielectric constant of the medium (78.4 for water at 20°C), ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$), r_p is the average radius of TiO_2 NPAs. ψ_p and ψ_c are the surface potentials of the TiO_2 NPAs and the collector (e.g., sand). Measured zeta potentials are frequently used in place of surface potentials. The air–water interface was always reported to be negatively charged and its zeta potential ranged from -15 to -65 mV (Chen and Flury, 2005). In this study, the zeta potential for the air–water interface was assumed to be -50 mV (Bradford and Torkzaban, 2008). κ is the Debye–Huckel parameter. Hamaker constant (A) for the sand–water– TiO_2 system was assumed to be 10^{-20} J in saturated condition (Yong et al., 2009), and for air–water– TiO_2 system it was assumed to be -10^{-20} J in unsaturated condition (Bradford and Torkzaban, 2008), and λ is the characteristic wavelength (100 nm) (Elimelech et al., 1995).

2.2. Two-site kinetic attachment model

The transport of TiO_2 NPAs through the sand columns was fitted using a modified form of the convection–dispersion equation with two-site kinetic retention, in which kinetic adsorption sites were considered for both attachment (Site 1) and straining (Site 2) processes. The mass balance equation is defined as (Gargiulo et al., 2007; Bradford et al., 2003):

$$\frac{\partial \theta c}{\partial t} + \rho_b \frac{\partial (s_1)}{\partial t} + \rho_b \frac{\partial (s_2)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial c}{\partial x} \right) - \frac{\partial qc}{\partial x} \quad (4)$$

where θ is the volumetric water content [–], c is the TiO_2 NPAs concentration in the aqueous phase [N L^{-3} , where N and L denote number and length, respectively], ρ_b is the bulk density of the porous matrix [M L^{-3} , where M denotes mass], t is the time [T], x is the vertical spatial coordinate [L], D is the hydrodynamic dispersion coefficient [$L^2 T^{-1}$], q is the flow rate [$L T^{-1}$], and s_1 [N M^{-1}] and s_2 [N M^{-1}] are the solid phase concentrations associated with sorption sites 1 and 2, respectively.

The two kinetic retention sites described mass transfer of TiO_2 NPAs between the aqueous and solid phase. The first kinetic site (site 1, Eq. (2)) assumes reversible retention, whereas the second kinetic site (site 2, Eq. (3)) assumes irreversible, depth-dependent retention as (Gargiulo et al., 2007; Wang et al., 2011):

$$\rho_b \frac{\partial (s_1)}{\partial t} = \theta k_{1a} c - \rho_b k_{1d} s_1 \quad (5)$$

$$\rho_b \frac{\partial (s_2)}{\partial t} = \theta k_{2\text{str}} \psi_x c \quad (6)$$

where k_{1a} [T^{-1}] and k_{1d} [T^{-1}] are the first-order attachment and detachment coefficients on site 1, respectively. $k_{2\text{str}}$ [T^{-1}] is the first-order straining coefficient on site 2, and ψ_x [–] is a dimensionless function to account for depth-dependent retention. Note that the detachment process occurs only

from the first sorption sites. In this analysis, attachment to the solid phase and air–water interface can be lumped in the k_{1a} term. Similarly, straining in pores and water films are also considered to be lumped using the $k_{2\text{str}}$ term. The value of ψ_x is given as (Bradford et al., 2003):

$$\psi_x = \left(\frac{d_c + x - x_0}{d_c} \right)^{-\beta} \quad (7)$$

where d_c is the median diameter of the sand grains [L], x_0 is the coordinate [L] of the location where the depth-dependent retention starts, and β is an empirical factor controlling the shape of the spatial distribution. Bradford et al. (2003) found that a value of $\beta = 0.432$ provides an optimum for experiments in which significant depth-dependency occurred.

The experimental data (BTCs) were characterized using the HYDRUS-1D code (Simunek et al., 2008), which allowed us to fit TiO_2 NPAs transport parameters (k_{1a} , k_{1d} , and $k_{2\text{str}}$) using a nonlinear least square optimization routine based on the Levenberg–Marquardt algorithm (Marquardt, 1963). The code numerically solves the Richards equation for saturated–unsaturated water flow. The pore water velocity and dispersivity used in the Hydrus-1D code were obtained by fitting the tracer (bromide) BTCs.

3. Materials and methods

3.1. Granular medium

Fine river sand was sieved to obtain size of 0.1 – 0.3 mm (median grain size of 0.2 mm), and then served as the granular media in the column experiments. To remove metal and organic impurities, the sand was cleaned sequentially by tap water, 10% nitric acid and deionized water (DI water) rinsing, and then oven-dried (550°C). Zeta potential of the cleaned fine sand was measured using a ZetaSizer Nano Series Instrument (Malvern Instrument Ltd., U.K.). The zeta potential of the cleaned fine sand was measured with ZetaSizer Nano Series Instrument (Malvern Instruments Ltd.) and found to be -22 mV , indicating that the sand surface was negatively charged.

3.2. TiO_2 NPAs suspensions

TiO_2 NPs were purchased from Hangzhou Wanjiang New Materials Company (Zhejiang, China) with an anatase purity of 99.9% and a primary particle size of 15 nm . Following the protocol developed from our previous work (Fang et al., 2009), the TiO_2 NPAs suspensions were prepared by sonicating and settling. Briefly, a portion of 500 mg TiO_2 NPs was added to 250 mL DI water, and subsequently sonicated for 30 min . After that, samples were settled down for 10 days . Supernatant contained unsettled TiO_2 NPAs were collected and used for the transport experiments. The concentration of TiO_2 NPAs suspensions in the supernatant was about 35 mg L^{-1} by measuring the concentration of titanium metal ion using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Electron Company, USA). The size and zeta potential of the TiO_2 NPAs suspensions were measured by

dynamic light scattering (DLS) (ZetaSizer Nano Series Instrument, Malvern Instruments Ltd.).

3.3. Column experiments

The transport of TiO₂ NPAs and bromide (tracer) were performed in an open vertical glass column with inner diameter of 22 mm. The column was packed to a height of 10 cm. In saturated column experiment, the column was initially saturated with DI water that was injected from the bottom of the column to remove any air pockets. Inflow was introduced vertically from the top of the column using a peristaltic pump (Longer BT100-2J) and a sprinkler head. Outflow from the bottom was connected to another peristaltic pump to adjust flow rate. A 1-cm constant water head was maintained throughout the experiments. In unsaturated column experiments, two peristaltic pumps at the column inlet and outlet were used to regulate the column moisture content and to control the downward flow rate. To prepare the unsaturated condition, an initially saturated column was drained for approximately 4 h to reach the target moisture content (70% water saturation) by elevating the outflow rate 5% higher than the inflow rate (Tian et al., 2011). A uniform hydraulic gradient was established through the column by equalizing the inflow and outflow rate. The percent moisture saturation was calculated from the ratio of θ (water-filled porosity) to the total porosity.

Once the column moisture stabilized, DI water was pumped through the column for about 3 pore volumes to stabilize the pore-water chemistries. The breakthrough experiment was then initiated by switching DI water into TiO₂ NPAs suspensions or bromide solution (tracer). The outflow samples were collected from the bottom of the column using a fraction collector. The absorbance of TiO₂ NPAs in the inflow and outflow were monitored by an UV–vis spectrophotometer (Agilent 8453) at a wavelength of 550 nm. A calibration curve was constructed by diluting the 35 mg L⁻¹ TiO₂ suspension, which was linear within the range of 0–35 mg L⁻¹. Additionally, a sand column leached with DI water was used for control experiment. Control column outflow absorbance in real time was detected to monitor the background colloid release. The concentration of TiO₂ NPAs in the outflow was calculated by

the difference between the concentration in TiO₂ NPAs transport experiment and that in the control experiment. The bromide concentration was measured by ion chromatography (Dionex, ICS-90 Chromatography System).

To investigate the effect of IS on the transport of TiO₂ NPAs, NaCl solutions with different concentrations (1.0 mM, 10 mM, and 50 mM) were applied. To study the effect of pH on TiO₂ NPAs transport, the pHs of TiO₂ NPAs suspensions were adjusted to 2.6, 7.1, and 9.6 by adding HCl or NaOH. Detailed physical parameters of the columns are given in Table 1.

4. Results and discussion

4.1. Characterization of TiO₂ NPAs

Although the nominal size of TiO₂ NPs purchased from the company (Hangzhou Wanjiang New Materials Company) was in the vicinity of 15 nm, the TiO₂ NPs existed in suspensions were aggregates rather than individual primary particles. As shown in Fig. 1, the aggregate size of TiO₂ NPAs varied with both suspension ISs and pHs. Larger aggregates formed at higher ISs. The average aggregates size increased from 247 nm to 427 nm when suspension IS was increased from 1.0 mM to 10 mM, and reached 1952 nm when suspension IS was 50 mM (Table 1). It can be well explained by the DLVO theory prediction, i.e., increases in suspension IS will decrease the thickness of the electrostatic double layer and thereby promote the aggregation of NPs due to a reduction in the height of the repulsive energy barrier (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948).

The zeta potential of TiO₂ NPAs in water is a function of pH and referred as an indication of the stability of the suspension (Guzman et al., 2006). When the suspension pH was 2.6, the zeta potential of TiO₂ NPAs was 2.4 mV, indicating that the net surface charges of TiO₂ were positive (Table 1). However, the zeta potentials of TiO₂ NPAs reversed to become negatively charged and its zeta potential increased from –34.7 to –36.1 mV (more negative) as the suspension pH increased from 7.1 to 9.6. Elimelech et al. (1995) pointed out that higher absolute values of zeta potentials are unfavorable for particles homo-aggregation. As shown in Table 1 and Fig. 1b, when pH

Table 1 – Physical and chemical conditions of the packed columns and TiO₂ NPAs used in this study.

Water saturation	Flow velocity (cm h ⁻¹)	IS (mM)	pH	Zeta potential of TiO ₂ NPAs (mV)	Average size of TiO ₂ NPAs (nm)	Ratio of TiO ₂ NPAs and collector grain (sand) diameter (d_p/d_c)
1.0	10.6	1.0	7.1	–36.4 ± 0.9	247 ± 31	0.001
0.7	9.9	1.0	7.1	–36.4 ± 0.9	247 ± 31	0.001
1.0	10.9	10	7.1	–34.3 ± 1.3	427 ± 26	0.002
0.7	10.0	10	7.1	–34.3 ± 1.3	427 ± 26	0.002
1.0	10.8	50	7.1	–34.6 ± 2.4	1952 ± 45	0.009
0.7	10.5	50	7.1	–34.6 ± 2.4	1952 ± 45	0.009
1.0	10.4	0.1	2.6	2.4 ± 1.1	1208 ± 53	0.006
0.7	10.2	0.1	2.6	2.4 ± 1.1	1208 ± 53	0.006
1.0	10.6	0.1	7.1	–34.7 ± 0.5	243 ± 23	0.001
0.7	10.3	0.1	7.1	–34.7 ± 0.5	243 ± 23	0.001
1.0	10.7	0.1	9.6	–36.1 ± 1.0	278 ± 19	0.001
0.7	10.9	0.1	9.6	–36.1 ± 1.0	278 ± 19	0.001

Fig. 1 – Particle size distributions of TiO₂ NPAs at varying suspension ISs (a) and pHs (b).

was 2.6, the smallest absolute value of zeta potential (2.4 mV) resulted in the largest aggregate size (1208 nm), even at the lowest IS (0.1 mM). When pH was 7.1 and 9.6, the absolute values of zeta potentials were above 30 mV which were considered as stable for TiO₂ NPAs suspensions. Thus the aggregate sizes were much smaller (243 nm and 278 nm when pH was 7.1 and 9.6, respectively) than the one (1208 nm) when pH = 2.6.

4.2. Calculation of DLVO interaction energies

The calculated DLVO interaction energies in both sand–water–TiO₂ and air–water–TiO₂ systems at different suspension ISs and pHs are presented in Fig. 2. In saturated conditions, high energy barriers (100–170 kT) existed between TiO₂ NPAs and sand grains with all the tested ISs (Fig. 2a), suggesting unfavorable conditions for TiO₂ NPAs deposition

Fig. 2 – Calculated DLVO interaction energies for sand–water–TiO₂ and air–water–TiO₂ systems under varying suspension ISs (a, b) and pHs (c, d). (b) and (d) were calculated under unsaturated conditions.

and/or retention. However, when IS was increased to 50 mM, there was a secondary minimum (-15 kT) at the distance greater than that of the primary energy barrier, where represented favorable deposition conditions. In unsaturated conditions, the DLVO theory predicted that the interaction energies for air–water–TiO₂ interface were significantly higher (>700 kT) than those for sand–water–TiO₂ system with all ISs tested (Fig. 2a, b), indicating that TiO₂ NPAs were not likely to deposit onto the repulsive air–water surface.

As indicated in previous studies, pH is another key factor that influences the DLVO interaction energy. Variations in pH altered both the magnitude and the separation distance (h) of the repulsive energy barrier in the DLVO interaction (Fig. 2c, d). When pHs were 7.1 and 9.6, large energy barriers (>100 kT) existed in both sand–water–TiO₂ and air–water–TiO₂ systems, indicating unfavorable attachment conditions. However, as the pH was as low as 2.6, substantially deep primary energy well (<-200 kT) occurred for interaction energies in both sand–water–TiO₂ and air–water–TiO₂ systems, which were favorable for the deposition and/or retention of TiO₂ NPAs.

4.3. Effect of IS on the transport of TiO₂ NPAs through saturated and unsaturated columns

Fig. 3 presents BTCs of TiO₂ NPAs being advected through the sand with suspension ISs of 1.0 mM, 10 mM, and 50 mM, respectively, under both saturated ($\theta = 1.0$) and unsaturated ($\theta = 0.7$) conditions. The BTCs are plotted as dimensionless concentration (C_f/C_0) of TiO₂ NPAs as a function of pore volume (PV, the real pore volume). The corresponding mass recovery of TiO₂ NPAs in the effluent is shown in Table 2. At IS of 1.0 mM, the TiO₂ NPAs were first detected in the effluent when $PV < 1$ in both saturated and unsaturated columns. And then, the C_f/C_0 value increased sharply and then reached a plateau relative concentration of 1 ($C_f/C_0 \approx 1.0$, Table 2) when $PV = 4.0$. It demonstrated that after the surface of sand grain was covered with TiO₂ NPAs, then the surface characteristics of sand does not affect further deposition of NPAs. Interestingly, the BTCs of TiO₂ NPAs for saturated and unsaturated columns were almost overlapped, suggesting

Table 2 – Mass balance percentages for TiO₂ NPAs in both saturated and unsaturated columns at varying IS and pH.

Water saturation	IS (mM)	pH	^a C_f/C_0	^b Recovery (%)
1.0	1.0	7.1	0.998 ± 0.003	92.3 ± 4.6
0.7	1.0	7.1	0.997 ± 0.003	93.6 ± 4.7
1.0	10	7.1	0.947 ± 0.004	74.7 ± 3.7
0.7	10	7.1	0.955 ± 0.007	76.1 ± 3.9
1.0	50	7.1	NB	15.3 ± 0.8
0.7	50	7.1	NB	26.7 ± 1.3
1.0	0.1	2.6	0 ± 0	0 ± 0
0.7	0.1	2.6	0 ± 0	0 ± 0
1.0	0.1	7.1	0.999 ± 0.002	94.1 ± 4.7
0.7	0.1	7.1	0.997 ± 0.004	94.1 ± 4.7
1.0	0.1	9.6	0.999 ± 0.004	93.0 ± 4.7
0.7	0.1	9.6	0.999 ± 0.003	95.1 ± 4.8

a Refers to the transport plateau concentration of TiO₂ NPAs.

b Refers to the recover percentage of TiO₂ NPAs. NB: not observed.

that the presence of air in the unsaturated conditions had no effect on TiO₂ NPAs transport at the IS of 1.0 mM. This is further approved by the similar high recovery rate (92.3% and 93.6% for saturated and unsaturated conditions, respectively, Table 2) at this IS. When the solution IS was increased to 10 mM, TiO₂ NPAs were first detected when $PV = 2$ in the effluent. Then the C_f/C_0 value increased monotonically to the identical plateau value of 0.95 when $PV > 10$ in both saturation conditions. However, the breakthrough rate of TiO₂ NPAs in unsaturated condition was inferior to that in saturated condition during 2–7 PV (the right shift of BTCs for unsaturated column). The high breakthrough concentrations of TiO₂ NPAs at ISs of 1 mM and 10 mM suggested that TiO₂ NPAs had high mobility in low ISs conditions. When the IS was as high as 50 mM, however, the mobility of TiO₂ NPAs exhibited a substantively retention, compared to those with lower ISs. When $PV = 15$, the C_f/C_0 value was only 0.32 in saturated condition and 0.37 in unsaturated conditions. Interestingly, the breakthrough rate of TiO₂ NPAs in unsaturated condition was slightly higher than that in saturated condition, indicating that TiO₂ NPAs were more mobile in the presence of air–water interface. In addition, the recovery of TiO₂ NPAs

Fig. 3 – Measured (dots) and fitted (lines) BTCs of TiO₂ NPAs in saturated (saturation of 1.0) and unsaturated (saturation of 0.7) sand columns under the indicated ISs of 1.0 mM (a), 10 mM (b), and 50 mM (c), respectively (pH = 7.1). The pore volume used here for unsaturated columns was the real pore volume (the total pore volume in the saturated conditions was multiplied by 0.7). Fitted curves were obtained using the two-site kinetic attachment model.

markedly decreased with increasing IS, indicating the retention of TiO_2 NPAs significantly increased with IS. This is consistent with previous studies (Ben-Moshe et al., 2010; Chowdhury et al., 2011). The possible retention mechanisms of TiO_2 NPAs will be discussed in the following sections.

Although DLVO had shown that high energy barrier (>100 kT, Fig. 2a, b) existed at suspension IS of 1.0 mM, a small amount of TiO_2 NPAs ($\approx 7\%$, Table 2) was still retained in the granular media (sand), consistent with the results reported elsewhere under similar unfavorable attachment conditions (Bradford et al., 2003; Chowdhury et al., 2011; Fang et al., 2009; Jaisi et al., 2008). In this study, the retention mechanisms of TiO_2 NPAs such as surface charge heterogeneities, aggregation and straining that were neglected by classical DLVO theory, would play important roles in TiO_2 NPAs retention. Though the surface charge of sand was generally negative, there were still some positive sites provided by the iron or aluminium oxide (positively charged) in the sand surfaces (Bouchard et al., 2012). This surface charge heterogeneity is likely to create locally favorable retention sites for TiO_2 NPAs retention, which could explain the weak retention of TiO_2 NPAs at low IS (i.e., 1.0 mM) condition. Straining occurred within mobile-water conduits that are too narrow for particles to pass through. Particles would be intercepted if the ratio of diameters of particle to collector (d_p/d_c) (where d_p and d_c are the diameters of NPs aggregates and collector, respectively) was above 0.002 (Bradford et al., 2003; Sakthivadivel, 1966). In this study, the average size of TiO_2 NPAs increased with increasing IS. When IS was 10 mM, the value of d_p/d_c was higher than 0.002 ($d_p/d_c = 427 \text{ nm}/0.2 \text{ mm} = 0.0021$). Hence, straining was involved in the retention of TiO_2 NPAs during the transport when IS was 10 mM. The straining effect became more pronounced with a higher IS (50 mM). The d_p/d_c value increased to 0.009 at IS 50 mM due to the increasing size of TiO_2 NPAs, and thus caused more retention of TiO_2 NPAs than those with lower ISs (Table 2). Additionally, a secondary minimum (~ 15 kT) existed in the DLVO profile when IS was 50 mM in sand–water– TiO_2 NPAs interfaces also provided favorable sites for TiO_2 NPAs deposition, though particle deposition in such secondary minimum was demonstrated to be reversible (Godinez and Darnault, 2011; Tufenkji and Elimelech, 2005; Wang et al., 2011).

In unsaturated conditions, there were high energy barriers between TiO_2 NPAs and air–water interface, indicating that unfavorable attachment condition existed for TiO_2 NPAs deposition on air–water interface (Fig. 2b). Chen and Flury (2005) found that colloids did not adhere to the air–liquid interface under unsaturated conditions through a light microscope observations. Therefore, the presence of air in the unsaturated sand columns would not increase the retention of TiO_2 NPAs. This prediction was proved by the transport results in this study that the recovery rate in unsaturated columns was similar to those in saturated columns (Table 2) and the final mobility of TiO_2 NPAs (plateau C_f/C_0) in unsaturated columns was also similar to those in saturated columns (Fig. 3).

Previous studies also demonstrated that the retention of colloids under unsaturated conditions were attributed to film straining that refers to the retention of colloids in thin water films when the thickness of the water film was smaller than the colloid diameter (Bradford and Torkzaban, 2008; Chen et al., 2008; Chen and Flury, 2005). The reported thickness of the thin water film was in the vicinity of 50 nm during steady-state water flow condition (Torkzaban et al., 2008). However, colloid would be retained by thin water film as its thickness was comparable to the size of colloid particles (Chen and Flury, 2005). In this study, film straining was unlikely to occur in the unsaturated column through all the tested ISs. Because TiO_2 NPAs (>200 nm) was too large to be bound within a thin water film. And this assumption was further proved by the experimental data. The mass recovery in unsaturated columns was slightly higher in unsaturated columns than those in saturated ones (Table 2).

4.4. Effect of pH on the transport of TiO_2 NPAs through saturated and unsaturated columns

Fig. 4 presents BTCs for TiO_2 NPAs with suspension pHs of 2.6, 7.1, and 9.6 when IS = 0.1 mM, respectively, under both saturated ($\theta = 1.0$) and unsaturated ($\theta = 0.7$) conditions. pH was found to have a marked role in the transport of TiO_2 NPAs. When pH = 2.6, deep primary energy wells existed for both sand–water– TiO_2 and air–water– TiO_2 interfaces, suggesting favorable attachment conditions (Fig. 2c, d). The deposition in primary energy minimum was considered to be irreversible

Fig. 4 – Measured (dots) and fitted (lines) BTCs of TiO_2 NPAs in saturated (saturation of 1.0) and unsaturated (saturation of 0.7) sand columns under the indicated pHs of 2.6 (a), 7.1 (b), and 9.6 (c), respectively (IS = 0.1 mM). The pore volume used here for unsaturated columns was the real pore volume (the total pore volume in the saturated conditions was multiplied by 0.7). Fitted curves were obtained using the two-site kinetic attachment model.

Fig. 5 – Measured (dots) and fitted (lines) BTCs of Br^- in saturated (saturation of 1.0) and unsaturated (saturation of 0.7) sand columns. The pore volume used here for unsaturated columns was the real pore volume (the total pore volume in the saturated conditions was multiplied by 0.7). Fitted curves were obtained using the two-site kinetic attachment model.

(Tufenkji and Elimelech, 2005). Furthermore, the average size of TiO_2 NPAs at pH 2.6 was as high as 1208 nm and the value of d_p/d_c reached 0.006, which resulted in significant pore straining. As expected, TiO_2 NPAs were completely retained in both unsaturated and saturated conditions when pH = 2.6.

At pHs of 7.1 and 9.6, the breakthrough of TiO_2 NPAs increased quickly and then reached a plateau. The plateau-concentrations (C_f/C_0) for both saturated and unsaturated columns were about 1.0. Both the mass recoveries of TiO_2 NPAs at pHs of 7.1 and 9.6 were more than 93%, suggesting low retention. This is consistent with the DLVO theory prediction, which indicated the sand surface was unfavorable for particle deposition. As stated above, straining was also unlikely to be involved in the retention of TiO_2 NPAs because of small size of TiO_2 NPAs and low d_p/d_c value (0.001) (Table 1). However, the low retention (in the vicinity of 7%) was probably attributed to

other retention mechanisms such as chemical heterogeneity of colloids, surface charge heterogeneity on the sand grain, surface roughness, colloid aggregation, and enhanced colloid retention in low velocity regions. These retention mechanisms are worthy further study, but are beyond the scope of this study. In addition, the elution of TiO_2 NPAs in unsaturated columns was still demonstrated to be almost the same to those in saturated columns at pHs of 7.1 and 9.6 (Fig. 4b and c, Table 2), which further confirming that the presence of air in unsaturated column had insignificant effect on the retention of TiO_2 NPAs.

4.5. Modeling TiO_2 NPAs transport in saturated and unsaturated columns

A two-site kinetic retention model was applied to fit the BTCs of TiO_2 NPAs in both saturated and unsaturated sand columns. The mean pore-water velocity and dispersivity were obtained by fitting the tracer (bromide) BTCs (Fig. 5). The fitted model parameters are provided in Table 3. The two-site kinetic attachment model provided a good description for the BTCs of TiO_2 NPAs under both saturated and unsaturated conditions ($r^2 > 0.97$) (Figs. 3 and 4 and Table 3). The model parameters (k_{1a} , k_{1d} and k_{2str}) were subsequently compared and discussed to gain additional insight on the TiO_2 NPAs retention mechanisms.

At a fixed saturation, the values of k_{2str} increased with increasing IS, suggesting that the greater straining occurred at higher ISs (Table 3). This was consistent with the results observed by Gargiulo et al. (2007) and Wang et al. (2011). Under low ISs of 0.1 and 10 mM, the values of k_{2str} were very small and the predicted retention contribution by straining process were less than 1% ($k_{2str}/(k_{1a} - k_{1d} + k_{2str})$, see Table 3). However, when IS was increased to 50 mM, the values of k_{2str} increased significantly and the predicted retention contribution by straining process exceeded 10%, indicating that straining played an important role in the retention of TiO_2 NPAs at the IS of 50 mM. This prediction was consistent with the experimental data in this study. The size of TiO_2 NPAs at IS of 50 mM was the largest, which led to the strongest straining during TiO_2 NPAs transport. The retention of TiO_2 NPAs on the first kinetic site (site 1) was assumed to be

Table 3 – Measured and fitted parameters for the transport of TiO_2 NPAs in various conditions.

Water saturation	IS (mM)	pH	k_{1a} (h^{-1})	k_{1d} (h^{-1})	k_{1d}/k_{1a}	k_{2str} (h^{-1})	$k_{2str}/(k_{1a} - k_{1d} + k_{2str})$ (%)	r^2
1.0	1.0	7.1	21.11	16.58	0.785	0.012	0.26	0.998
0.7	1.0	7.1	168.00	122.00	0.726	0.063	0.14	0.997
1.0	10	7.1	55.91	20.22	0.362	0.276	0.77	0.995
0.7	10	7.1	196.00	42.23	0.215	0.271	0.18	0.999
1.0	50	7.1	29.11	3.21	0.110	3.63	12.29	0.997
0.7	50	7.1	38.72	4.11	0.106	4.01	10.38	0.997
1.0	0.1	2.6	nf	nf	nf	nf	nf	nf
0.7	0.1	2.6	nf	nf	nf	nf	nf	nf
1.0	0.1	7.1	7.55	7.47	0.989	0.0004	0.50	0.973
0.7	0.1	7.1	356.00	285.00	0.801	0.071	0.10	0.988
1.0	0.1	9.6	62.22	57.6	0.926	0.031	0.67	0.995
0.7	0.1	9.6	27.14	24.73	0.911	0.061	2.47	0.979

nf: not fitted.

reversible and when $k_{1d}/k_{1a} = 1$, the attachment was approaching linear equilibrium (Gargiulo et al., 2007; van Genuchten and Wagenet, 1989). In this study, the value of k_{1d}/k_{1a} decreased from 0.989 to 0.110 and from 0.801 to 0.106, respectively, when the IS increased from 0.1 mM to 50 mM in saturated and unsaturated conditions. The reduction in k_{1d}/k_{1a} value indicated that the equilibrium attachment was reduced and the retention of TiO_2 NPAs on site 1 was enhanced with increasing IS.

For a given IS, the values of k_{1d}/k_{1a} under unsaturated conditions were slightly smaller than those under saturation conditions, suggesting the reversible detachment decreased and the retention of TiO_2 NPAs on site 1 enhanced with decreasing water saturation. The results were consistent with those reported in the literature (Gargiulo et al., 2007). However, the values of k_{2str} for the unsaturated conditions were quite similar to those in the saturated conditions, indicating that the presence of air–water interface did not enhance the straining of TiO_2 NPAs in sand columns.

Because TiO_2 NPAs were completely retained in the columns under acidic condition (pH 2.6) for both saturated and unsaturated conditions, the two site kinetic retention model could not adequately fit the BTCs. Under neutral/alkaline conditions, the k_{1d}/k_{1a} values generally approached 1 for both saturations, suggesting that the attachment of TiO_2 NPAs on site 1 was almost reversible and the retention of TiO_2 NPAs on site 1 was insignificant. In addition, the values of k_{2str} were very small and the percentage of colloid retention by straining was less than 3% (Table 3). This prediction was quite consistent with the experimental results that very small retention (<7%) of TiO_2 NPAs was found in neutral/alkaline conditions for both saturations (Table 2).

5. Conclusions

Results of this study have several implications for the understanding of TiO_2 NPAs transport and deposition in saturated and unsaturated granular media. TiO_2 NPAs were highly mobile in both saturated and unsaturated porous media under most of the experimental conditions. Both IS and pH were found to have remarkable effects on the transport and retention of TiO_2 NPAs. Lower ISs (1.0 and 10 mM) and higher pHs (7.1 and 9.6) were unfavorable for TiO_2 NPAs deposition and resulted in their high mobility in sand columns, which was consistent with DLVO prediction. A High IS (50 mM) and a low pH (2.6) resulted in high retention of TiO_2 NPAs because of the enhanced aggregation and straining. Presence of air in the unsaturated conditions had little effect on the retention and transport of TiO_2 NPAs in sand columns. The two-site kinetic retention model provided a good description for the BTCs of TiO_2 NPAs in both saturated and unsaturated conditions. The model fitting parameters could be successfully used to explain the retention process of TiO_2 NPAs under various solution chemistries. This study also suggested that in most natural systems with moderate IS (<10 mM) and pH (neutral), TiO_2 NPAs were high mobile through subsurface even under unsaturated conditions. More attention should be paid to the risk of TiO_2 NPAs in unsaturated natural system due to their high mobility.

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