



# Stability and transport of titanium dioxide nanoparticles in three variable-charge soils

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## Abstract

**Purpose** The exposure pathways and environmental impacts of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) released into soils could be significantly influenced by their stability and transport behaviors. The aim of this study was to investigate the stability and transport of TiO<sub>2</sub> NPs in three variable-charge soils and to determine the key factors controlling these behaviors.

**Materials and methods** Three surface (0~15 cm) variable-charge soils derived from quaternary red clay, humid ferralsols and stagnic anthrosols collected from Yingtan, Jiangxi Province (YT-H and YT-S, respectively), and humid ferralsols collected from Fuyang, Zhejiang Province (FY-H), were used in this study. Batch sedimentation experiments of TiO<sub>2</sub> NPs in soil suspensions were performed for 10 h to quantify their stability. Transport of TiO<sub>2</sub> NPs in soil columns was conducted with and without the presence of fulvic acid (FA).

**Results and discussion** Apart from soil organic matter (SOM) and iron oxides, there was no significant difference between the tested soils. Batch experiments showed that TiO<sub>2</sub> NPs were more stable in the YT-S soil suspension with high dissolved organic matter than in the YT-H and FY-H soil suspensions. In the column experiments, all TiO<sub>2</sub> NPs were retained in YT-H and YT-S, while 11% of the TiO<sub>2</sub> NPs were eluted from FY-H with a low amorphous iron oxide content. The significant retention of TiO<sub>2</sub> NPs in the soils could be attributed to the straining and adsorption of TiO<sub>2</sub> NPs on the surface of soil particles. FA enhanced the transport of TiO<sub>2</sub> NPs in YT-H and FY-H by dispersing the TiO<sub>2</sub> NPs and reducing their adsorption onto soil particles, while all the TiO<sub>2</sub> NPs dispersed in the FA solution were still deposited in YT-S with a high amorphous iron oxide content.

**Conclusions** The stability of TiO<sub>2</sub> NPs in three variable-charge soil suspensions was dependent on the SOM. However, the mobility of TiO<sub>2</sub> NPs in soils was not directly related to their stability in the soil suspensions. The difference in amorphous iron oxide content could induce the disparity in mobility of TiO<sub>2</sub> NPs in soils.

**Keywords** Amorphous iron oxide · Retention · Stability · Titanium dioxide nanoparticles · Transport · Variable-charge soil

## 1 Introduction

Titanium dioxide nanoparticles (TiO<sub>2</sub> NPs), one of the most widely used engineered nanomaterials in industry and daily

life, are inevitably released into the natural environment. Exposure modeling suggested that engineered nanoparticle concentrations in soil were higher than those in water and air, implying that soil might be a major sink for nanoparticles

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released into the environment (Ge et al. 2011; Gottschalk et al. 2009). TiO<sub>2</sub> NPs enter the soil environment through intentional and unintentional releases, such as nanomaterial usage for environmental remediation, atmospheric deposition, industrial and domestic wastewater discharge, treatment and disposal of solid waste, and accidental spillage during manufacturing and transportation of nanoparticles (Ray et al. 2009; Menard et al. 2011). It has also been estimated that the environmental concentrations of TiO<sub>2</sub> NPs in sludge-treated soil may increase at rates as great as 42–89 μg kg<sup>-1</sup> y<sup>-1</sup> (Gottschalk et al. 2009). With the further development of nanotechnology and the nanoindustry, it could be reasonably predicted that the concentration of TiO<sub>2</sub> NPs in soil will increase even further in the future (Fang et al. 2011).

Once released into the soil, TiO<sub>2</sub> NPs can adversely affect the metabolic activity of animals, plants, and microorganisms in the environment (Du et al. 2011; Ge et al. 2011; Menard et al. 2011; Ma et al. 2019). TiO<sub>2</sub> NPs could also increase the transport and bioavailability of pollutants (Sun et al. 2007; Fang et al. 2011; Fang et al. 2013; Yang et al. 2014). The bioavailability and toxicity of nanoparticles released into the environment are strongly influenced by their stability and mobility behaviors (Zhang et al. 2015). A substantial number of studies have provided insights into the effects of environmental conditions, such as pH, ionic strength, and valence state, and the presence of dissolved organic matter (DOM), clay minerals, and coexisting nanoparticles, on the stability and transport of TiO<sub>2</sub> NPs. High concentrations of DOM and low ionic strength facilitated the transport of TiO<sub>2</sub> NPs in saturated porous media (Zhang et al. 2015), while iron oxides inhibited the mobility of TiO<sub>2</sub> NPs in quartz columns (Han et al. 2014; Wang et al. 2016). However, natural soils, crucial environmental media, are complex assemblies of various components, and soil properties such as pH, size, surface area, base saturation, mineral type, and organic matter composition can greatly affect the stability and mobility of nanoparticles (Kretzschmar et al. 1997; Sun et al. 2015c). The environmental behaviors of TiO<sub>2</sub> NPs in soil may be different from those in simulated porous media (Sun et al. 2015a). Hence, it is urgent to explore the stability and transport of TiO<sub>2</sub> NPs in soil under the comprehensive effects of environmental conditions and to determine the critical factor affecting these behaviors. Some researchers have previously investigated the stability and mobility of engineered nanoparticles in soil. Fang et al. (2009) found that the stability of TiO<sub>2</sub> NPs in soil suspensions was positively correlated with the DOM concentration and clay content of the soils but was negatively correlated with ionic strength, pH, and zeta potential; additionally, a significant portion of the TiO<sub>2</sub> NPs (18.8–83.0%) has readily passed through the soil columns containing soil particles of relatively larger diameters and lower solution ionic strengths, while TiO<sub>2</sub> NPs were significantly retained by soils with higher clay contents and salinity. Darlington et al. (2009) suggested that although

many factors influenced the transport of aluminum nanoparticles, the size, charge, and agglomeration rate of the nanoparticles were predictive of their mobility in soils. However, transport of TiO<sub>2</sub> NPs in real soils is still inconclusive, and very few systematic studies have focused on the stability and transport of TiO<sub>2</sub> NPs in variable-charge soils with a high iron oxide content, commonly higher than 30 g kg<sup>-1</sup> (Xu et al. 2003; Xu and Zhao 2013; Zhu et al. 2019). Variable-charge soils are widely distributed in economically developed regions and major grain-producing areas in southern China and are more likely to be a sink for intentionally or unintentionally released nanoparticles. Consequently, more attention should be paid to the stability and mobility behaviors in these soils.

The objective of this study was to investigate the stability of TiO<sub>2</sub> NPs in suspensions of three variable-charge soils and the transport of the nanoparticles in these soils and to determine the key factors controlling the stability and mobility of TiO<sub>2</sub> NPs. The results of this work will hopefully provide insights into the environmental behaviors of TiO<sub>2</sub> NPs in variable-charge soils.

## 2 Materials and methods

### 2.1 Soils

Three surface (0–15 cm) variable-charge soils were collected from a section of dry land (YT-H) and a paddy field (YT-S) in Yingtan, Jiangxi Province, and a section of dry land (FY-H) in Fuyang, Zhejiang Province, China. The soils were air-dried, grounded, and passed through a 2-mm sieve prior to use. Soil pH was determined with a pH meter (FB10, Mettler Toledo) at a soil/deionized water (18.2 MΩ cm) ratio of 1:2.5 (w/v<sup>-1</sup>). Soil organic matter (SOM) was measured using potassium dichromate oxidation-ferrous sulfate titrimetry. The cation exchange capacity (CEC) of the soils was analyzed by the ammonium acetate method. The free iron oxide and aluminum oxide contents were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Pekin Elmer Optima 7000 DV) after extraction by sodium dithionite. The amorphous iron oxide and aluminum oxide contents were determined by ICP-OES after being extracted by ammonium oxalate. All measurements above are referred to Lu (2000). Soil texture (sand, silt, and clay contents) parameters were measured using a laser particle analyzer (Malvern Mastersizer 2000F). The clay fraction (< 2 μm) separated from the soils by the sedimentation method was used for the determination of zeta potential of the soils with a Zetasizer Nano ZS 90 (Malvern).

### 2.2 TiO<sub>2</sub> NPs and fulvic acid

The TiO<sub>2</sub> NPs used in this study were the same as those used in our previous work (Zhang et al. 2015). In brief, the

nanoparticles were spherical with a nominal size of  $30 \pm 10$  nm and a specific surface area of  $80.8 \text{ m}^2 \text{ g}^{-1}$ . The point of zero charge was determined to be at pH 6.2 in deionized water by a Zetasizer Nano ZS 90. A stock suspension of  $\text{TiO}_2$  NPs was prepared by adding 250 mg  $\text{TiO}_2$  NPs to 1.0-L deionized water. The suspension was sonicated for 30 min (500 W, 40 kHz) with vigorous stirring at room temperature ( $25^\circ\text{C}$ ) and stored no longer than 2 days at  $4^\circ\text{C}$ . The fulvic acid (FA) obtained from the Fluka Regent Chemical Corporation was used as a model natural organic matter. Stock solutions of FA were prepared at  $1 \text{ g L}^{-1}$  in deionized water.

### 2.3 Sedimentation of $\text{TiO}_2$ NPs in water leachate and suspensions of soils: batch experiments

The soil suspensions in this study were obtained by mixing soils with deionized water at a ratio of 1:20 (w/v) and equilibrating in a rotating shaker at 180 rpm at  $25^\circ\text{C}$  for 24 h. The suspensions were centrifuged at  $3500 \times g$  for 30 min and then filtered through a  $0.45\text{-}\mu\text{m}$  cellulose acetate filter membrane. The filtrates were referred to as soil leachates. The pH of the soil leachates was measured with a pH meter, and the electrical conductivity (EC) was determined using a conductivity meter (FE38, Mettler Toledo). The ionic strength (IS) of the soil suspensions was calculated using an empirical equation of IS and EC (Morrisson et al. 1990):  $\text{IS} = 0.0127 \times \text{EC}$ , where IS and EC are in  $\text{mmol L}^{-1}$  and  $\text{mS cm}^{-1}$ , respectively. The DOM concentration in the soil suspensions was analyzed using a total organic carbon analyzer (Shimadzu TOV-VCPH).

The stability of  $\text{TiO}_2$  NPs in soil leachates and suspensions was quantified by their sedimentation behaviors in this study. Ten milligrams of  $\text{TiO}_2$  NPs was added to soil leachates or soil suspensions to obtain a final  $\text{TiO}_2$  NPs concentration of  $50 \text{ mg L}^{-1}$ . The mixtures were sonicated vigorously for 30 min (500 W, 40 kHz), transferred into 250-mL graduated cylinders, and allowed to settle undisturbed for 10 h. Throughout the sedimentation process, aliquots of supernatant liquid (1 mL) were carefully periodically sampled from the top of the cylinders (2 cm below surface), and the concentration of  $\text{TiO}_2$  NPs was measured. The aggregate size distribution and zeta potential of  $\text{TiO}_2$  NPs in soil leachates were determined using a Zetasizer Nano ZS 90. After sedimentation, soil particles settled out and suspended in suspensions were analyzed on a scanning electron microscope (SEM, Hitachi S-4800 FE) equipped with an energy dispersive X-ray spectroscopy (EDS, Horiba EMAX-7000) detector for examining the combination of these particles with  $\text{TiO}_2$  NPs.

Analysis of  $\text{TiO}_2$  NPs concentrations in aqueous samples is referred to Zhang et al. (2007). Briefly, the  $\text{TiO}_2$  NPs suspension was first evaporated to dryness in glass tubes, followed by digestion with 5 mL of a sulfuric acid-ammonium sulfate solution by heating. The sulfuric acid-ammonium sulfate solution was prepared by mixing 400 g ammonium sulfate with

700-mL hot, concentrated sulfuric acid. Ti in digested samples was determined by ICP-OES, and the concentration of  $\text{TiO}_2$  NPs in the suspensions was calculated by the mass balance between Ti and  $\text{TiO}_2$ .

### 2.4 Transport of $\text{TiO}_2$ NPs in soils: column experiments

Glass columns (2.5 cm in inner diameter and 10 cm in length) were packed uniformly with soils. The resulting porosity of the packed columns was gravimetrically measured to be 0.41–0.44 (Table 2). Once packed, the column was flushed with 20 pore volumes (PVs) of deionized water, and the absorbance of the outflow at 420 nm was determined to be less than 0.006, suggesting that the soil colloids in the outflow were negligible. Immediately prior to the next step, an aqueous suspension containing a final  $\text{TiO}_2$  NPs concentration of  $50 \text{ mg L}^{-1}$  and a desired FA concentration of 0, 5, or  $10 \text{ mg L}^{-1}$  were produced by diluting the  $\text{TiO}_2$  NPs stock suspension and FA stock solution in deionized water. Subsequently, the prepared  $\text{TiO}_2$  NPs suspension was pumped into the columns, and the effluent was collected at regular time intervals using a BS-110A fraction collector (Huxi Analytical Instrument Factory Co., Ltd.). The concentration of  $\text{TiO}_2$  NPs in influent ( $C_0$ ) and effluent ( $C$ ) was determined by ICP-OES after digestion with sulfuric acid-ammonium sulfate. All solutions were introduced into columns upward by peristaltic pumps at a Darcy velocity of  $0.39\text{--}0.44 \text{ cm min}^{-1}$  for all experiments. All transport experiments were conducted in duplicate, and one representative breakthrough curve for each batch is shown in the results.

## 3 Results and discussion

### 3.1 Characterization of soils

The selected properties of the soils used in this study are summarized in Table 1. All three variable-charge soils are derived from quaternary red clay. The pH of the soil varied from 4.28 to 4.90. The SOM content of YT-S was approximately three times as much as that of YT-H and FY-H. The free iron oxide content of YT-S was lower than that of YT-H and FY-H, but the amorphous iron oxide content was two and four times as much as that of YT-H and FY-H, respectively. Due to the anaerobic environment of paddy fields, a portion of crystalline iron oxide could be transformed to an amorphous state, and hence, the amorphous iron oxide content in paddy fields was generally higher than that in sections of dry land (Ma and Xu 2010). No significant distinction in texture was found among the three soils. According to Ley et al. (1994), the average soil particle diameters were the sum of the sand, silt, and clay particle diameters of 0.175, 0.02, and 0.0015 mm, respectively, and multiplied by their respective

**Table 1** Physicochemical properties of the soils

	YT-H	YT-S	FY-H
Sampling sites	Yingtang, Jiangxi	Yingtang, Jiangxi	Fuyang, Zhejiang
Agrotype	Humid ferralsols	Stagnic anthrosols	Humid ferralsols
Parent materials	Quaternary red clay		
Land use types	Dry land	Paddy field	Rain-fed cropland
pH	4.76	4.90	4.28
SOM (%) <sup>1</sup>	1.12	3.86	1.18
CEC (cmol kg <sup>-1</sup> )	8.42	8.33	9.12
Free iron oxide (g kg <sup>-1</sup> )	44.1	20.5	48.2
Free aluminum oxide (g kg <sup>-1</sup> )	13.9	8.47	10.5
Amorphous iron oxide (g kg <sup>-1</sup> )	2.04	3.92	1.07
Amorphous aluminum oxide (g kg <sup>-1</sup> )	1.73	1.90	1.66
Texture (%)			
Clay	22.5	20.4	21.4
< 2 μm)			
Slit (2–20 μm)	42.9	43.7	40.6
Sand (20–2000 μm)	34.6	35.9	38.0
Zeta potential (mV)	– 12.7	– 19.6	– 15.6

<sup>1</sup> SOM (%) refers to the dry weight of soils

percentage contents in the soil. Consequently, the average particle diameters of YT-H, YT-S, and FY-H were 69, 72, and 75 μm, respectively.

### 3.2 Stability of TiO<sub>2</sub> NPs in soil leachates and soil suspensions

The essential physicochemical properties of soil leachates are shown in Tables 2 and 3. The pH varied from 4.89 to 5.50, slightly higher than that of the corresponding soil. The IS was lower than 0.5 mmol L<sup>-1</sup>. The DOM of YT-S was approximately twice that of the other two soils.

Take the ratio between the concentration of TiO<sub>2</sub> NPs suspended in soil leachates, C, and the initial concentration of TiO<sub>2</sub> NPs, C<sub>0</sub>, at specific time intervals as sedimentation behaviors index. Sedimentation curves of TiO<sub>2</sub> NPs in soil leachates are profiled in Fig. 1. The sedimentation of TiO<sub>2</sub>

NPs in soil leachates could be divided into two stages: a rapid settling period followed by a stable suspension period. After 3 h of rapid settling, 6.3% ± 1.9%, 50% ± 17%, and 8.9% ± 1.5% of the TiO<sub>2</sub> NPs were still suspended in the YT-H, YT-S, and FY-H soil leachates, respectively. After 10 h of sedimentation, 38% ± 0.4% of the TiO<sub>2</sub> NPs still stably existed in the YT-S soil leachate, while the TiO<sub>2</sub> NPs in YT-H and FY-H soil leachates were less than 5%. All these results above were in accordance with the size of TiO<sub>2</sub> NPs measured in soil leachates (Table 3). The aggregation size of TiO<sub>2</sub> NPs in the YT-H and FY-H soil leachates reached 583 and 574 nm, respectively, larger than the 473 nm in the YT-S soil leachate. According to previous reports (Chowdhury et al. 2011; Shih et al. 2012; Zhang et al. 2015), an IS of soil leachate that was lower than 0.5 mmol L<sup>-1</sup> had an ignorable effect on TiO<sub>2</sub> NP aggregation and sedimentation. Because of the higher DOM and pH, the zeta potential of the TiO<sub>2</sub> NPs was lower (the absolute value

**Table 2** Physicochemical parameters of the soil columns

	Soil	TiO <sub>2</sub> NPs (mg L <sup>-1</sup> )	FA (mg L <sup>-1</sup> )	Average particle size of soil (μm)	Porosity	Flow velocity (cm min <sup>-1</sup> )	Elution rate
EX-01	YT-H	50	0	69	0.41	0.44	0
EX-02			5		0.42	0.40	0.003
EX-03			10		0.41	0.39	0.208
EX-04	YT-S	50	0	72	0.44	0.40	0
EX-05			5		0.43	0.39	0
EX-06			10		0.43	0.41	0
EX-07	FY-H	50	0	75	0.41	0.41	0.025
EX-08			5		0.43	0.43	0.159
EX-09			10		0.42	0.40	0.378

was greater, Table 3); therefore, the TiO<sub>2</sub> NPs were more stable in the YT-S soil leachate.

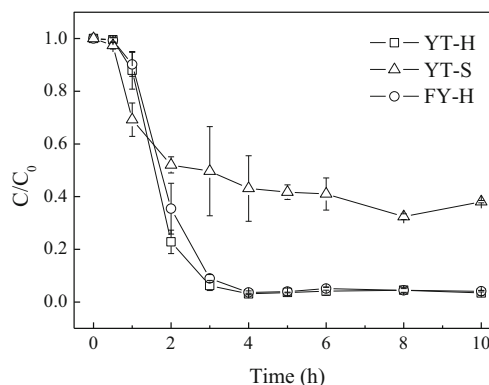
Except for the properties identical to those of soil leachates, such as ion and DOM contents, the soil particles in soil suspensions should interact with TiO<sub>2</sub> NPs and affect their stabilization (Fang et al. 2009; Sun et al. 2015b). Sedimentation curves of TiO<sub>2</sub> NPs in soil suspensions are presented in Fig. 2. Similar to the settling behaviors in soil leachates, TiO<sub>2</sub> NPs were more stable in the YT-S soil suspension. However, the sedimentation of the TiO<sub>2</sub> NPs was rapid, being completed in 1 h. One hour later, 43% ± 3.1% of TiO<sub>2</sub> NPs existed stably in the YT-S soil suspension, while over 99% of TiO<sub>2</sub> NPs in the YT-H and FY-H soil suspensions had already settled out. After 10 h of sedimentation, 27% ± 4.4% of TiO<sub>2</sub> NPs remained stable in the YT-S soil suspension. Fang et al. (2009) found that the TiO<sub>2</sub> NPs in suspension after 24 h were positively correlated with the DOM and clay contents of the soils but negatively correlated with the ionic strength, pH, and zeta potential. After settling for 24 h, 31.1–35.8% of the TiO<sub>2</sub> NPs particles were suspended in soil suspensions with a higher DOM content and lower IS, while more than 98% of the initial TiO<sub>2</sub> NPs had been deposited in soil suspensions with a higher IS and lower DOM content. There was almost no significant difference in the clay contents among the three soils in this study, and therefore, the clay content was not the main reason for the distinct settling behaviors of TiO<sub>2</sub> NPs. The lower zeta potential of TiO<sub>2</sub> NPs in the YT-S soil suspension was reasonably attributed to the higher DOM content derived from the higher SOM. Hence, the higher SOM of YT-S stabilized TiO<sub>2</sub> NPs in the soil suspension.

During sedimentation, the Fe and Al contents of the suspended mixture were also measured with ICP-OES after digestion with HF–HNO<sub>3</sub>–HClO<sub>4</sub> to represent the settling behaviors of soil particles. As demonstrated in Fig. 3, the deposition of soil particles coincided with that of TiO<sub>2</sub> NPs. According to the results of a Pearson correlation analysis (SPSS version 20.0), there was a significant positive correlation between suspended TiO<sub>2</sub> NPs and the contents of Fe ( $r = 0.984, p < 0.01$ ) and Al ( $r = 0.993, p < 0.01$ ) in the suspension, which indicated the cosedimentation of TiO<sub>2</sub> NPs and soil particles. SEM-EDS analysis of small suspended soil particles and large deposited soil particles demonstrated that the surface of both small and large soil particles adsorbed TiO<sub>2</sub> NPs

**Table 3** Properties of the soil leachates

	pH	IS (mmol L <sup>-1</sup> )	DOM (mgC L <sup>-1</sup> )	Zeta potential <sup>1</sup> (mV)	Particle size <sup>1</sup> (nm)
YT-H	5.22	0.45	22.6	-25.3	583
YT-S	5.50	0.40	43.1	-30.2	471
FY-H	4.89	0.36	23.7	-24.5	574

<sup>1</sup> Zeta potential and particle size of TiO<sub>2</sub> NPs in soil leachate

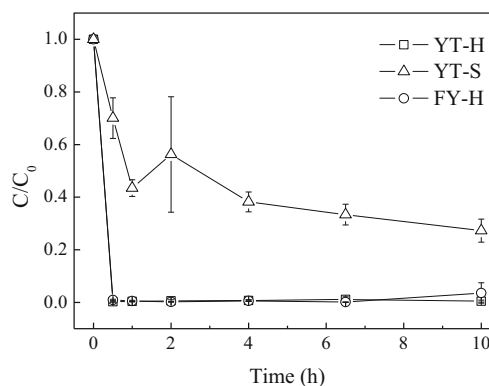


**Fig. 1** Sedimentation curves of TiO<sub>2</sub> NPs in the soil leachates

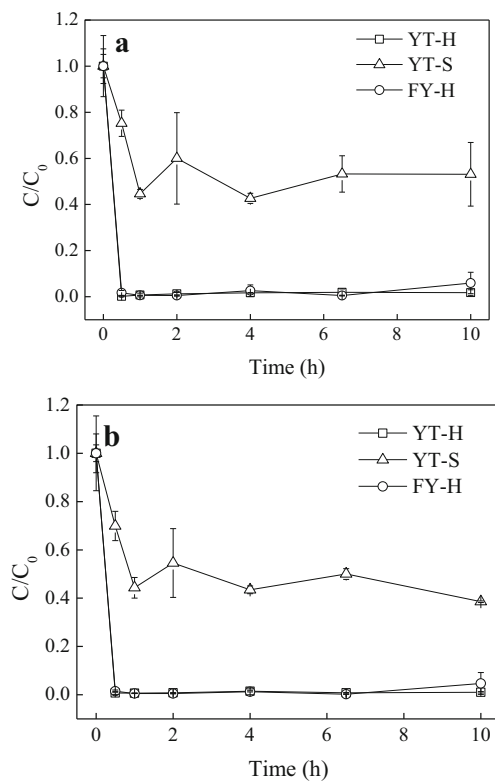
aggregates (Fig. 4), which confirmed the cosedimentation of TiO<sub>2</sub> NPs and soil particles. The positively charged iron and aluminum oxides on the surface of soil particles could electrostatically adsorb the negatively charged TiO<sub>2</sub> NPs. In addition, the roughness of the soil particle surface promoted the capture of TiO<sub>2</sub> NPs (Sun et al. 2015b).

### 3.3 Transport of TiO<sub>2</sub> NPs in soil columns

In column experiments, breakthrough curves of TiO<sub>2</sub> NPs in soils were plotted as dimensionless concentrations (C/C<sub>0</sub>) of TiO<sub>2</sub> NPs vs. PVs, as illustrated in Fig. 5. In the absence of FA, no TiO<sub>2</sub> NPs could be eluted from the YT-H and YT-S soil columns; TiO<sub>2</sub> NPs could be flushed from the FY-H soil column (C/C<sub>0</sub> > 0.01), but C/C<sub>0</sub> was merely 0.11 at 100 PVs; moreover, the elution rate of TiO<sub>2</sub> NPs was 0.025 throughout the transport experiment (Table 2). Previous studies also found that the mobility of nanoparticles in soils was weak. TiO<sub>2</sub> NPs were significantly retained in soils with higher clay contents and salinity and lower DOM contents (Fang et al. 2009). Zhao et al. (2012a, b) demonstrated that 93–99% of ZnO nanoparticles were retained in sandy loam soil. Wang et al. (2014) investigated the mobility of water-dispersed engineered nanoparticles in a red soil (Ultisol) and found that more than 90% of



**Fig. 2** Sedimentation curves of TiO<sub>2</sub> NPs in the soil suspensions



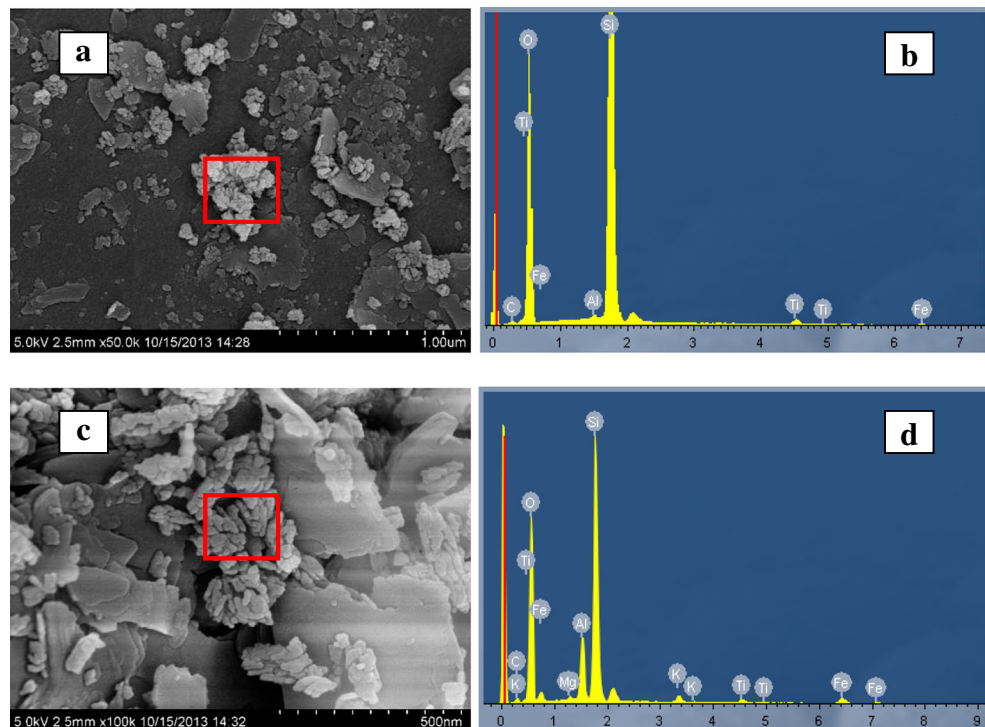
**Fig. 3** Relative concentrations of Fe (a) and Al (b) in the soil suspensions during sedimentation

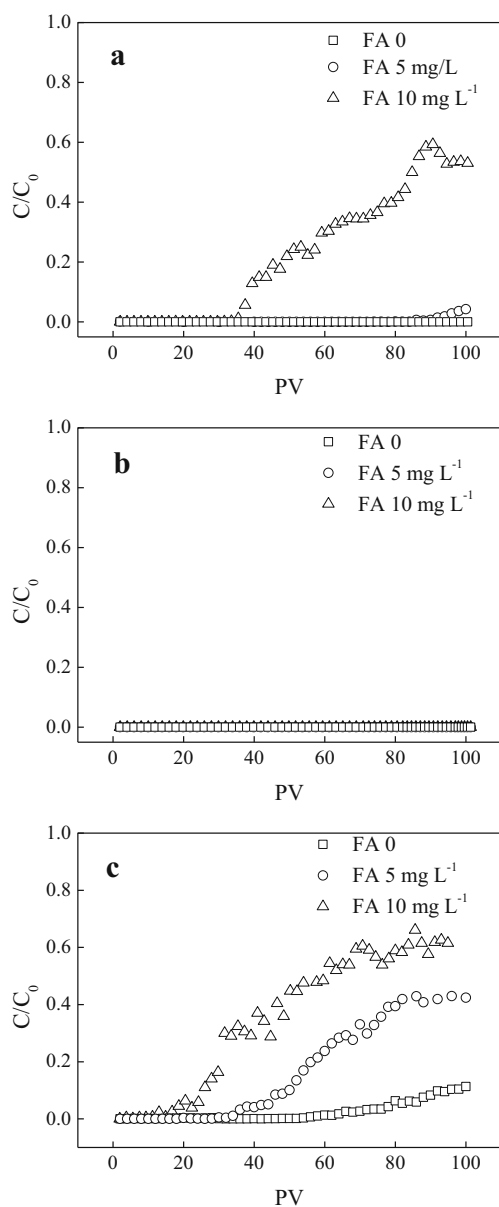
TiO<sub>2</sub> NPs, Ag nanoparticles, buckminsterfullerenes, and single-walled carbon nanotubes could not pass through the soil columns.

Generally, it is the physical filtration and physicochemical interactions between nanoparticles and soil particles that mainly contribute to the retention of nanoparticles in soils (Jaisi et al. 2008; Darlington et al. 2009; Fang et al. 2009). Straining is the trapping of the particles in the downgradient mobile-water conduits that are too narrow to allow particles to pass (Mcdowellboyer et al. 1986). In principle, straining is governed by the size of the particles and the pore size distribution of the porous media (Zhang et al. 2015). Empirically, particles were retained if their diameter exceeded 0.2–5% of the diameter of the porous media grains (Redman et al. 2004; Jaisi et al. 2008). However, straining has also been considered to be an important particle retention mechanism when the ratio of the particle diameter to the media grain diameter is larger than 0.0017 (Bradford et al. 2002; Chen et al. 2012), and straining could even be more important if the collector grains were rough and irregular in shape (Bradford et al. 2002; Tufenkji and Elimelech 2004). In this study, the aggregate size of TiO<sub>2</sub> NPs in deionized water without FA was up to 498 nm, which was 0.66–0.72% of the mean size of the three soil particles. Therefore, it could be reasonably inferred that straining was inevitably involved in the retention of TiO<sub>2</sub> NPs in the soils. In addition, the straining potential of the porous soil media was significantly increased due to the high heterogeneity and shape irregularity of the soils.

TiO<sub>2</sub> NPs with a zeta potential of –18.2 mV in deionized water and in the absence of FA were prone to be adsorbed onto the positively charged surface of soil particles, which was another crucial reason for the significant retention of TiO<sub>2</sub>

**Fig. 4** SEM-EDS of YT-S soil particles deposited (a, b) and suspended (c, d)





**Fig. 5** Breakthrough curves of TiO<sub>2</sub> NPs in YT-H (a), YT-S (b), and FY-H (c) soil columns

NPs in the soils. Zhao et al. (2012a, b) suggested that although ZnO nanoparticles exhibited low mobility in a sandy loam soil, soil colloids might act as carriers of strongly adsorbed nanoparticles and enhance their passage away from the soil. Another investigation also found that kaolin and bentonite increased the transport of TiO<sub>2</sub> NPs in porous quartz sand in the presence of NaCl (Cai et al. 2014). However, although a portion of TiO<sub>2</sub> NPs adsorbed onto the surface of soil particles suspended stably in the YT-S soil suspension, the adsorbed TiO<sub>2</sub> NPs were finally retained in soils, resulting from the lack of soil particle migration throughout the transport experiments. Thus, the mobility of TiO<sub>2</sub> NPs in soils was not directly related to their stability in soil suspensions in this study. Wang et al. (2018) suggested that the retention capacity of Ag

nanoparticles in soils was positively correlated with the iron oxide content. Generally, the specific area of amorphous iron oxide is larger than that of free iron oxide, and it was reasonably concluded that the positively charged amorphous iron oxide could exert stronger inhibition of the transport of the negatively charged TiO<sub>2</sub> NPs than free iron oxide due to the greater adsorption of nanoparticles. Unlike the complete retention in YT-H and YT-S soils, a small amount of TiO<sub>2</sub> NPs could be eluted from the FY-H soil column because of the lower adsorption by the lower amorphous iron oxide content. It was suggested that the difference in the amorphous iron oxide content influenced the disparity in the transport behaviors of TiO<sub>2</sub> NPs in the three variable-charge soils. Despite the high content of SOM, no mobility of TiO<sub>2</sub> NPs was observed in YT-H soil, which indicated that SOM was not a key factor affecting the migration of TiO<sub>2</sub> NPs in soils in this study.

In general, except for the physicochemical properties of soil, the transport and retention behaviors of nanoparticles were remarkably affected by their characteristics (Jaisi et al. 2008; Fang et al. 2009). Nanoparticles modified by organic matter or surfactants exhibited high mobility in soils or well-controlled porous quartz sand. Compared to pristine nanoparticles, the maximum relative concentration ( $C/C_0$ ) of ZnO nanoparticles modified with sodium citrate increased elution from sandy soils and sandy loam soils by 0.04 and 0.02, respectively (Zhao et al. 2012a). DOM coating facilitated the transport of nanoparticles in saturated porous quartz- and iron oxide-coated quartz sand (Han et al. 2014; Zhang et al. 2015). As shown in Fig. 5, FA enhanced the mobility of TiO<sub>2</sub> NPs in YT-H and FY-H soils. In the YT-H assay, the elution rate of TiO<sub>2</sub> NPs dispersed by 5 mg L<sup>-1</sup> of FA was 0.3%, and it increased to 20.8% when increasing the FA concentration to 10 mg L<sup>-1</sup>. Meanwhile, the breakthrough time (the PVs when  $C/C_0 > 0.01$ ) shifted earlier from 90 PVs to 36 PVs. Likewise, FA induced the increase in elution and the advance of the breakthrough time of TiO<sub>2</sub> NPs in FY-H soil columns. The promotion of the TiO<sub>2</sub> NPs mobility in soil columns by FA could be summarized as follows: (1) FA dispersed TiO<sub>2</sub> NPs, and nanoparticles of smaller size tended to exhibit higher mobility (Guzman et al. 2006; Solovitch et al. 2010; Chinnapongse et al. 2011; Rottman et al. 2013). The aggregate size of TiO<sub>2</sub> NPs dispersed in 10 mg L<sup>-1</sup> FA was 448 nm, smaller than that in 5 mg L<sup>-1</sup> FA (505 nm) and in deionized water (529 nm). (2) Unbonded FA in suspension could be adsorbed onto the surface of soil particles neutralizing the positive charge of the grain, occupying the available adsorption sites, and, therefore, diminishing the adsorption of TiO<sub>2</sub> NPs onto the soil particles. The lack of DOM determined in the outflow after removal of TiO<sub>2</sub> NPs suggested the complete adsorption of free FA by the soil particles in columns. Unlike the mobility in YT-H and FY-H soils, no FA-dispersed TiO<sub>2</sub> NPs could be flushed from YT-S soil columns, which further confirmed that a higher content of amorphous iron oxide was

the major factor accounting for the total retention of TiO<sub>2</sub> NPs in YT-S.

## 4 Conclusions

The stability and transport behaviors of TiO<sub>2</sub> NPs in three variable-charge soil samples were studied in batch and column experiments. The stability of TiO<sub>2</sub> NPs in soil suspensions was strongly associated with the SOM of the tested soils, and better stability of TiO<sub>2</sub> NPs was observed in the YT-S suspension, with a higher SOM content. However, the transport of TiO<sub>2</sub> NPs in soils was not directly related to their stability in soil suspensions. The difference in the positively charged amorphous iron oxide content induced the disparity in the mobility of TiO<sub>2</sub> NPs in the tested soils. A small amount of TiO<sub>2</sub> NPs was eluted from FY-H, with a low amorphous iron oxide content, while all TiO<sub>2</sub> NPs were retained in YT-H and YT-S. Moreover, FA facilitated TiO<sub>2</sub> NPs transport in soils by dispersing TiO<sub>2</sub> NPs and reducing the adsorption of TiO<sub>2</sub> NPs onto soil particles.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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