

**Effect of Surfactants on the Behaviors and Transport of Metal Oxide  
Nanomaterials in Aqueous Matrices and Porous Media**

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# CHAPTER 1

## Background introduction

### 1.1 Research background

Currently, engineered nanomaterials (ENMs) are being widely applied to a plenty of industrial and consumer products. However, the large-scale industrial production and application of ENMs will inevitable result in their release into environment and generate potential environmental risks (Gardea-Torresdey et al., 2014; Rathnayake et al., 2014; Van Koetsem et al., 2015; Zhang et al., 2008). ENMs are being applied to products such as sunscreens, cosmetics, paints, pigments, foods and medicine, etc (Han et al., 2016; Ma et al., 2013; Tong et al., 2014). In addition, consumer products containing ENMs reached as many as 1317 in the year of 2011, a number 521% higher compared to the year 2006 (Bandyopadhyay et al., 2013). In a research released in 2012, it was reported the median of the annual world production of TiO<sub>2</sub> and ZnO ENMs were 3000 and 500 tons, respectively, which ranked the top two among various metallic ENMs (Piccinno et al., 2012). Along with the huge production and application of metallic ENMs, some researchers estimated the environmental concentration of ZnO ENMs in United Kingdom could range from less than 100 µg/L (in water) to a few mg/kg (in soil) (Boxall et al., 2007). Considering the increasing industrial application, the environmental levels of TiO<sub>2</sub> and ZnO ENMs are expected to grow significantly in the following years (Ma et al., 2013). As the report concerning about the toxicities of TiO<sub>2</sub> and ZnO ENMs to bacterial (Kasemets et al., 2009; Li et al., 2013; Read et al., 2016), fish (Chen et al., 2014; Kool et al., 2011; Wiench et al., 2009; Xiong et al., 2011;

Yu et al., 2011), algae (Aruoja et al., 2009; Ji et al., 2011; Manzo et al., 2013; Metzler et al., 2011; Tang et al., 2015), *Daphnia* (Adam et al., 2015; Oleszczuk et al., 2015; Poynton et al., 2011; Yang et al., 2014), soil organisms (Canas et al., 2011; Heggelund et al., 2014; Kool et al., 2011) etc. are increasing rapidly in recent years, the risks of ENMs to biosphere cannot be ignored. Consequently, researches on the behaviors and fate of TiO<sub>2</sub> and ZnO ENMs in environment are becoming more and more important. Surfactants are commonly used in both industry and household, which can usually be detected in the wastewater with high concentration. For instance, Narkis and Sun et al. reported that the detergents' concentration in industrial wastewater can range from few hundreds to thousands of ppm (Narkis and Ben-David, 1985; Sun et al., 2015). Meanwhile, surfactants are well known to be able to promote the dispersion of ENMs in aqueous solutions for industrial or laboratorial purposes. The dispersive effect of surfactants on ENMs make it necessary to study the effect of surfactant on the environmental behaviors and transports of ENMs. For example, Liu et al. found surfactants of dodecyl benzene sulfonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) improved the dispersion and stability of graphene ENMs even at a low concentration of 0.004% (w:v). Besides, surfactant concentration was also proved to exert significant impact on the retention and transport of graphene ENMs in saturated porous media (Liu et al., 2015). Similarly, Yang et al.'s study also showed that CTAB enhanced the suspension of Al<sub>2</sub>O<sub>3</sub> nanoparticles in aqueous solutions (Yang et al., 2011). At a pH of 7.0, Triton X-100 and SDBS increased of steric repulsive forces and inhibited the uncontrollable aggregation of nano-TiO<sub>2</sub>. Along with the increase of

surfactant concentration, the transport distances of nano-TiO<sub>2</sub> in porous media column also increased at pH 9.0 (Godinez and Darnault, 2011).

Considering the wide application of ENMs and surfactant in the industries and households, it is reasonable to assume the co-existence of ENMs and surfactant in natural environment may happen. Therefore, the effect of surfactants on the environmental behaviors and transport of ENMs are necessary to be studied.

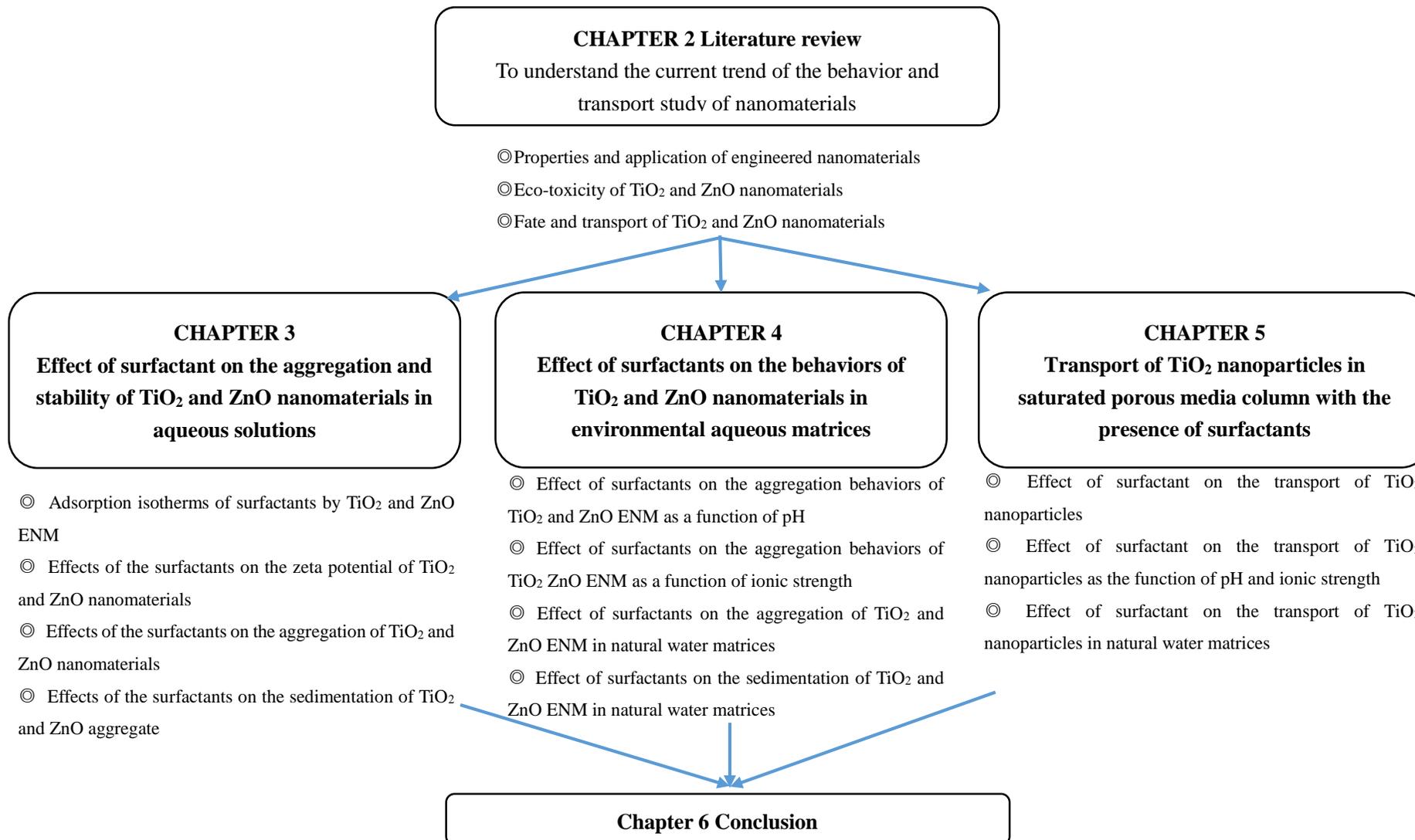
## **1.2 Research aims**

The aims of this research is to investigate the environmental behavior and fate of typical TiO<sub>2</sub> and ZnO ENMs under the effect surfactants.

The specific objectives:

- 1) To understand the effect of surfactants on the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENMs in a realistic dynamic aqueous environment, and reveal the mechanisms of how ionic and nonionic surfactants impact those behaviors of the above-mentioned ENMs.
- 2) To understand the effect of surfactants on behaviors of TiO<sub>2</sub> and ZnO ENMs in suspensions of various pH or ionic strength, and natural aqueous matrices.
- 3) To understand the effect of surfactant on the transport of TiO<sub>2</sub> and ZnO ENMs in a porous media.

## **1.3 Research structure**



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## CHAPTER 2

### Literature review

Nanomaterial refers to the materials which particle size range from 1 to 100 nanometers. Because of the unique physicochemical properties such as small size, large surface areas, surface activity, high thermal and energy conductivity, ENMs is widely applied in a lot of field. The applications of ENMs led to the inventions of numerous consumer products with new functions and improved people's daily life. However, the inevitable release of engineered nanomaterials into natural environment also brings potential risks to the environment. In this chapter, a literature review concerning the application, fate/transport, and environmental risks of engineered nanomaterials is provide.

#### 2.1 Properties and application of engineered nanomaterials

Engineered nanomaterials can be classified into four types: carbon-based, metal-based, dendrimers and nanocomposites (US Environmental Protection Agency, 2007), among which the former two kinds of ENMs are most widely applied in industries. Carbon-based ENMs mainly include carbon nanotubes (CNTs) and fullerene (C<sub>60</sub>). Whereas the metal-based ENMs are much more diverse, which include metal nanomaterials (nano Ag, Au, Zero valent iron, ect.), metal oxide nanomaterials (TiO<sub>2</sub>, ZnO), and quantum dots.

Table.1. lists a general description of the properties, applications of several engineered nanomaterials. In general, it is the small size that gives nanomaterials those physico-chemical properties. Because of the nanometer-grade particle size, the nanomaterials

owns a remarkable specific surface area and much higher surface atoms than normal-sized materials, which make nanomaterials usually more reactive than other materials. Hence, the engineered nanomaterials have a lot of unique characteristics and various applications.

**Table.1 The property and application of common engineered nanomaterials**

Category	Nanomaterial	Property	Application	Reference
<b>Carbon-based</b>	CNTs	Hydrophobic surface; hollow tube structure; modifiable surface; thermal conductivity and stability; mechanical and electrical properties; strong tensile strength and high elasticity.	Composites; sensors and probes; field emission devices; flat panel displays; energy storage devices; nanometer-sized electronic devices.	(Bouchard et al., 2012; Hyung et al., 2007; Lu et al., 2014; Paradise and Goswami, 2007)
	Fullerene	Hydrophobic surface; modifiable surface; hollow cage structures; chemically equivalent carbon atoms.	Solar cell; fuel cells; polymer composite; conductive thin fill; lubrication enhancement; pharmaceuticals; photodetectors.	(Cai et al., 2013; Lee et al., 2009; Liu et al., 2015; Nalwa et al., 2010)
<b>Metal-Based</b>	Silver nanomaterial	Antibacterial; antifungal; antiviral; anti-inflammatory activity; pH-dependent	Food packaging materials; food supplements; odor-resistant textiles; electronics;	(Ge et al., 2014; Haider et al., 2015; Schluesener and

<b>Metal-Based (continued)</b>	Silver nanomaterial (continued)	partitioning to solid and dissolved particulate matter.	household appliances, cosmetic; medical devices; water disinfectants.	Schluesener, 2013; Wijnhoven et al., 2009)
	Gold nanomaterial	High S/V ratio; low cytotoxicity; unique tunable optical properties; manipulable surface and core properties; chemically stable.	Biosensing; photothermal therapeutic; diagnostic; drug delivery; electron transfer; labelling and visualizing; Catalysis.	(and and El-Sayed*, 2006; Chen et al., 2008, 2008; Sperling et al., 2008)
	Zero valent iron nanomaterial	High S/V ratio; cheap cost; high reactivity for contaminant removal; sufficient mobility within porous media; sufficient reactive longevity; low toxicity; environmental compatibility.	Ground water and soil remediation.	(Crane et al., 2011; Crane and Scott, 2012; Fu et al., 2014; Grieger et al., 2010; Kanel et al., 2008; Klimkova et al., 2011;)
	TiO <sub>2</sub> nanomaterial	High S/V ratio; photo-catalytic activity; wide-bandgap;	Sunscreen, cosmetics, paints, Pigments; coatings; foods;	(Godinez and Darnault, 2011;

<b>Metal-Based (continued)</b>	TiO <sub>2</sub> nanomaterial (continued)	porosity; ion exchange properties.	pharmaceuticals; adsorbent; photo-catalysis; environmental remediation.	Henderson, 2011; Kanakaraju et al., 2015; Li et al., 2015; Sygouni and Chrysikopoulos, 2015; Yang et al., 2008; Zhang et al., 2011)
	ZnO nanomaterial	High S/V ratio; photo-catalytic activity; Antibacterial and antifungal activities.	Ultra-violet lasers; gas sensors; energy conversion; biomedical sciences; photo- catalysis; sunscreens; cosmetics; paints; pigments; foods; medicine.	Chung et al., 2009; Fatehah et al., 2014; Oleszczuk et al., 2015; Peng et al., 2015; Poynton et al., 2011; Sharma et al., 2010.

<b>Metal-Based (continued)</b>	Quantum dot	Photoluminescence; emitting light over a wide range of wavelengths; high extinction coefficients and high brightness; exhibiting a pronounced resistance to both chemical and photo-degradation; large surface area; offering multiple functionalization sites.	Bioanalytical applications, imaging, labelling and sensing; solar cells; photovoltaics; memory chips; <u>miniature lasers</u> ; displays.	(Medintz et al., 2005; Medintz and Mattoussi, 2009)
<b>Dendrimer</b>	Dendrimer	Highly-branched structures; high densities of peripheral functionalities; monodisperse structure; chemical versatility.	Drug delivery; catalysis.	(Abbasi et al., 2014; Zhu and Shi, 2013)
<b>Nanocomposites</b>	Graphene-based nanocomposites	Introducing controlled functional building blocks to graphene	Solar energy conversion; electrochemical energy devices; removal of heavy metal ions, organic pollutants.	(Chang and Wu, 2013; Georgakilas et al., 2012; Pumera, 2011)

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## 2.2 Eco-toxicity of TiO<sub>2</sub> and ZnO nanomaterials

According to a report by Piccinno et al, among the commercialized ten different ENMs (TiO<sub>2</sub>, ZnO, FeO<sub>x</sub>, AlO<sub>x</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, Ag, quantum dots, CNT, and fullerenes), TiO<sub>2</sub> and ZnO nanomaterials shared the highest production among all the above ENMs (Piccinno et al., 2012). Although the application of TiO<sub>2</sub> and ZnO nanomaterials offers a plenty of functionalized products to the global market, the potential environmental risks of these two nanomaterials are also attracting more and more attention.

Some studies have demonstrated that inhalation of TiO<sub>2</sub> nanoparticles leads to pulmonary inflammation for mice (Warheit et al., 2007a, 2007b). Wang et al. reported that after the exposure to different sizes (25 and 80 nm) of TiO<sub>2</sub> nanoparticles for 2 weeks, hepatic injury and myocardial damage also occurred for adult mice (Wang et al., 2007). In a study of cytotoxicity, anatase TiO<sub>2</sub> nanoparticles were proved to cause oxidative DNA damage, lipid peroxidation, and micronuclei formation, as well as to increase hydrogen peroxide and nitric oxide production in a human bronchial epithelial cell line (Gurr et al., 2005). In addition, after 12 to 72-h exposure of syrian hamster embryo cells to 1 µg L<sup>-1</sup> TiO<sub>2</sub> nanoparticles, a significant dose-dependent increase in the formation of micronuclei and apoptosis was observed (Rahman et al., 2002).

As to the eco-toxicity of TiO<sub>2</sub> ENMs, it was found that TiO<sub>2</sub> inactivated algae possibly by generating reactive oxygen species (ROS) (Ochiai et al., 2010). In addition, some reports shows that TiO<sub>2</sub> ENM aggregates might entrap algal cells because of the toxic effects (Aruoja et al., 2009; Sharma, 2009). As the first group to examine the impact of nanoparticles on invertebrates, Lovern et al. reported that exposure to filtered TiO<sub>2</sub>

nanoparticles resulted in an increase in the mortality of invertebrates (Lovern and Klaper, 2006). According to a research conducted by Li et al., apart from the photocatalytic oxidation and physical hindering, presence of nanoparticles such as TiO<sub>2</sub> resulted in the disruption of the energy budget of *C. dubia*, which led to adverse effects on their physical conditions and reproductivity as a result (Li et al., 2011). Kim et al. applied hollow glass beads coated with TiO<sub>2</sub> nanomaterials to batch culture of *Anabaena*, *Microcystis*, and *Melosira* under black UV lamps. It was found <sup>14</sup>C-assimilation rate decreased, which indicated the growth of the above-mentioned were inhibited (Kim and Lee, 2005). Linkous et al. coated TiO<sub>2</sub> nanomaterial on cement substrates and applied those coated substrates to growth media containing *Oedogonium*. They found that nano-TiO<sub>2</sub> coated cement particles increased the non-specific breakdown of the *Oedogonium*' cellular structure, and concluded that the breakdown of cellular structure was likely to be related to the ROS interaction with the cells (Linkous et al., 2000). In a research of the toxicological impact of TiO<sub>2</sub> nanomaterials on *Desmodesmus subspicatus*, Hund-Rinke et al. found with the addition of 25 nm sized TiO<sub>2</sub> nanoparticles, the EC<sub>50</sub> ranged from 44 to 50 mg L<sup>-1</sup>, but no toxicity was observed if the primary particle size of TiO<sub>2</sub> was 100nm (Hund-Rinke and Simon, 2006).

Eco-toxicological effect ZnO ENMs had also been reported by many researchers. For example, Jones et al., reported that smaller ZnO particles (8 nm, 50–70 nm) were found to increase the growth inhibition to *S. aureus* than larger particles (>1 μm) (Jones et al., 2008). The Gram-positive bacterium of *S. aureus* is more sensitive to ZnO ENM toxicity than the Gram-negative bacteria of *E. coli* and *Pseudomonas aeruginosa*

(Premanathan et al., 2011), because of the differences in bacteria's cell membrane structure which controls the access of toxicants to action sites. In addition, there are also reports concerning the toxicity of ZnO ENMs to the yeast, and the soluble Zn<sup>2+</sup> was deemed as the major reason for the toxicity. For example, Kasamets et al. reported that ZnO ENMs (particle size 50–70 nm) showed toxicity to the *Saccharomyces cerevisiae*, and experiment found the 24-h EC50s was 131 mg/L (Kasemets et al., 2009). With the presence of 1 mg/mL ZnO ENM, the growth inhibition rate of a pathogenic yeast *Candida albicans* was observed to exceed 95% (Mortimer et al., 2010).

What is more, many studies had focused on the eco-toxicities of ZnO to plants and algae. For instance, Xing et al. found that the seed germination and the root elongation of ryegrass were significantly inhibited with the presence of 2000 mg/L ZnO ENM, the toxicity were considered to be resulted from both dissolved free Zn<sup>2+</sup> and particle-dependent effect (Lin and Xing, 2007). Similarly, Manzo et al. also reported that ZnO ENM remarkably affected the root elongation of garden cress and lead to the genotoxicity to the broad bean (Manzo et al., 2011). A study conducted by Miller et al. showed that ZnO ENM could retard the growth of four marine algae species. The growth rate of *Thalassiosira pseudonana*, *Dunaliella tertiolecta*, *Skeletonema marioni*, and *Isochrysis galbana* were found to be 50–75% reduced with the introduction of 1 mg/L ZnO ENM (20–30 nm). Similarly, the dissolution, release and uptake of free Zn<sup>2+</sup> were presumed to be the major reason of toxicities (Miller et al., 2010).

Toxicity studies of ZnO ENMs on aquatic biosphere was also conducted by some researchers. For instance, a study reported that the 48-h LC50s of ZnO ENM (50–70

nm) to *D. magna* and *T. platyurus* were 3.2 mg/L and 0.18 mg/L, respectively (Heinlaan et al., 2008). Using the same ZnO ENM reported by Heinlaan et al., Blinova et al. discovered the 48-h EC50 to *D. magna* and 24-h LC50 to *T. platyurus* were 2.6 mg/L and 0.14 mg/L, respectively (Blinova et al., 2010). The researched of both Blinova et al. and Heinlaan et al. proved that the toxicity of ZnO ENM to zebrafish embryo resulted from the dissolved Zn<sup>2+</sup>.

Some researchers reported that ZnO ENM can be significantly toxic to the embryo of zebrafish at early development stage. Bai et al. studied the toxicity of a 30-nm ZnO ENM to the embryo of zebra fish, they concluded that dissolved free Zn<sup>2+</sup>, small ZnO aggregates, and big ZnO aggregates exerted a combined effect on the early development of zebrafish embryos. When the exposed to 50 and 100 mg/L ZnO ENM, increased mortalities of the zebrafish embryo were observed, and exposures to 1–25 mg/L ZnO ENM led to reduced hatching rate (Bai et al., 2010). Similarly, Zhu et al. demonstrated that the 96-h LC50 and 84-h EC50 (hatching rate) of a 20-nm ZnO ENM were 1.79 mg/L and 2.06 mg/L, respectively. Besides, approximately 30% of the ZnO ENM dissolved during a dissolution experiment, and this dissolved Zn<sup>2+</sup> is believed be responsible for the toxicity of ZnO ENM to the zebrafish embryos (Zhu et al., 2008).

### **2.3 Fate and transport of TiO<sub>2</sub> and ZnO nanomaterials**

To understand the behaviors and transport of engineered nanoparticles in water environment and saturated subsurface environments is critical for evaluating the risks of ENM's release into environment. Aggregation and sedimentation are important

processes that affect the fate and risk of ENMs in aquatic environment; transport and deposition behaviors of colloids and nanoparticles are of importance to understand the mobility and fate of nanoparticles in the subsurface environment. By unveiling the mechanisms responsible for the behaviors and transport of particles, researchers can gain a more comprehensive method to conduct risk assessments engineered nanomaterials.

The key factors affecting the environmental behaviors and transport of TiO<sub>2</sub> nanomaterials in aquatic and subsurface mainly lies on pH of matrix, ionic strength, and surfaces coatings (Brunelli et al., 2013; Fang et al., 2009). As the pH of TiO<sub>2</sub> nanomaterial suspensions changed toward the point of zero charge (pHpzc), the aggregates size of TiO<sub>2</sub> increased significantly while their mobility reduced (Sygouni and Chrysikopoulos, 2015). When the pH of dispersions is closed to the pHpzc, the surface ionization of nanoparticles will be suppressed and the surface charge will reduce to zero, consequently weakening the repulsive forces between nanoparticles and promoting the aggregation of TiO<sub>2</sub> nanoparticles. The aggregation of TiO<sub>2</sub> ENM is remarkably affected by the ionic strength and electrolyte types (Cupi et al., 2016). In the situation of increasing the ionic strength or the valency of the ions, the compression of the electrical double layer of nanoparticle will be enhanced, hence reducing the repulsive force and promoting the aggregation of nanoparticles (Brunelli et al., 2013; French et al., 2009; Godinez and Darnault, 2011; Liu et al., 2013). Some researched studied the aggregation and stability of a TiO<sub>2</sub> ENM in several soil suspensions, and also the transport of those ENM in saturated soil columns. They found that the retention

of TiO<sub>2</sub> ENM was more remarkable in those soils which contained higher percentage of clay and higher salinity (Fang et al., 2009). In addition, the stability of ENMs in natural water environments is also reported to be significantly affected by the presence of natural organic matter (NOM). Some studies also showed NOM can affect the stability of ENMs such as fullerenes, carbon nanotubes or quantum dots, indicating the introduction of NOM may impact the stability and transport of ENMs in porous media (Hoon Hyung et al., 2006; Li et al., 2009; Navarro et al., 2009). NOM stabilizes ENMs by the ways of both electrical repulsions and steric inhibition. However, the presence of high concentration of divalent ions will significantly affect stability of ENMs because of the bridging effect between divalent cations and surface adsorbed NOM. Surfactants may also be adsorbed to ENMs and alter their stability and mobility in porous media by changing their surface charge and hydrophilicity. Surfactant may be adsorbed by the porous media and thereby alter the hydraulic characteristics and interaction forces of the media filled in (Abu-Zreig et al., 2003; Brown and Jaffé 2001). For instance, the application of sodium dodecylbenzene sulfonate (SDBS), an anionic surfactant, to the stabilization of ENMs led to the increase of nanoparticles' mobility in saturated porous media. Both nonionic and ionic surfactants are widely applied to the coating of TiO<sub>2</sub> ENM to enhance dispersion or stability in industries (Tkachenko et al., 2006).

The increasing application of ZnO ENMs also inevitably results in their release into environment, which redoubles the need of the study on the fate and transport of the ZnO ENM in environment. For instance, Zhang et al. studied the effect of natural organic

matter (NOM) and divalent cations ( $\text{Ca}^{2+}$ ) on the stability of ZnO ENM, it was found that on one side the NOM retarded the aggregation of ZnO ENM, on other side  $\text{Ca}^{2+}$  promoted the aggregation (Zhang et al., 2009). Other researchers studied the adsorption behavior of humic acids (HA) by ZnO ENM and the impact of pH for the adsorption, it was found that the presence of HA stabilized the ZnO ENM but the pH value of the suspension remarkably affected the stability of ZnO ENM (Scheckel et al., 2010). Similarly, the dispersion of ZnO ENM in different natural waters including seawater, lagoon, river, and groundwater was studied. It was found that the NOM could be adsorbed by the nanoparticles and significantly retarded their aggregation and sedimentation (Keller et al., 2010). Generally, water chemistry conditions such as ion valence, ionic strength, and pH exert significant impact on the transport and deposition of ZnO ENM, and mobility of ZnO ENM was observed to be low in the typical water environment. The straining resulted by simultaneous aggregation and deposition was discovered to dominate the mechanisms that affecting the transport of ZnO ENM. In addition, NOM was proved to significantly promote the mobility of ZnO ENM in quartz sand packed porous media by altering the particle–surface and particle–particle interaction (Jiang et al., 2013).

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## CHAPTER 3

### **Effect of surfactants on the aggregation and stability of TiO<sub>2</sub> and ZnO engineered nanomaterials**

#### **Abstract**

In the first part of study, the adsorption of surfactants and the resulted effect on the behaviors of TiO<sub>2</sub> and ZnO engineered nanomaterials (ENMs) were studied after a 24-h batch reactor experiment, and then the sedimentation of the aggregates of TiO<sub>2</sub> and ZnO ENMs were observed with a UV-spectrophotometer at a wavelength of 378 nm. It was found that both SDS and NP-9 surfactant can be apparently adsorbed by TiO<sub>2</sub> and ZnO ENMs, and Langmuir model can be well applied to the fitting of the adsorption isotherms. Next, the presence of both surfactants effectively reduced the aggregation of two ENMs when surfactant concentration exceeded 0.015% as observed by both dynamic scattering lightening (DSL) and scanning electronic microscopy (SEM). The SDS surfactant remarkably affected the zeta potential of TiO<sub>2</sub> and ZnO nanomaterials, and the absolute value of nanomaterials' zeta potential decreased at first and then significantly increased with growth of SDS concentration. This process remarkably increased the electrical repulsive forces between nanoparticles, and hence reduced the aggregation and increased the stabilities of the aggregates of both TiO<sub>2</sub> and ZnO nanomaterials. As for the non-ionic NP-9 surfactant, the surfactant covered the surface of nanomaterials, hence reduced the aggregation and increased the stability of both nanomaterials. In a 24-h sedimentation observation, it was found the presence of both surfactants significantly retarded the sedimentation of TiO<sub>2</sub> and ZnO aggregate, and the

increase of concentration of surfactants resulted stronger retardation on the sedimentation of the aggregate of ENMs.

### **3.1. Introduction**

Currently, engineered nanomaterials (ENMs) are being widely applied to a plenty of industrial and consumer products. However, the large-scale industrial production and application of ENMs will inevitable result in their release into environment and generate potential environmental risks (Gardea-Torresdey et al., 2014; Rathnayake et al., 2014; Van Koetsem et al., 2015; Zhang et al., 2008). Consequently, researches on the behaviors and fate of TiO<sub>2</sub> and ZnO ENMs in environment are becoming more and more important.

Surfactants are commonly used in both industry and household, which can usually be detected in the wastewater with high concentration. For instance, Narkis and Sun et al. reported that the detergents' concentration in industrial wastewater can range from few hundreds to thousands of ppm (Narkis and Ben-David, 1985; Sun et al., 2015). Meanwhile, surfactants are well known to be able to promote the dispersion of ENMs in aqueous solutions for industrial or laboratorial purposes. The dispersive effect of surfactants on ENMs make it necessary to study the effect of surfactant on the environmental behaviors and transports of ENMs. For example, Liu et al. found surfactants of dodecyl benzene sulfonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) improved the dispersion and stability of graphene ENMs even at a low concentration of 0.004% (w:v). Besides, surfactant concentration was also proved

to exert significant impact on the retention and transport of graphene ENMs in saturated porous media (Liu et al., 2015). Similarly, Yang et al.'s study also showed that CTAB enhanced the suspension of Al<sub>2</sub>O<sub>3</sub> nanoparticles in aqueous solutions (Yang et al., 2011). At a pH of 7.0, Triton X-100 and SDBS increased of steric repulsive forces and inhibited the uncontrollable aggregation of nano-TiO<sub>2</sub>. Along with the increase of surfactant concentration, the transport distances of nano-TiO<sub>2</sub> in porous media column also increased at pH 9.0 (Godinez and Darnault, 2011).

In this chapter, ionic SDS and non-ionic NP-9 were chosen to study their effect on the aggregation and stability of TiO<sub>2</sub> and ZnO ENMs. The adsorption and zeta potential studies were conducted to elucidate the mechanisms of the how surfactant affect the behaviors of TiO<sub>2</sub> and ZnO ENMs.

## **3.2. Materials and methods**

### **3.2.1 Chemicals**

Aeroxide P25 TiO<sub>2</sub> (718467,  $\geq 99.5\%$  trace metals basis ) with a primary particle size of 21 nm (TEM) and surface area (BET) of 35–65 m<sup>2</sup> g<sup>-1</sup> was purchased from Sigma-Aldrich. The point of zero charge (PZC) of this TiO<sub>2</sub> is reported to be approximately 6.2 (Jiang et al., 2008; Kosmulski, 2009; Suttiponparnit et al., 2010). ZnO ENM (351-34492,  $\geq 99.9\%$ ) with a primary particle size of 20 nm was obtained from WAKO Pure Chemical Industries. SDS (436143, ACS reagent,  $\geq 99.0\%$ ) and NPEO (521078, Tergitol NP-9,  $>97\%$ ) surfactants were obtained from Sigma-Aldrich.

TiO<sub>2</sub> and ZnO nanoparticle stock solution were prepared by adding 0.5 g of TiO<sub>2</sub> or ZnO nanoparticle powder into 1 L of ultrapure water (Milli-Q), respectively, and then sonicating for 30 min in a bath sonicator (300 W, 38 KHz, US-5, SND), the nanoparticle stock solutions were prepared and used for following experiment immediately. The working solutions were prepared by diluting the TiO<sub>2</sub> or ZnO stock solution to 50 mg L<sup>-1</sup>. Next, 1.0 g SDS and NPEO surfactants were added into 200-mL beakers, respectively. After completely dissolving in milli-Q water, the solutions in beakers were transferred in to 1-L volume flasks to form 0.1% (w:v) stock solutions of each surfactant. The stock solutions of surfactants were stored at room temperature before use.

### ***3.2.2 Adsorption study***

In order to understand the adsorption behaviors of surfactants on the surface of TiO<sub>2</sub> and ZnO nanoparticles, adsorption experiments were conducted through batch-equilibrium experiments at 25 °C. Firstly, stock solutions of SDS and NP-9 were diluted in 100-mL vials to form 50 mL working solutions which surfactant concentration ranged from 0 to 100 mg L<sup>-1</sup>. Next, 50 mg of TiO<sub>2</sub> and ZnO nanoparticle powder were added into the above solutions, respectively. After 24-h equilibrium at 140 rpm in a shaker, finally 15mL of the equilibrated suspensions were collected in centrifuge tube and centrifuged at a speed of 10,000 rpm. After 20 min, the supernatants were collected for TOC analysis.

### ***3.2.3 Effect of surfactants on the zeta potential and aggregation TiO<sub>2</sub> and ZnO ENMs***

The effects of SDS and NP-9 surfactants on the aggregation of TiO<sub>2</sub> and ZnO nanoparticles in solution were studied after a 24-h batch reactor experiment. In general, 5 mL of TiO<sub>2</sub> and ZnO stock solutions and certain volume of surfactant stock solutions were diluted to 50-mL mixed suspensions, which contained 50 mg L<sup>-1</sup> TiO<sub>2</sub> or ZnO nanoparticles and 0-0.03% surfactants. After preparing all the suspensions and 10-min sonication, the zeta potential of the TiO<sub>2</sub> and ZnO nanoparticles in each suspension were measured by a dynamic light scattering (DLS) analyzer (ELSZ-2plus, Otsuka Electronics).

Next, the above-mentioned suspensions were placed in a shaker and shaken at a speed of 140 rpm. After 24-h reaction at a constant temperature of at 25 °C, 2.5-mL aliquots of the above suspensions were added to disposable cuvettes. The average hydrodynamic particle sizes of TiO<sub>2</sub> and ZnO aggregate in SDS or NP-9 solutions were measured by DLS. In addition, to better confirm the impact of surfactants on the aggregation behaviors of TiO<sub>2</sub> and ZnO nanoparticles after 24-h batch reactor experiment, the aggregate sizes of TiO<sub>2</sub> and ZnO nanoparticles were observed by a scanning electron microscope (SEM, JSM-5600T, JEOL).

### ***3.2.4 Effect of surfactants on the sedimentation process of aggregates of TiO<sub>2</sub> and ZnO ENM***

Following experiment 2.3, the equilibrated nanoparticle-surfactant suspensions were then used to study the effect of surfactants on the sedimentation of TiO<sub>2</sub> and ZnO ENM's aggregate, the sedimentation process of the ZnO aggregate was observed by a

UV-Vis spectrophotometer. In general, 2.5 mL aliquots of the 24-h equilibrated mixed suspensions were transferred into 3 mL cuvettes and measured at a wavelength of 378 nm. The UV absorbencies of each suspension were recorded at different time intervals for 24 hours. The sedimentation of ZnO aggregate was expressed by  $C_t/C_0$ , where  $C_0$  is the initial absorbency and  $C_t$  is the absorbency recorded at different intervals during the 24-h experimental period.

### **3.3 Results and discussion**

#### ***3.3.1 The adsorption isotherms of surfactants by TiO<sub>2</sub> and ZnO ENM***

If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. The adsorption isotherm is an equation or curve relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. Therefore, to understand the adsorption capacities and patterns of SDS and NP-9 surfactants onto the TiO<sub>2</sub> and ZnO nanoparticles respectively, the most commonly used Langmuir and Freundlich isotherms were applied and compared.

Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) with no transmigration of the adsorbate in the plane of the surface (Foo and Hameed, 2010).

The Langmuir isotherm model is expressed as Eq. 1:

$$Q_e = Q_{max}bC_e/(1 + bC_e) \quad \text{Eq.1}$$

In Eq.1,  $Q_e$  (mg/g) is the amount of solute adsorbed per unit weight of TiO<sub>2</sub> or ZnO nanomaterial at equilibrium,  $Q_{max}$  (mg/g) is the maximum adsorption capacity,  $C_e$  (mg/L) is the equilibrium concentration of solute in the liquid phase, and  $b$  (L/mg) is the constant related to the molar heat of adsorption.

Freundlich isotherm is an empirical equation that can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Ahmaruzzaman, 2008).

$$Q_e = K_F C_e^{1/n} \quad \text{Eq.2}$$

The Freundlich isotherm model is expressed as Eq. 2:

In Eq.2,  $Q_e$  (mg/g) is the amount of solute adsorbed per unit weight of TiO<sub>2</sub> or ZnO nanomaterial at equilibrium,  $C_e$  (mg/L) is the equilibrium concentration of solute in the liquid phase,  $K_F$  is Freundlich isotherm constant (mg/g) (dm<sup>3</sup>/g)<sup>n</sup> related to adsorption capacity,  $1/n$  is the measure of adsorption intensity.

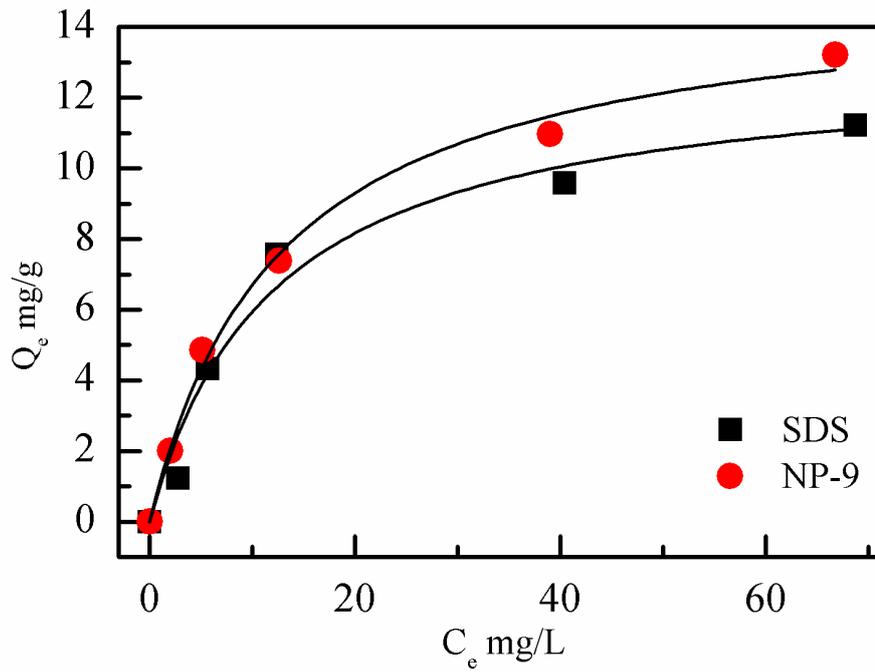


Fig.1 Langmuir adsorption isotherms of SDS and NP-9 surfactants by TiO<sub>2</sub> nanoparticles

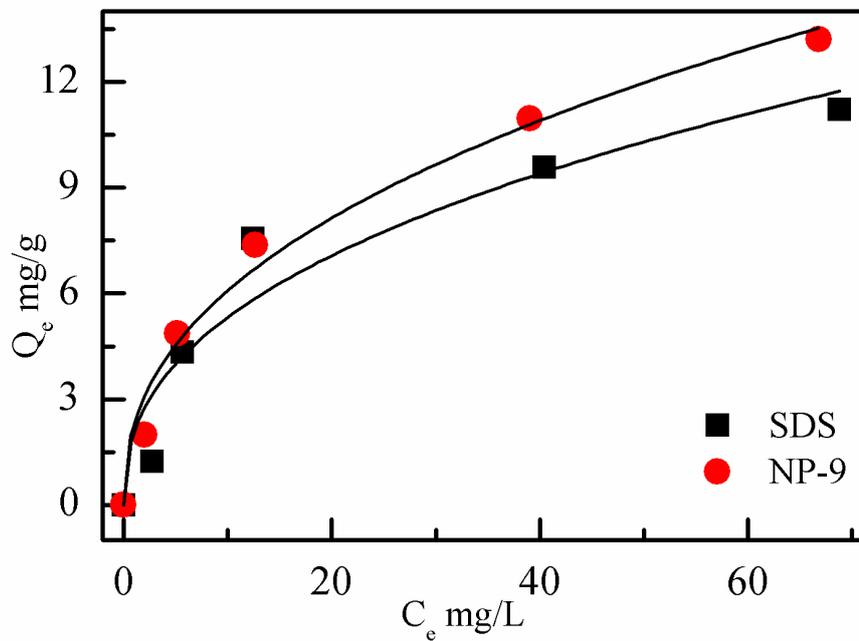


Fig.2 Freundlich adsorption isotherms of SDS and NP-9 surfactants by TiO<sub>2</sub> nanoparticles

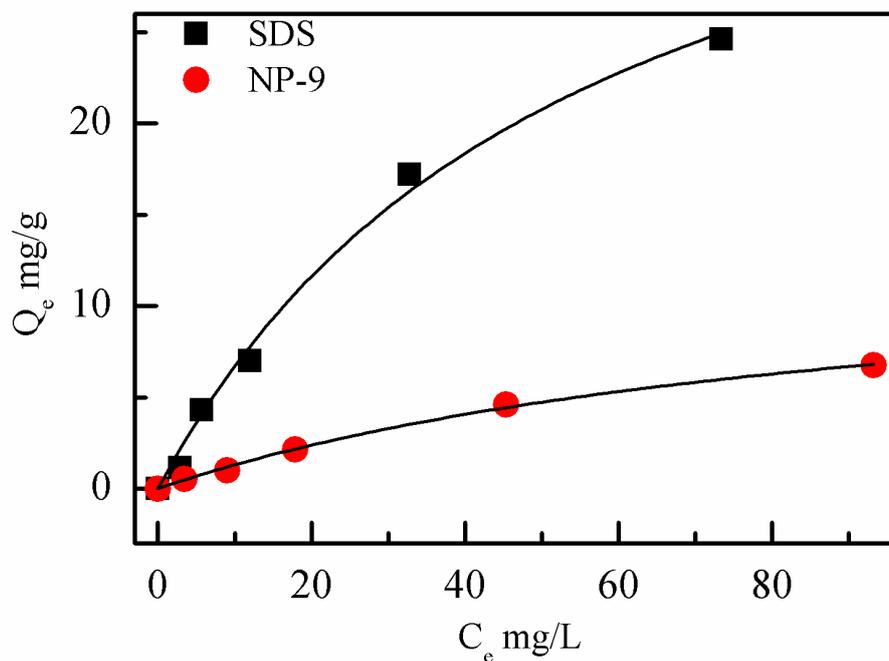


Fig.3 Langmuir adsorption isotherms of SDS and NP-9 surfactants by ZnO nanoparticles

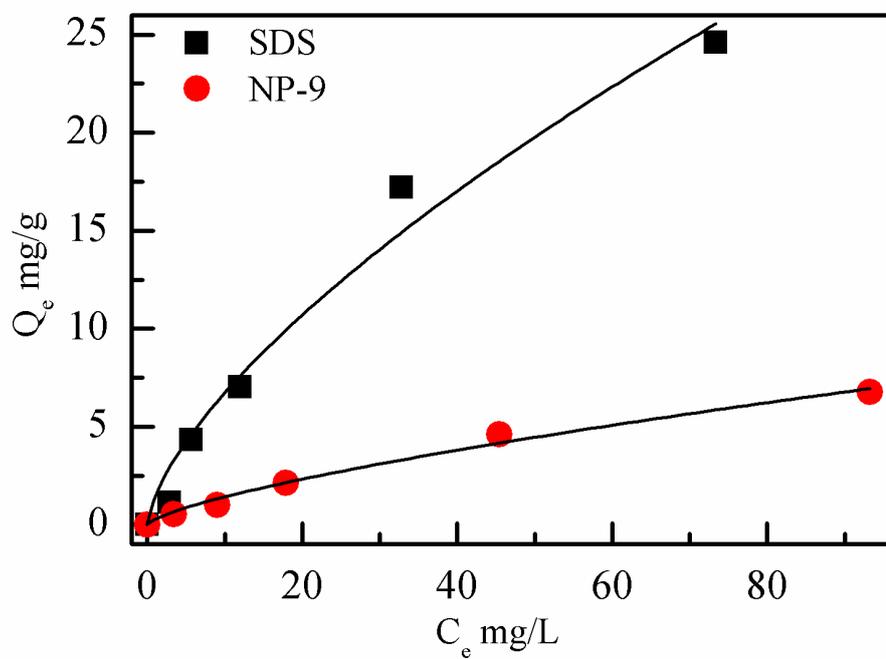


Fig.4 Freundlich adsorption isotherms of SDS and NP-9 surfactants by ZnO nanoparticles

Table 3.1 The adsorption isotherms parameters of surfactants onto nanoparticles

Nanoparticle and surfactant	Langmuir mode		Freundlich mode		
	$Q_{\max}$ mg/g	$R^2$	$K_f$ (mg/g) (dm <sup>3</sup> /g) <sup>n</sup>	n	$R^2$
TiO <sub>2</sub> /SDS	13.05	0.969	2.30	2.37	0.982
TiO <sub>2</sub> /NP-9	15.20	0.993	2.07	2.44	0.916
ZnO/SDS	43.73	0.993	1.44	1.49	0.975
ZnO/NP-9	13.79	0.997	0.27	1.40	0.988

Fitting the experimental data according to Eq.1 and Eq.2, the Langmuir and Freundlich adsorption isotherms of the two surfactant by TiO<sub>2</sub> and ZnO nanoparticles were shown in Fig.1 to Fig.4, and the adsorption isotherms parameters of surfactants onto nanoparticles were listed in Table.1. Generally, Langmuir adsorption model shows a better regression coefficients for the adsorption of surfactants onto TiO<sub>2</sub> and ZnO nanoparticles. According to the Langmuir adsorption isotherm model, it was found that the adsorption capacity of NP-9 was slightly higher than SDS when using TiO<sub>2</sub> nanomaterial as the adsorbent. However, as for adsorption by ZnO nanomaterial, the adsorption capacity of SDS was found significantly higher than that of NP-9 surfactant. Considering the point of zero charge (PZC) of ZnO nanomaterial were reported to generally range between 8.7 to 9.4 (Keller et al., 2010; Peng et al., 2015; Zhou and Keller, 2010), and the pH of the surfactant-ZnO mixed suspensions were measured to be around 7.02 (pH of MilliQ water), therefore ZnO nanoparticles carried positive charges in the adsorption experiment. With the presence of electrostatic force, the

maximum adsorption capacity of the ionic SDS was significantly higher than the nonionic NP-9 surfactant.

### ***3.3.2 Effects of the surfactants on the zeta potential of TiO<sub>2</sub> and ZnO nanomaterials***

The adsorption of surfactants exerted different effects on the zeta potential of TiO<sub>2</sub> and ZnO nanoparticles in aqueous solutions. As shown in Fig.5, the zeta potential of nano-TiO<sub>2</sub> decreased from 14.72 to - 42.67 mV with the increase in the SDS concentration from 0% to 0.030%. In contrast, the zeta potential remained unchanged, showing only small fluctuations, with the increase in the NP-9 concentrations. Similarly, as portrayed in Fig.6, the zeta potential of ZnO the zeta potential of ZnO ENM decreased from 17.56 to -27.96 mV as the SDS concentration increased from 0 to 0.030%. In contrast, with the introduction of same concentrations of NP-9, the zeta potential of ZnO ENM remained stable with only small fluctuations being observed.

Because of the adsorption of the anionic SDS surfactant, the introduction of SDS remarkably reduced the zeta potential of both TiO<sub>2</sub> and ZnO nanoparticles. With the increase of SDS concentration, the zeta potential of both nanoparticles followed a continuous negative trajectory, and the absolute value of both both TiO<sub>2</sub> and ZnO nanoparticles firstly declined and then increased. In contrast, although the nonionic NP-9 can also be adsorbed by both TiO<sub>2</sub> and ZnO nanoparticle, the increase of NP-9 did not significantly alter the zeta potential.

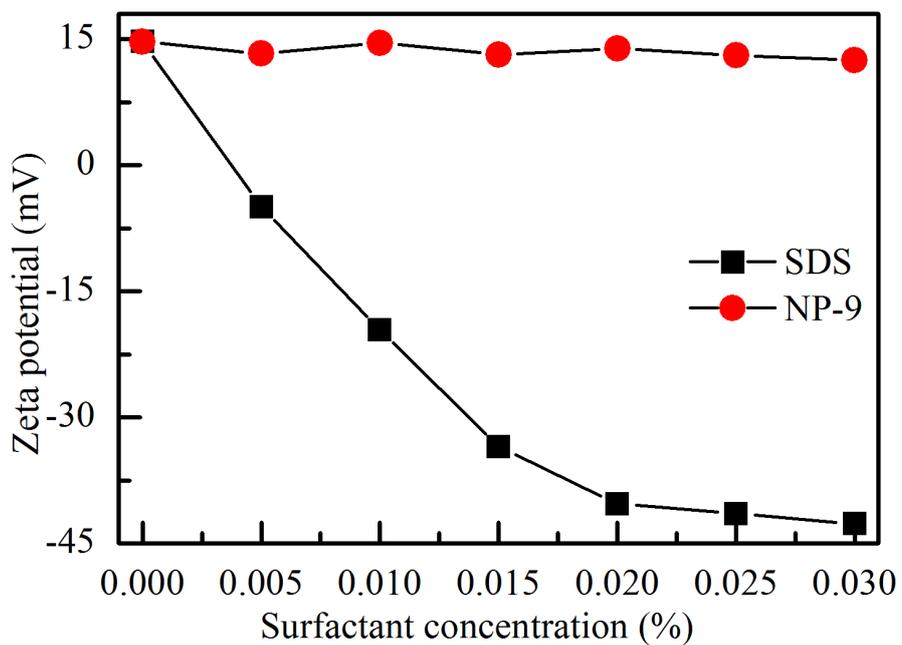


Fig.5 Effect of surfactants on the zeta potential TiO<sub>2</sub> nanoparticles

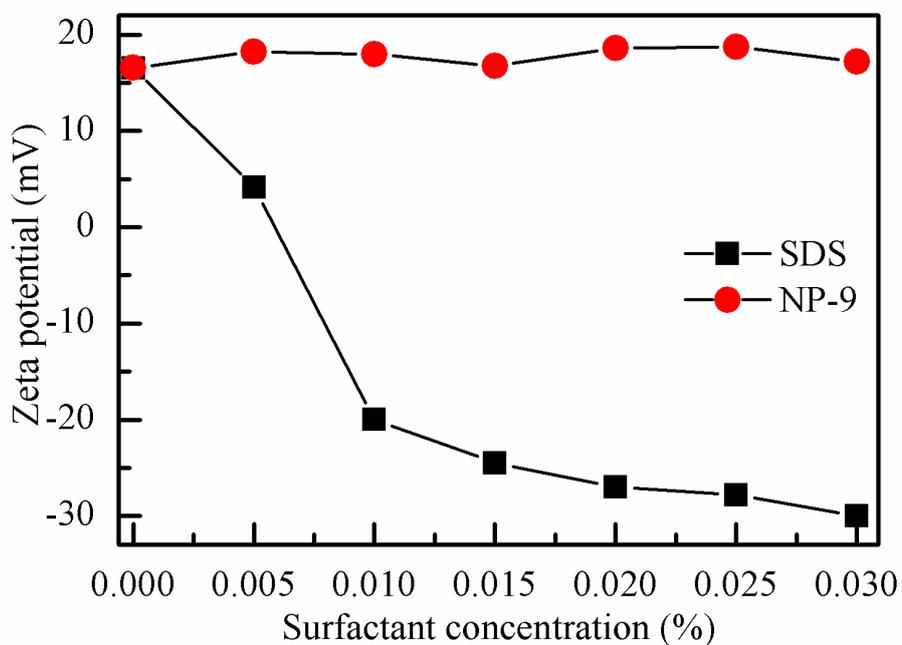


Fig.6 Effect of surfactants on the zeta potential of ZnO nanoparticles

### ***3.3.3 Effects of the surfactants on the aggregation of TiO<sub>2</sub> and ZnO nanomaterials***

The existence of surfactants also significantly affected the average particle size of TiO<sub>2</sub> and ZnO aggregates in solutions after 24-h batch reactor experiment. Fig.7 and Fig.8 show the effect of surfactants on the average particle size of TiO<sub>2</sub> and ZnO nanoparticles, respectively. For example, aggregation size of TiO<sub>2</sub> and ZnO nanoparticles increased to 1250.2 nm and 2766.0 nm in Milli-Q water respectively, showing the 24-h continuous shaking process remarkably facilitated the aggregation of nanoparticles. With the introduction of SDS, in contrast, the particle size of the TiO<sub>2</sub> aggregates increased sharply at the outset and continued to reach a peak size of 3268.7 nm at an SDS concentration of 0.005%. Similarly, the aggregate size of ZnO increased sharply and reached a maximum value of 3844.1 nm in the presence of same concentration of SDS. However, despite the further increase in the SDS concentration, the particle size rapidly decreased. The sizes of TiO<sub>2</sub> and ZnO aggregates were much smaller than that measured in bare Milli-Q water, as the SDS concentration reached 0.015% and 0.010%, respectively. At an SDS concentration of 0.030% after the 24-h batch experiment, aggregate sizes as small as 241.7 nm and 332.4 nm were recorded for TiO<sub>2</sub> and ZnO nanoparticles, respectively.

In comparison, the increasing NP-9 surfactant concentration in the solution reduced the particle size of the TiO<sub>2</sub> and ZnO aggregates relatively smoothly. For example, when the NP-9 concentration reached 0.030%, a TiO<sub>2</sub> aggregate of 676.0 nm, a diameter 45.9% smaller than that observed in Milli-Q water was detected. As for ZnO, as the

NP-9 concentration reached 0.030%, the ZnO aggregate size was detected as 546.6 nm, 80.24% smaller than that observed in bare Milli-Q water.

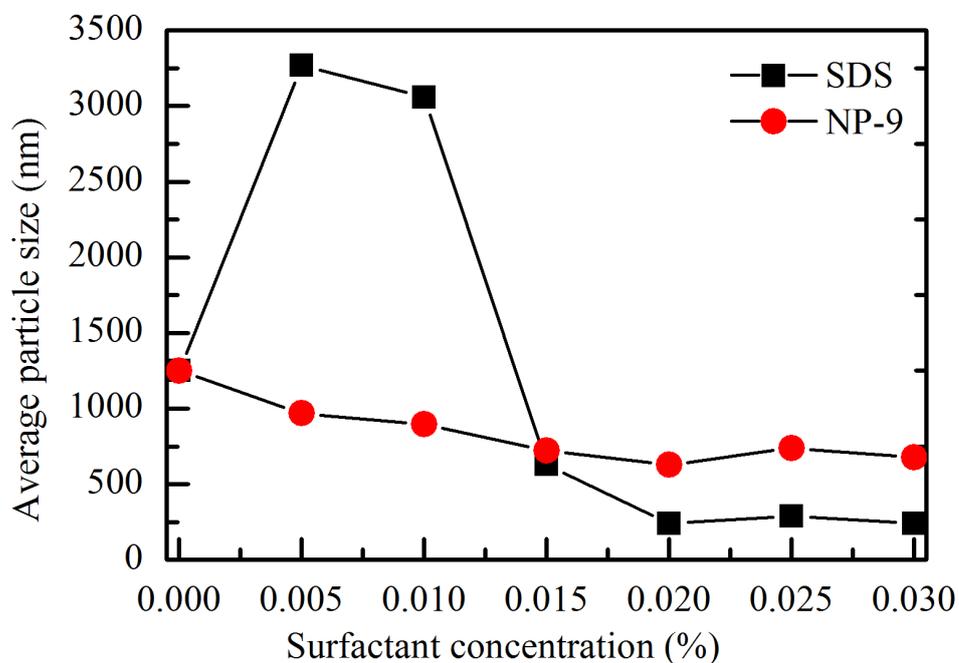


Fig.7 Effect of surfactants on the average particle size of nano-TiO<sub>2</sub>

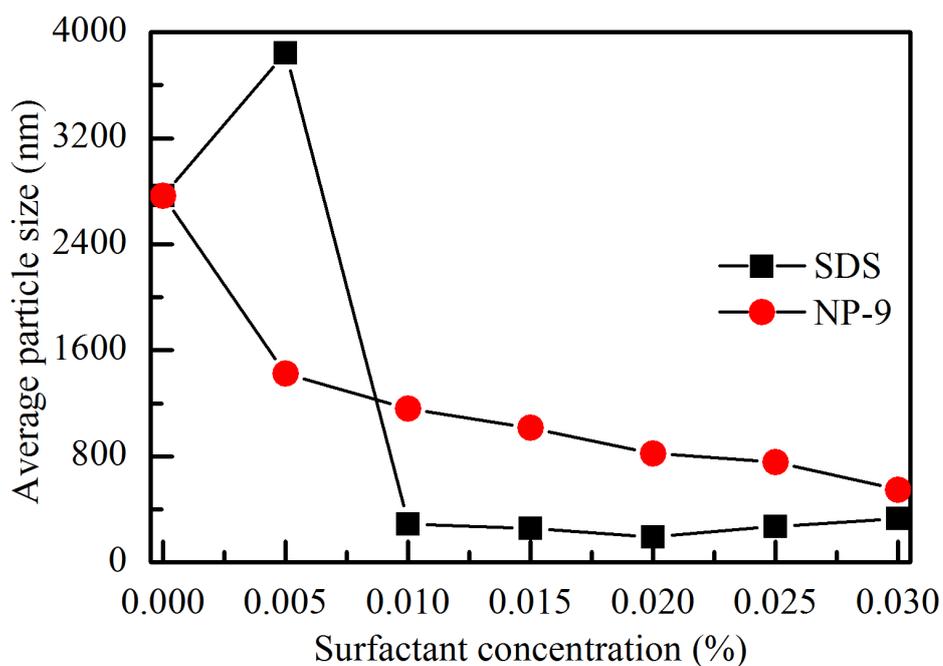


Fig.7 Effect of surfactants on the average particle size of nano-ZnO

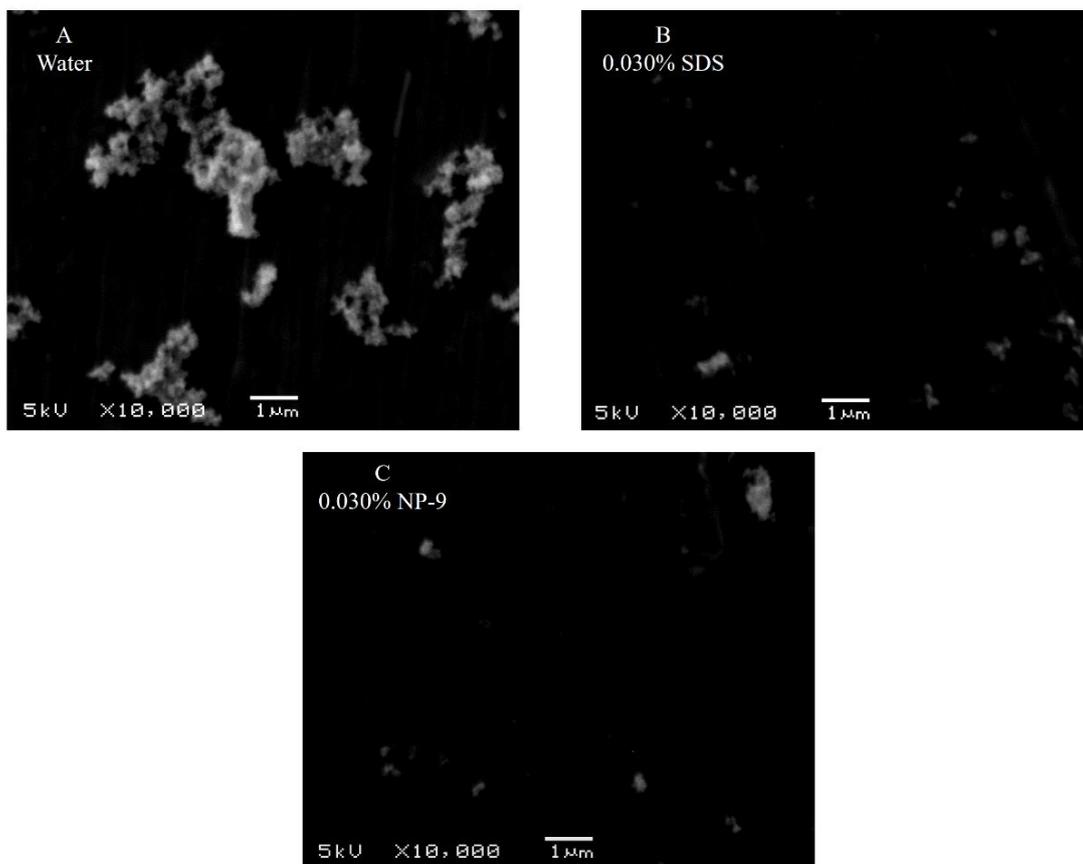


Fig.8. SEM images of TiO<sub>2</sub> aggregates after 24-h batch reactor experiment

The SEM image visually proved that the presence of surfactants remarkably reduced the sizes of the TiO<sub>2</sub> and ZnO aggregate after 24-h batch reactor experiment. As shown in Figure 8 (A), the TiO<sub>2</sub> aggregates formed in Milli-Q water after 24-h shaking were apparently beyond the micrometer grade. In comparison, the TiO<sub>2</sub> aggregate remained within the 100-nm range in the presence of both 0.030% SDS and 0.030% NP-9 as shown in Fig.8 (B) and (C). The above findings confirm the high capacity of the surfactants to affect the aggregate size of TiO<sub>2</sub> in aqueous solutions.

As demonstrated in Fig. 9 (A), the particle size of ZnO aggregate formed in Milli-Q water had already surpassed 5 μm. In contrast, Fig. 9 (B) and (C) shows the aggregate

sizes of the same ENM were much smaller with the presence of 0.030% SDS or 0.030% NP-9. The above comparison proved the ability of the surfactants in affecting the aggregation of ZnO ENM in aqueous environment.

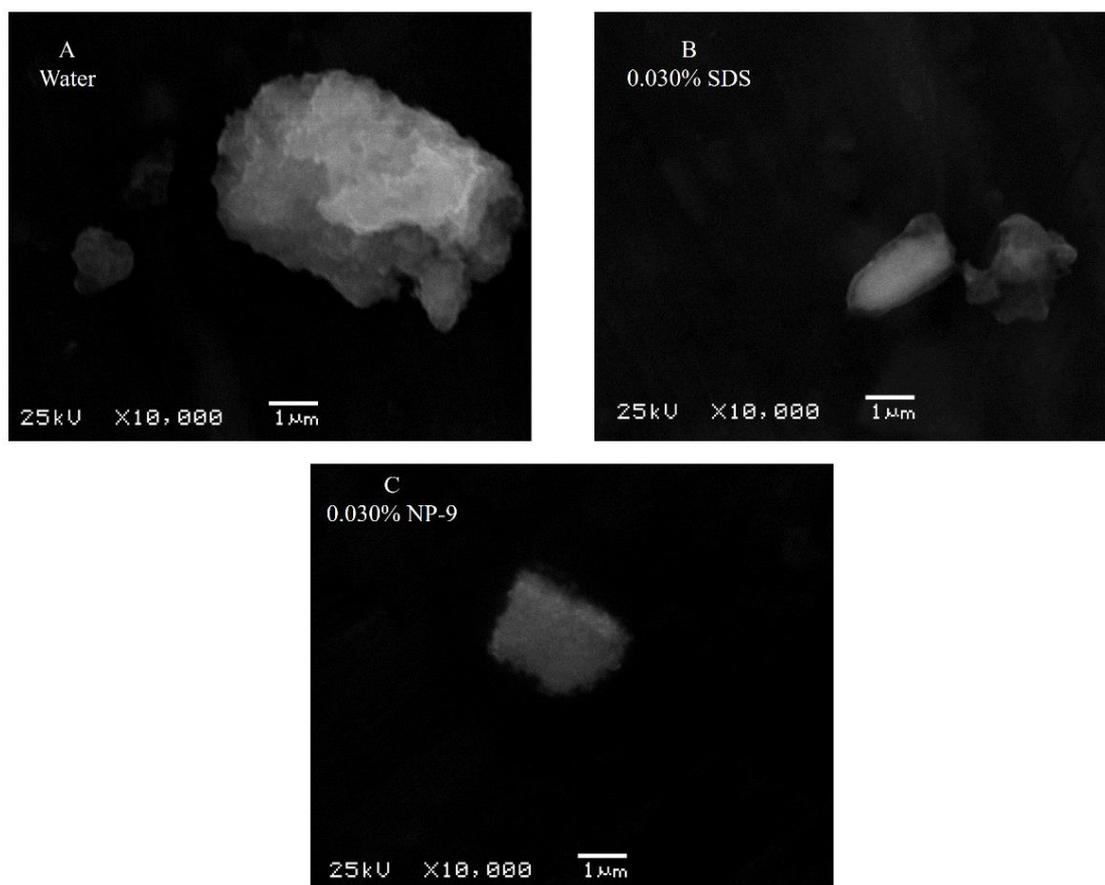


Fig.9. SEM images of ZnO aggregates after 24-h batch reactor experiment

It is reported that nanoparticles are unstable and tend to form bigger aggregates as their zeta potentials approach zero. If the absolute value of zeta potential is higher than 20 mV, nanoparticles tend to repel each other by electrical force and remain dispersed in the suspension (Hasani Bijarbooneh et al., 2013). With the introduction of 0.005% SDS initially, surfactant anions compressed the diffuse layer of nanoparticles, causing the absolute value of the zeta potential of TiO<sub>2</sub> and ZnO quickly dropped to -4.49 and

4.16 mV, respectively. Hence, the repulsive force between the TiO<sub>2</sub> and ZnO nanoparticles reduced significantly, leading to a much larger aggregate size after 24-h batch equilibrium. As the SDS concentration increased further, the zeta potential continuously moved toward the negative whereas the absolute value of the zeta potential increased. The accordingly stronger electrical repulsive force between the nanoparticles led to the decrease of the aggregate size of both TiO<sub>2</sub> and ZnO nanoparticles. In comparison, the introduction of NP-9 effectively retarded the aggregation of ZnO ENM without exerting obvious impact on the zeta potential. This can be explained by the adsorption of non-ionic NP-9 surfactant onto the surfaces of the TiO<sub>2</sub> and ZnO primary nanoparticles, a process that reduced the aggregation of TiO<sub>2</sub> and ZnO nanoparticles through steric inhibition during the batch experiment.

#### ***3.3.4 Effects of the surfactants on the sedimentation of TiO<sub>2</sub> and ZnO aggregate***

The sedimentation of TiO<sub>2</sub> and ZnO aggregates after 24-h continuous batch reactor experiment were observed using a UV-spectrophotometer at the wavelength of 378 nm (Keller et al., 2010; Zhou and Keller, 2010). Before measuring the suspensions containing TiO<sub>2</sub> and ZnO, the background solutions of SDS or NP-9 surfactant were measured at the same wavelength and no absorbency was recorded.

As shown in Fig. 10, the TiO<sub>2</sub> aggregates clearly settled in the Milli-Q water, leaving only 44.6% remaining in the suspension after 24 h. The sedimentation of TiO<sub>2</sub> aggregate significantly accelerated in the presence of SDS at 0.005% and 0.010% concentrations, leaving only 4.49% and 8.80% of the aggregate in the above suspensions after 24 h, respectively. The rate of TiO<sub>2</sub> sedimentation retarded remarkably, however, at SDS concentrations higher than 0.015%. At an SDS

concentration of 0.020%, over 95% of the TiO<sub>2</sub> was still suspended after 24 h. The effect of SDS on the sedimentation of TiO<sub>2</sub> correlated well with that on the particle size. At SDS concentration above 0.015%, the repulsive force generated by the surface-attached anionic surfactant retarded the aggregation of nano-TiO<sub>2</sub> particles during the batch experiment and prevented the quick sedimentation of nano-TiO<sub>2</sub> particles. Fig. 11 shows the effect of NP-9 surfactant on TiO<sub>2</sub> sedimentation. The figure clearly shows the effect of NP-9 in retarding the sedimentation of TiO<sub>2</sub>: as the concentration of NP-9 increased, the stability of TiO<sub>2</sub> in the suspension generally increased in parallel during the experimental period. In the presence of NP-9 at the concentration of 0.030%, as high as 83.65% of the TiO<sub>2</sub> remained in the suspension after 24 h.

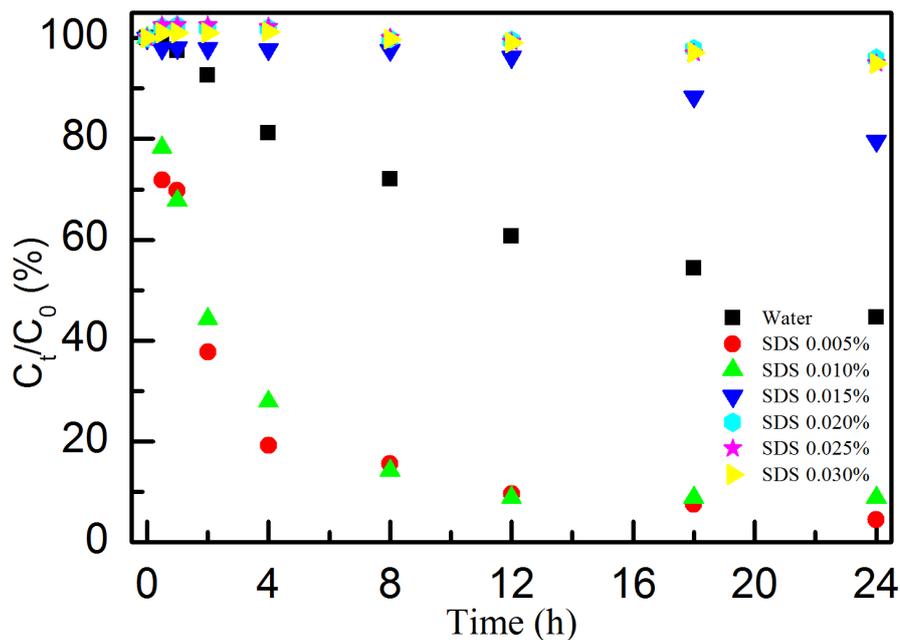


Fig.10 Effect of SDS surfactant on the sedimentation of TiO<sub>2</sub> aggregates

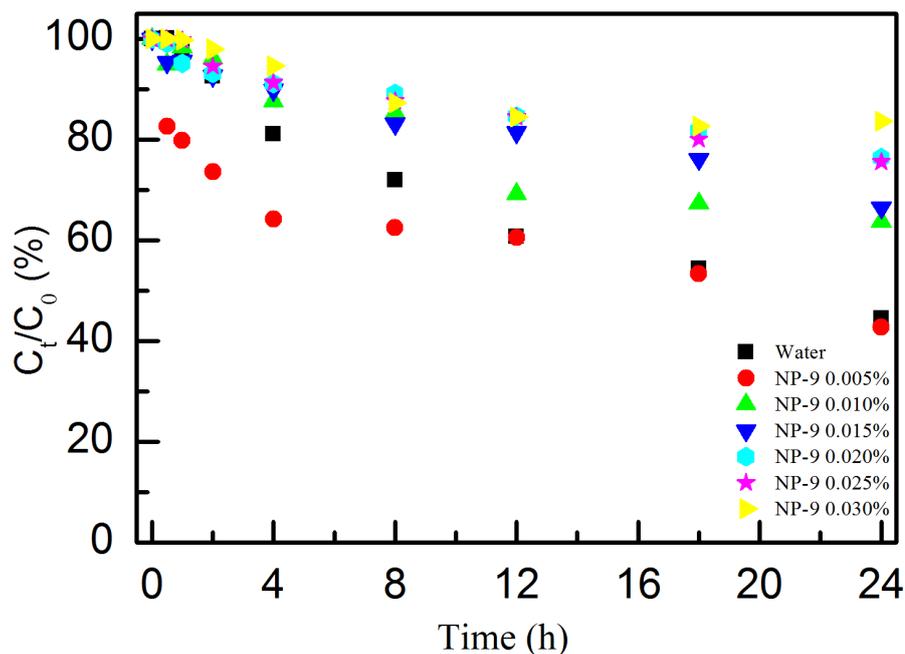


Fig.11 Effect of NP-9 surfactants on the sedimentation of TiO<sub>2</sub> aggregates

Fig. 12 shows the sedimentation of ZnO aggregates, it was found the ZnO aggregates settled significantly in bare Milli-Q water, leaving only 27.27% remaining in the suspension after 24 h. With the introduction of 0.005% SDS, the sedimentation of ZnO aggregate significantly accelerated with only 13.46% keeping suspended after 24 h. However, as the SDS concentration increased more, a remarkable retarded sedimentation of ZnO aggregate was observed after 24 h, and more than 50% of the ZnO aggregate was found kept suspended as SDS concentration exceeded 0.015%. Fig.13 clearly exhibits the retarding effect of NP-9 surfactant on the stability of ZnO ENM aggregate: with the increase of NP-9 concentration, the sedimentation of ZnO aggregate in the suspension slowed down during the 24-h experimental period. At a NP-9 concentration of 0.030%, for instance, 51.22% of the ZnO aggregate was kept suspended after 24 h, a ratio significantly higher than that in bare Milli-Q water.

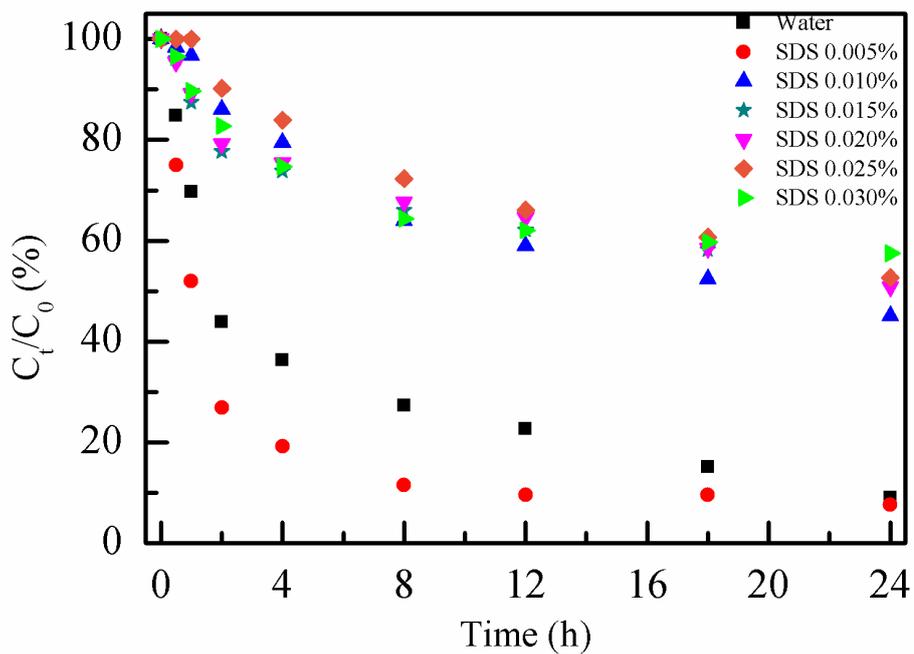


Fig.12 Effect of SDS surfactant on the sedimentation of ZnO aggregates

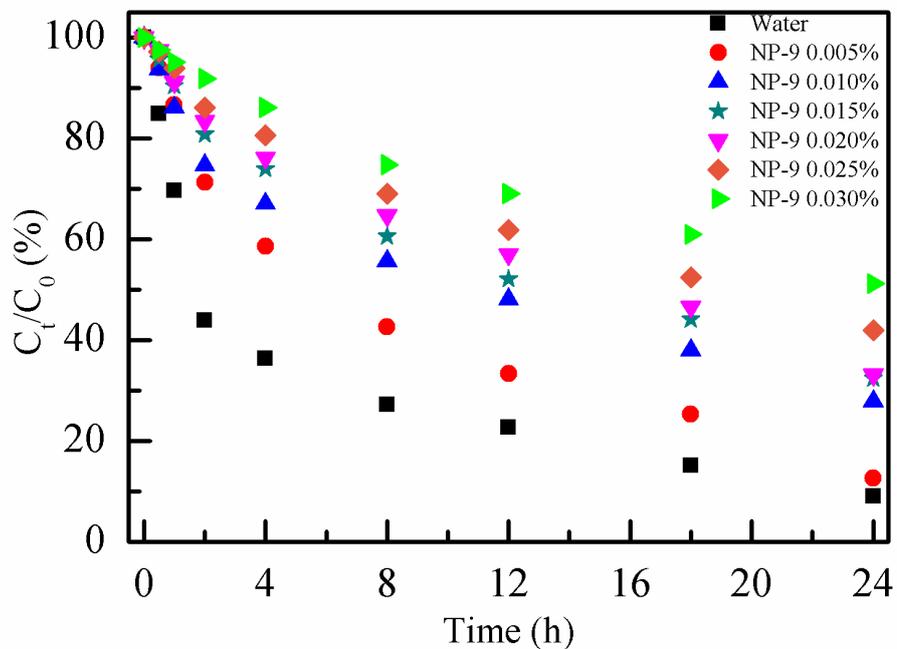


Fig.13 Effect of np-9 surfactant on the sedimentation of ZnO aggregates

From the results of the above experiments, SDS and NP-9 surfactants remarkably changed the aggregate size and sedimentation speed of TiO<sub>2</sub> aggregates. We can therefore reasonably assume that surfactants increase the environmental risk of TiO<sub>2</sub> nano-materials by changing their transport behavior and fate in aqueous environments.

### **3.4 Conclusion**

In this chapter, the effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO nanomaterials were studied after a 24-h batch reactor experiment, and the sedimentation of the aggregates of TiO<sub>2</sub> and ZnO nanomaterials were observed with a UV-spectrophotometer at a wavelength of 378 nm. It was found that the presence of both surfactants effectively reduced the aggregation of two nanomaterials when surfactant concentration exceeded 0.015%. The SDS surfactant affected the zeta potential of TiO<sub>2</sub> and ZnO nanomaterials, and the absolute value of nanomaterials' zeta potential decreased at first and then significantly increased with growth of SDS concentration. This process remarkably increased the electrical repulsive forces between nanoparticles, and hence reduced the aggregation and increased the stabilities of the aggregates of both TiO<sub>2</sub> and ZnO nanomaterials. As for the non-ionic NP-9 surfactant, the surfactant covered the surface of nanomaterials, hence reduced the aggregation and increased the stability of both nanomaterials.

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## CHAPTER 4

### Effect of surfactants on the behaviors of TiO<sub>2</sub> and ZnO nanomaterials in environmental aqueous matrices

#### Abstract

In this chapter, the effect of surfactants on the behaviors of TiO<sub>2</sub> and ZnO engineered nanomaterials (ENMs) in environmental conditions and six realistic water samples were explored. It was found that as pH increase from 6.0 to 9.0, the aggregate size of TiO<sub>2</sub> and ZnO ENMs varied significantly after 24-h batch reactor experiment. In addition, as the ionic strength increased to 50 mM, the aggregation of ENMs increased significantly. However, the introduction of surfactants reduced the aggregate size of both TiO<sub>2</sub> and ZnO ENMs as the function of pH and ionic strength. In six natural water matrices, the aggregation of both TiO<sub>2</sub> and ZnO ENMs were found most significant in Yangtze river water, and the ionic strength were thought to be a major reason for the increased aggregation of ENMs. With the presence of surfactant, however, both aggregation and sedimentation of ENMs were found to be retarded, and the ionic SDS were found more effective than nonionic NP-9 surfactant.

#### 4.1. Introduction

The eco-toxicities of engineered nanomaterials (ENMs) are arousing more and more research interest in recent years, and ENMs had been widely reported to be toxic to algae (Ji et al., 2011; Manzo et al., 2013), plants (Gardea-Torresdey et al., 2014; Miralles et al., 2012), fish (Bai et al., 2009; Wiench et al., 2009), *Daphnia* (Lovern and

Klaper, 2006; Zhu et al., 2010), and so on. Therefore, the study of the behaviors and fate of ENMs in natural aqueous environment are of great importance to assess the environmental risk of ENMs.

The behaviors of ENMs in aqueous environment were found to be mainly affected by pH, ionic strength or the dissolved natural organic matters (NOMs). Therefore, it is reasonable to consider the behaviors of ENMs in natural water is much different and complex than in laboratory solutions. For example, Wiench et al. found that an uncoated TiO<sub>2</sub> ENM formed virtually homogenous dispersions in double distilled water and pond water. However, sedimentation of the particles proceeded at different rates in these two media: after 40 h, the pond water dispersion had a slightly opaque supernatant and the double distilled water had no visible sedimentation. This could be confirmed by gravimetric measurements after 16 h, where the TiO<sub>2</sub> concentration for the double distilled dispersion and the pond water dispersion of 83 mg/L was measured (Wiench et al., 2009). Keller et al. dispersed three different metal oxide nanoparticles (TiO<sub>2</sub>, ZnO and CeO<sub>2</sub>) in samples taken from eight different aqueous media and measured their electrophoretic mobility, state of aggregation, and rate of sedimentation. The electrophoretic mobility of the particles in a given aqueous media was dominated by the presence of natural organic matter (NOM) and ionic strength, and independent of pH. NOM adsorbed onto these nanoparticles significantly reduces their aggregation, stabilizing them under many conditions (Keller et al., 2010). Brunelli et al. studied the stability and sedimentation of TiO<sub>2</sub> nanoparticle under conditions relevant for ecotoxicological testing, by using both synthetic and real seawater, as well as synthetic

freshwater. The tested TiO<sub>2</sub> nanomaterial was found to undergo a fast agglomeration as soon as it was dispersed in both synthetic and real aqueous dispersions, while sedimentation was slower. The extent and rate of sedimentation, over the tested 50 h, increased remarkably with increase in the initial TiO<sub>2</sub> concentration, thus decreasing the stability over time of nano TiO<sub>2</sub> dispersions moving from 0.1 to 10 mg/l. Both agglomeration and sedimentation were observed to depend mostly on TiO<sub>2</sub> initial concentration and, to a minor extent, on salt content, ionic strength, and dissolve organic carbon, under the investigated conditions (Brunelli et al., 2013).

Despite many studies have focused on the factors affecting the behaviors of ENMs in laboratory solutions, currently the studies concerning the behaviors of ENMs in realistic natural waters are still rare to find. However, considering the remarkable difference between the artificial solution and natural water, more researches about the behaviors of ENMs in natural waters are needed. In this chapter, the effect of surfactants on the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENMs in six natural waters were studied. In addition, the effect of surfactants on the behaviors of those two ENMs as the functions pH and ionic strength were also studied.

## **4.2. Materials and methods**

### ***4.2.1 Chemicals***

Aeroxide P25 TiO<sub>2</sub> (718467, ≥99.5% trace metals basis ) with a primary particle size of 21 nm (TEM) and surface area (BET) of 35–65 m<sup>2</sup> g<sup>-1</sup> was purchased from Sigma-Aldrich. ZnO ENM (351-34492, ≥99.9%) with a primary particle size of 20 nm was

obtained from WAKO Pure Chemical Industries. SDS (436143, ACS reagent,  $\geq 99.0\%$ ) and NPEO (521078, Tergitol NP-9,  $>97\%$ ) surfactants were obtained from Sigma-Aldrich. The preparation of the stock solutions were conducted in the same way written in chapter 3.2.1.

#### ***4.2.2 Experimental water samples***

To study the effects of the surfactants on the behaviors of TiO<sub>2</sub> and ZnO ENMs in environmental water matrices, six water samples from different origins were collected for experiment. Four natural surface water samples were collected from the Yangtze River (Wuhan, China), Xiangjiang River (Changsha, China), Biwa Lake (Otsu, Japan) and Katsuragawa River (Kyoto, Japan), which are important water sources in the South Central China and Kansai area of Japan. Another two samples were tap water (Kyoto University, Japan) and discharged water from a municipal wastewater treatment plant (MWTP; Kyoto Toba MWTP, Japan). All of the collected water samples were filtered through 0.2  $\mu\text{m}$  hydrophilic polytetrafluoroethylene membranes (Millipore) and stored at 4 °C before using for experiment.

The pH values of the above samples were measured by a pH meter (Horiba, D51). The TOC was measured by using a TOC-V analyzer (Shimadzu Corporation). The anions of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and cations of Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> in the water samples were determined by an ion chromatograph (Shimadzu Corporation), HCO<sub>3</sub><sup>-</sup> was determined by titration.

#### ***4.2.3 Effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENMs as the function of pH***

The pH is vital factor in affecting the behaviors of ENMs in aqueous environment, thereby the effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENM in suspensions varied in pH values were investigated. For one group of suspensions containing 50 mg L<sup>-1</sup> TiO<sub>2</sub> or ZnO ENM and certain concentration of SDS or NP-9 surfactant, the pH values were adjusted to range from 6.0 to 9.0 by adding 0.1 M HCl or NaOH solution. After 24-h batch experiment, the aggregate size of the TiO<sub>2</sub> or ZnO nanomaterial in the above two group of suspensions were measured by DLS.

Considering the ZnO nanomaterials can dissolve in the aqueous solutions, experiments to measure the dissolved Zn<sup>2+</sup> and pH change after 24-h batch experiment were conducted. The ZnO ENM stock solutions were diluted in 100-mL vials to form the suspensions containing 50 mg L<sup>-1</sup> ZnO ENM. Then the pH of the suspension were adjusted by the 0.1 M HCl or 0.1 M NaOH solution. To avoid the effect of ionic strength, we did not buffered the ZnO suspension in this experiment. After 24-h batch equilibrium, the suspensions were centrifuged at 10,000 rpm, and then the supernatants were collected. An ICP-MS (Thermo) was used to determine the dissolved Zn<sup>2+</sup>.

#### ***4.2.4 Effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENM as the function of ionic strength***

As another widely acknowledged factor that can impact the behaviors and fate of nanomaterials in natural water environment, the effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENM as the function of ionic strength were also studied. In brief, the

ionic strength of suspensions containing 50 mg L<sup>-1</sup> TiO<sub>2</sub> or ZnO ENM and certain concentration of surfactant were set to range from 0 to 50 mM with 1 M NaCl stock solution. After 24-h batch experiment, the aggregate size of TiO<sub>2</sub> and ZnO nanomaterial in the above two group of suspensions were measured by DLS.

#### ***4.2.5 Effect of surfactants on the behaviors of TiO<sub>2</sub> and ZnO ENM in natural waters***

In order to better understand the effect of surfactants on the behaviors and transport of TiO<sub>2</sub> and ZnO ENM in natural water environment as opposed to in laboratory-used Milli-Q water, I studied the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENM in environmental aqueous matrices collected from six different origins according to the method mentioned in chapter 2.4.

### **4.3. Results and discussion**

#### ***4.3.1 Effect of surfactants on the aggregation behaviors of TiO<sub>2</sub> and ZnO ENM as a function of pH***

The pH and ionic strength (IS) are two important factors which can significantly affect the aggregation and stability of ENMs in aqueous solutions (Bian et al., 2011; Godinez and Darnault, 2011; Mohd Omar et al., 2014; Raza et al., 2016). Fig.1 and Fig.2 show the effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENM under the variation of pH after 24-h batch equilibrium, respectively. It is reported that the point of zero charge (PZC) of the selected TiO<sub>2</sub> nanomaterial is approximately 6.2 (Jiang et al., 2008; Kosmulski, 2009; Suttiponparnit et al., 2010), and the PZC of ZnO nanomaterial were reported to generally range between 8.7 to 9.4 (Keller et al., 2010; Peng et al., 2015;

Zhou and Keller, 2010). If pH value of suspension equals to  $pH_{pzc}$ , the surface charge of nanoparticle will be zero and aggregation will be promoted because of the lack of electrical repulsion. Therefore, as the pH of suspension increased from 6.0 to 9.0, a trend of surpassing the  $pH_{pzc}$  of  $TiO_2$  ENM or a trend toward the  $pH_{pzc}$  of ZnO ENM, the particle size of  $TiO_2$  and ZnO aggregate changed in different trajectories. The aggregate size of  $TiO_2$  firstly increased and then decreased, whereas the aggregate size of ZnO increased constantly. However, the growth of both  $TiO_2$  and ZnO aggregate were remarkably retarded with the introduction of surfactants. For example, at a pH of 7.0, the aggregate size of  $TiO_2$  reached 3030.0 nm in suspension without surfactant. In comparison, with the presence 0.030% surfactants, the aggregate sizes of  $TiO_2$  in SDS and NP-9 containing suspensions are 596.0 and 1324.6 nm, respectively. As for ZnO ENM, at a pH of 9.0 for instance, the aggregate size of ZnO reached 4762.1 nm in suspension without surfactant. In comparison, with the presence 0.030% surfactants, the aggregate sizes of ZnO in SDS and NP-9 containing suspensions are 43.81% and 24.36% decreased, respectively.

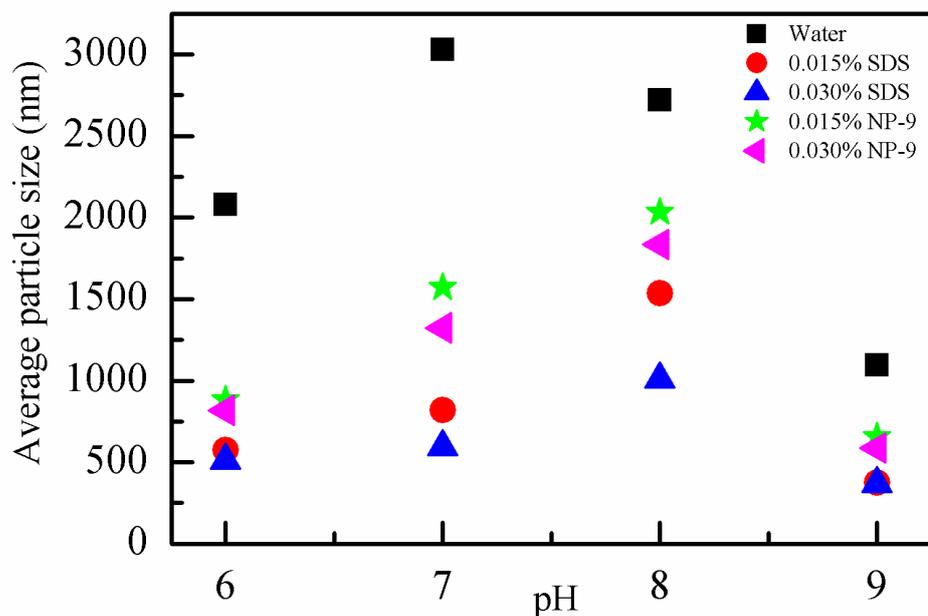


Fig.1 The effect of surfactants on the aggregate size of nano-TiO<sub>2</sub> as a function of pH

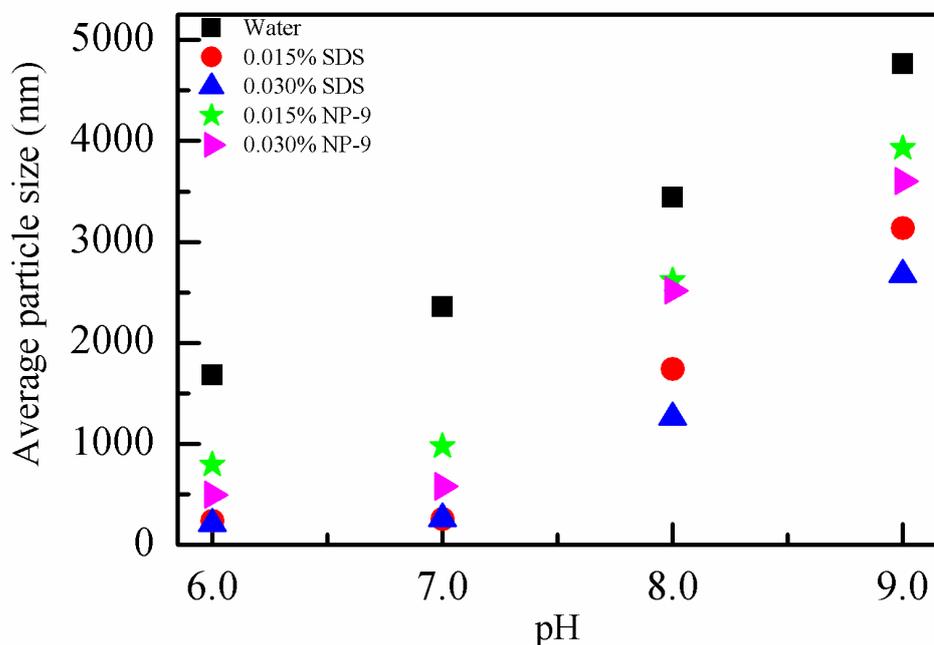


Fig.2 The effect of surfactants on the aggregate size of nano-ZnO as a function of pH

Table.1 shows the concentration of Zn<sup>2+</sup> and the pH change of the ZnO suspensions. In Milli-Q aqueous matrices with different initial pH values, the highest dissolution rate

were found to be 3.49% in the suspension of an initial pH 6.0. The increase of pH and aggregate size inhibited the further dissolution of ZnO. With the introduction of 0.030% SDS or 0.030% NP-9 surfactant, the dissolution rate of ZnO slightly increased to 4.28 and 4.47%, respectively. Although the surfactant-resulted reduction of aggregate size were considered to be responsible for the increase of the dissolution rate, the dissolution rate is still too small that the effect of dissolution on the particle size can be considered to be minor.

Table.1 The dissolution of ZnO ENM and the change of suspension pH

Initial suspension pH	6.0			7.0	8.0	9.0
Suspension matrices	Milli-Q water	0.030% SDS	0.030% NP-9	Milli-Q water		
Suspension pH after 24 h	7.44	7.72	7.65	7.61	7.83	8.26
Dissolved Zn <sup>2+</sup> mg L <sup>-1</sup>	1.401	1.712	1.787	1.218	0.909	0.669
ZnO nanoparticle dissolution rate (%)	3.49	4.28	4.47	3.04	2.29	1.81

#### ***4.3.2 Effect of surfactants on the aggregation behaviors of TiO<sub>2</sub> and ZnO ENM as a function of ionic strength***

Fig.3 and Fig.4 demonstrated the effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO nanoparticles as a function of ionic strength, respectively. As it has been generally proved that the introduction of electrolyte will compress the double layer of nanoparticles and promote the aggregation of nanoparticles in suspensions, we have also similarly observed a remarkable growth of the aggregate size of TiO<sub>2</sub> and ZnO as the NaCl concentration increased. As the concentration of NaCl increase from 0 to 50 mM, after 24-h equilibrium the aggregate size of TiO<sub>2</sub> and ZnO ENM correspondingly increased from 1250.2 nm to 2800.6 nm and 2793.1 nm to 5085.7 nm, respectively. With the introduction of surfactants, however, the aggregation of both TiO<sub>2</sub> and ZnO

ENM was found significantly retarded. In suspensions containing 10 mM NaCl, for example, the presence of 0.030% SDS and NP-9 reduced the aggregate size of TiO<sub>2</sub> by 82.87% and 20.67%, respectively; as the NaCl concentration further increased to 50 mM, the aggregate size of ZnO ENM were detected to be 73.50% and 48.15% decreased under the presence of 0.030% SDS and NP-9, respectively.

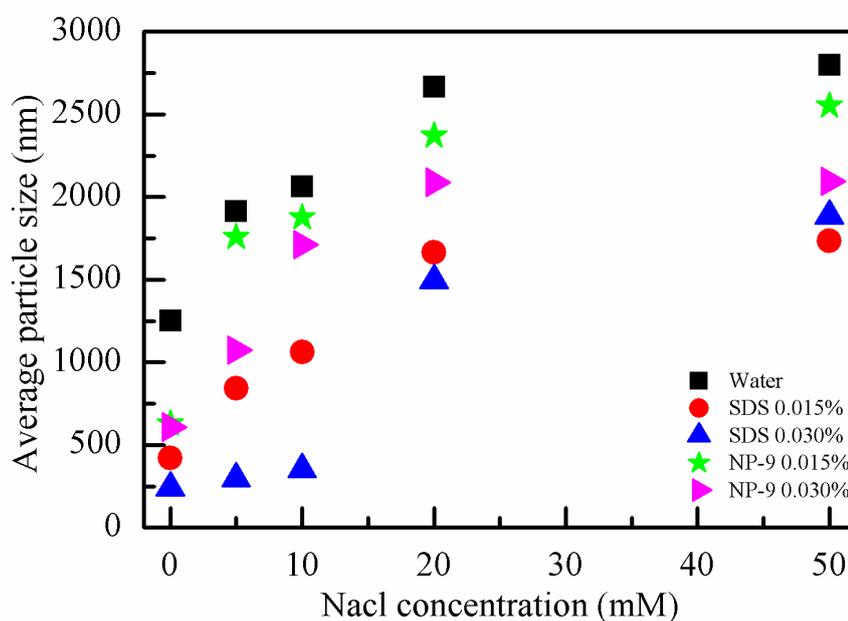


Fig.3 The effect of surfactants on the aggregate size of nano-TiO<sub>2</sub> as a function of ionic strength

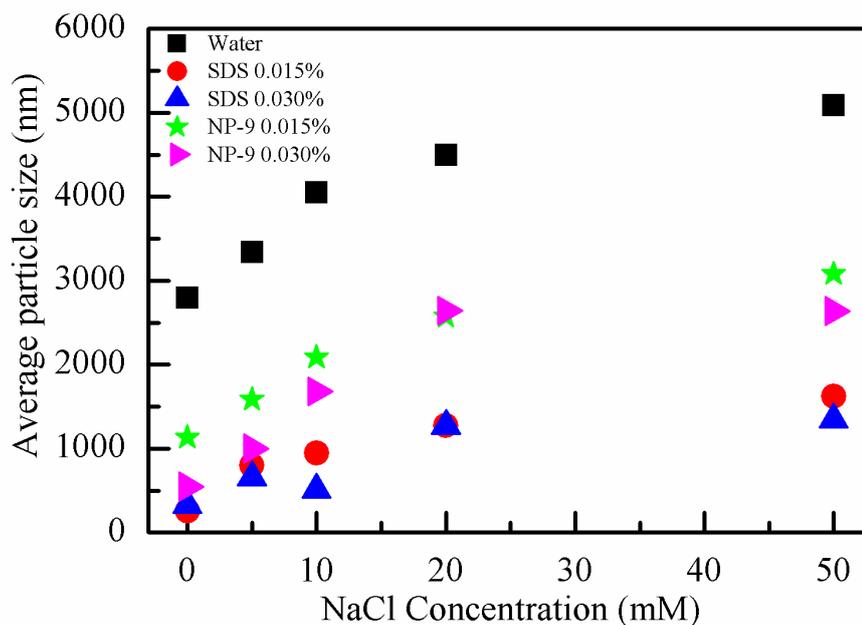


Fig.4 The effect of surfactants on the aggregate size of nano-ZnO as a function of ionic strength

#### 4.3.3 Characterization of experimental aqueous matrices

To better understand the effect of surfactants on the aggregation and stability of TiO<sub>2</sub> and ZnO ENM in real water environment, we collected six environmental water samples from different origins and studied the behaviors of TiO<sub>2</sub> and ZnO ENM in these water matrices. All the water samples were previously analyzed before being used for experiment. Table.2 lists the ion composition and properties of all the environmental water samples. Although collected from different origins, all the experimental aqueous matrices had similar pH values ranged from 6.65 to 6.99. The highest TOC value was detected in wastewater, whereas the highest concentration of multivalent ion and ionic strength were detected in the sample collected from Yangtze River.

Although some researchers reported the dissolved organic matter such as humic acid (HA) can stabilize the nanoparticles in laboratory study. However, in natural aqueous

matrices of low TOC value, the ionic strength rather than dissolved organic matter actually affects the aggregation and stability more significantly. For example, Keller et al. studied the stability and aggregation of metal oxide nanoparticles in several natural aqueous matrices. In four aqueous matrices of ionic strength (0.1 to 1 eq L<sup>-1</sup>) and low to medium TOC value (54-523 μM C), the aggregation and sedimentation of TiO<sub>2</sub>, ZnO, and CeO<sub>2</sub> nanoparticle were found accelerated (Keller et al., 2010). Brunelli et al. studied the agglomeration and sedimentation of TiO<sub>2</sub> nanoparticles in synthetic and real waters, they reported that both agglomeration and sedimentation were observed to depend mostly on the initial concentration of nano TiO<sub>2</sub>. Because of the low concentration of DOC in all the water samples ( $\leq 2.16$  mg L<sup>-1</sup>), the agglomeration and sedimentation of nano TiO<sub>2</sub> were not significantly affected by organic matter (Brunelli et al., 2013).

In the aqueous matrices of this study, the ENM concentration was 50 mg L<sup>-1</sup> and initial surfactant concentrations was 150 mg L<sup>-1</sup>, but the highest TOC value in the selected natural water matrices was only 2.54 mg L<sup>-1</sup>. Therefore, the effect of dissolved organic matter on the behaviors of nanoparticles in the selected aqueous matrices are deemed to be minor.

1

Table.2 Chemical composition and physico-chemical properties of water samples

	<i>Yangtze River</i>	<i>Xiangjiang River</i>	<i>Katsuragawa River</i>	<i>Lake Biwa</i>	<i>Tap Water</i>	<i>Waste Water</i>
Ionic composition (mg L <sup>-1</sup> )						
F <sup>-</sup>	0.26	0.28	0.13	0.18	0.09	0.19
Cl <sup>-</sup>	20.08	19.83	6.33	10.98	11.09	46.46
NO <sub>3</sub> <sup>-</sup>	7.18	10.36	2.82	1.94	0.93	17.53
SO <sub>4</sub> <sup>2-</sup>	26.18	24.51	16.91	19.95	11.90	28.84
HCO <sub>3</sub> <sup>-</sup>	133.21	112.55	89.18	95.24	37.15	148.33
Na <sup>+</sup>	23.10	22.23	18.36	13.26	14.29	25.53
K <sup>+</sup>	2.26	3.04	2.12	2.75	1.69	8.14
NH <sub>4</sub> <sup>+</sup>	1.67	1.51	0.20	0.49	0.12	31.24
Mg <sup>2+</sup>	9.79	5.39	2.53	3.09	1.79	3.18
Ca <sup>2+</sup>	45.23	39.17	12.91	12.86	7.31	16.36
pH	6.65	6.70	6.99	6.93	6.89	6.83
TOC (mg L <sup>-1</sup> )	1.20	1.09	1.27	1.40	0.67	2.54
Conductivity at 25 °C (μS)	390	330	139	132	86	330
Ionic strength (mM)	5.57	4.71	2.47	2.59	1.56	4.35

2

#### ***4.3.4 Effect of surfactants on the aggregation of TiO<sub>2</sub> and ZnO ENM in natural water matrices***

Fig.5 and Fig.6 portrays the ratios of TiO<sub>2</sub> and ZnO aggregate size after 24-h batch equilibrium in natural aqueous matrices with and without surfactants, respectively. The  $D_s$  and  $D_0$  are the aggregate sizes of the two nanoparticles with and without the introduction of surfactants, respectively. In all the natural water matrices, the presence of both SDS and NP-9 obviously reduced the aggregate size of the TiO<sub>2</sub> and ZnO ENM. For TiO<sub>2</sub> ENM, in the MWTP discharged water for instance, the presence of 0.015% and 0.030% SDS reduced the TiO<sub>2</sub> aggregate sizes by 42.72% and 50.98%, respectively. In comparison, the presence of 0.015% and 0.030% NP-9 reduced the aggregate size by 36.18% and 46.99%, respectively.

For ZnO nanoparticles, generally, the retarding effect of surfactants on the growth of aggregates was found most remarkable in tap water, and least pronounced in Yangtze River water. In tap water, for instance, the presence of 0.030% SDS and NP-9 reduced the aggregate size of ZnO by 57.67% and 50.91%, respectively. In comparison, the presence of same concentration of SDS and NP-9 in Yangtze River water only reduced the aggregate size by 27.77% and 19.41%, respectively.

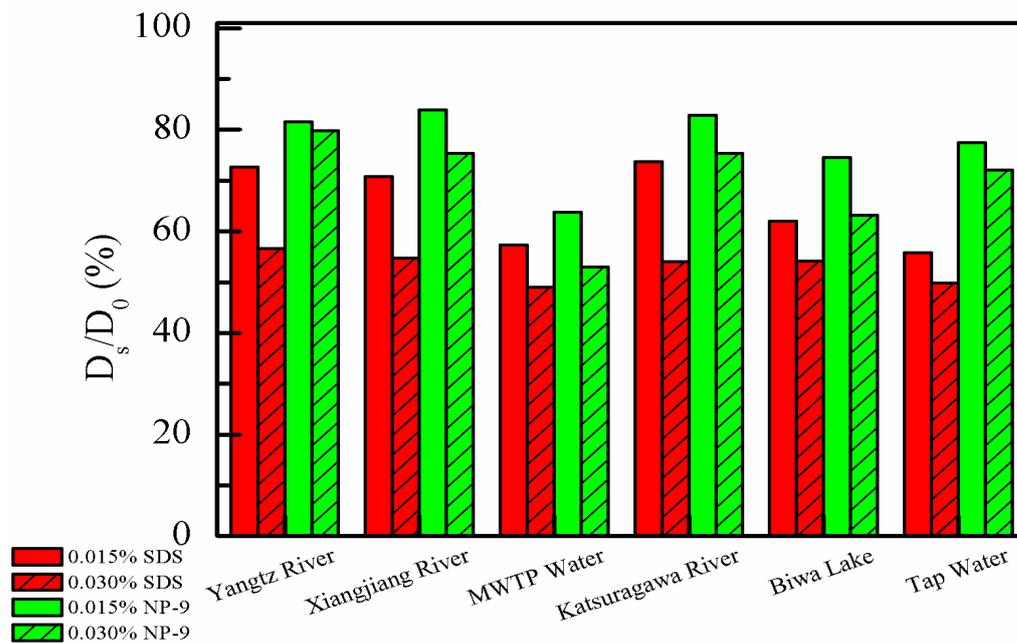


Fig.5 Effect of surfactants on the size ratios of TiO<sub>2</sub> aggregates in natural waters

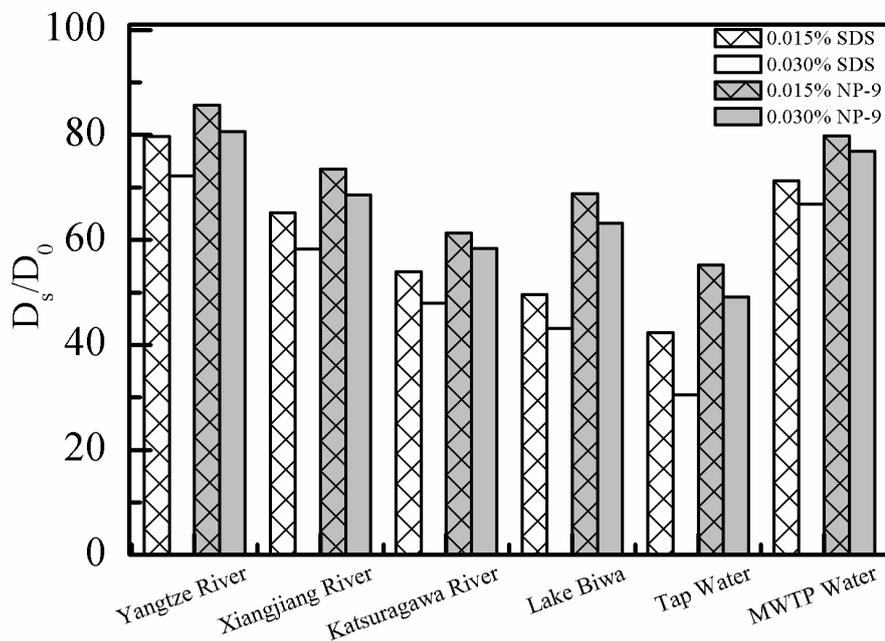


Fig.6 Effect of surfactants on the size ratios of ZnO aggregates in natural waters

### 4.3.5 Effect of surfactants on the sedimentation of TiO<sub>2</sub> and ZnO ENM in natural water matrices

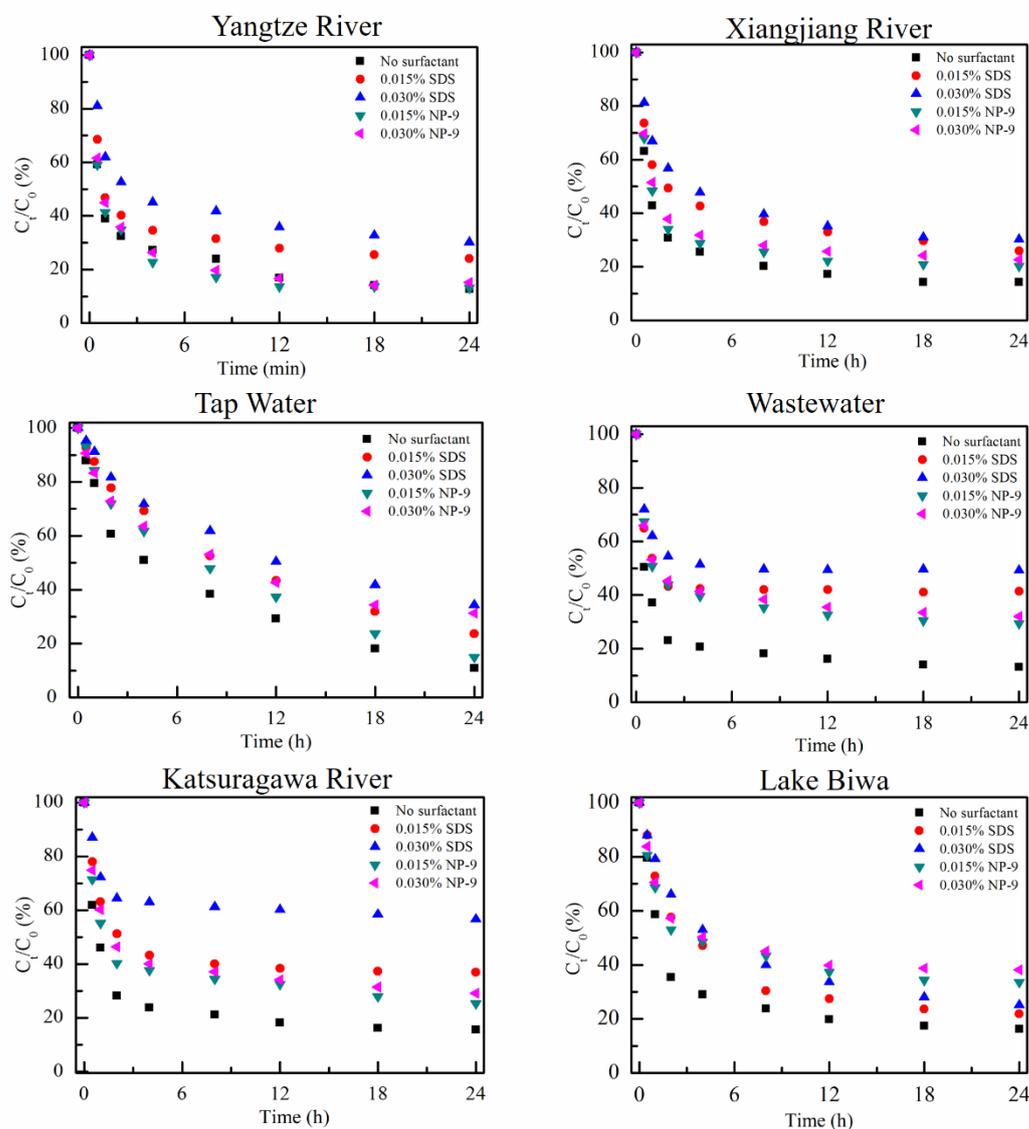


Fig.7 Effect of surfactants on the sedimentation of TiO<sub>2</sub> aggregates in natural waters

Despite retarding effect of surfactants on the aggregation and sedimentation of TiO<sub>2</sub> and ZnO aggregates were observed in natural aqueous matrices, the effectiveness of surfactants are not as pronounced as that in Milli-Q water. As shown in Fig.7, in the presence of SDS or NP-9 at 0.030% concentration in tap water, for instance, 52.97% and 39.58% of the TiO<sub>2</sub> remained in the suspension after 24 h, respectively. In

comparison, the corresponding values in Milli-Q water were 96.01% and 83.65%. As for ZnO nanomaterials, with the presence of SDS or NP-9 at a concentration of 0.030% in Xiangjiang river water, for instance, only 31.19% and 22.04% of the ZnO remained in the suspension after 24 h, respectively. In comparison, the corresponding values in Milli-Q water were 57.47% and 51.22%, respectively. Some studies have reported that factors such as pH value, ionic strength and natural organic matters (NOMs) are able to affect the behaviors and fate of ENMs in the water environment (Chowdhury et al., 2013; Domingos et al., 2013; Loosli et al., 2013; Mohd Omar et al., 2014; Raza et al., 2016). In our study, however, no significant differences of pH values were observed between the Milli-Q water (pH 7.02) and natural water samples. In addition, the TOC of all the experimental water samples ranges from 0.67 to 2.54 mg L<sup>-1</sup> according to Table.2, suggesting concentrations of NOMs were much lower than surfactants in the experimental suspensions, thus the sorption competition between NOMs and surfactants are deemed to be minor.

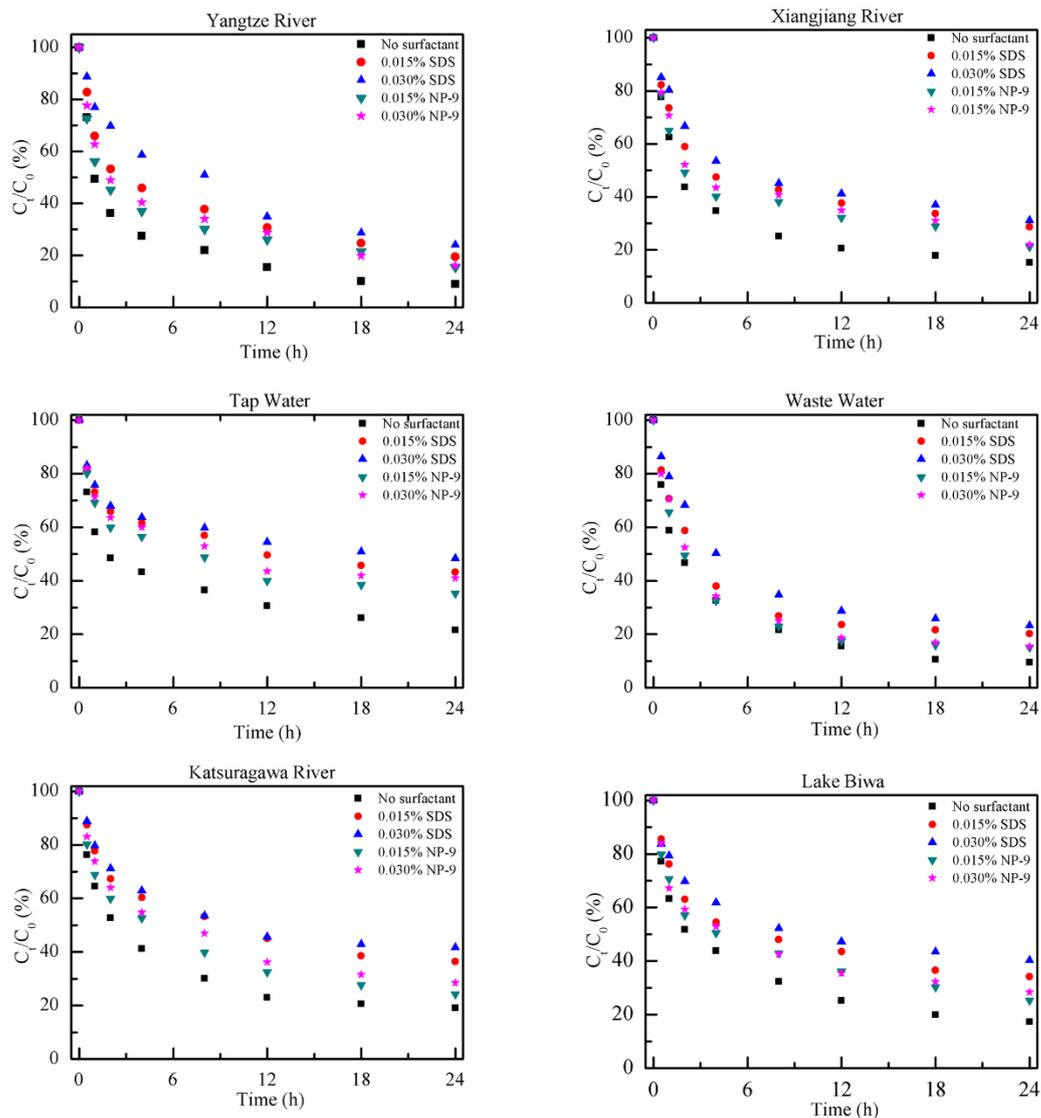


Fig.8 Effect of surfactants on the sedimentation of ZnO aggregates in natural waters

The discrepant behaviors of TiO<sub>2</sub> or ZnO ENM in Milli-Q water and environmental aqueous matrices are deemed to be caused by the factor of ionic strength. It has been proved that an increase in ionic strength will lead to stronger compression of the electrical double layer of nanoparticles, thereby reducing the repulsive force between nanoparticles and increasing the size of the aggregates and speed of the sedimentation. For example, Dickson et al. reported that an increase of ionic strength to 10 mM NaCl resulted in rapid aggregation and sedimentation of hematite nanoparticles in dispersion

within 8 h (Dickson et al., 2012). With the increase of ionic strength from 0 to 10 mM NaCl, Han et al. found that the sedimentation of ZnO nanoparticles was significantly accelerated (Han et al., 2014). French et al. discovered in a suspension containing NaCl (ionic strength 0.0165 M), the mean aggregate size of a stable nano-TiO<sub>2</sub> (50-60 nm) increased to 150 nm after only 5 min (French et al., 2009). Similarly, we also observed a promoted aggregation of TiO<sub>2</sub> and ZnO ENM as the increase of ionic strength in chapter 4.3.1. In addition, the remarkable presence of divalent ions in natural water samples further promoted the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENM. In one side, the multivalent ions exert stronger compressive effect on the electrical double layer than monovalent ions. In the other side, the bridging effect of multivalent ions also increase the aggregation and reduce the stability of nanoparticles in aqueous environment.

Generally, two findings were observed in all the tested aqueous matrices: higher surfactant concentration retarded the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENM more, and the effect of ionic SDS surfactant was more pronounced than non-ionic NP-9 surfactant. When only nonionic NP-9 was used, the TiO<sub>2</sub> nanoparticles cannot be stabilized with additional repulsive force. Besides, the pH values of all the environmental water samples were higher than the PZC value (6.2), indicating the minus charge on the surface of TiO<sub>2</sub> nanoparticles. Therefore, the intermolecular bridging through Ca<sup>2+</sup> and Mg<sup>2+</sup> weakened the steric inhibition effect of NP-9. With regard to SDS surfactant, although surface-covered SDS anions exerted strong repulsive forces between the TiO<sub>2</sub> nanoparticles, cations were also attracted by the

negative surface charge. Finally, with the suppression of the double layer, the repulsive force between TiO<sub>2</sub> nanoparticles decreased. These effects, in turn, remarkably increased the chances for nanoparticle collision in natural aqueous matrices during the batch experiments, promoting aggregation and sedimentation in both SDS and NP-9 suspensions.

As for ZnO nanomaterials, considering the pH values of all the water samples (6.65 to 6.99) were apparently lower than the p*H*<sub>ZPC</sub> (8.7 to 9.4), the ZnO nanoparticles were supposed to be positively charged in all the six natural aqueous matrices. With the introduction of SDS, the anionic surfactant attached to the surface of ZnO nanoparticles and exerted repulsive forces between those nanoparticles, thereby reduced the aggregation and sedimentation of ZnO ENM in the natural waters. However, cations in the natural water matrices were also attracted by the surface-covered anions. Finally, under the compression of the electrical double layer and bridging effect by divalent Ca<sup>2+</sup> and Mg<sup>2+</sup>, the retarding effects of SDS on the aggregation and sedimentation of ZnO ENM in natural water matrices were not as prominent as that in Milli-Q water. In comparison, the nonionic NP-9 surfactant could not offer electrical repulsive force to reduce the collision of ZnO nanoparticles. With the compression of the electrical double layer and the bridging effect of anions, therefore, the retarding effects of NP-9 on the aggregation and sedimentation of ZnO ENM in natural water matrices were not as pronounced as SDS.

#### 4.4 Conclusions

In this chapter, the effect of surfactants on the aggregation and sedimentation of TiO<sub>2</sub> and ZnO ENM as the function of pH and ionic strength were studied, it was found that both ENMs tended to aggregate more as the suspension pH closed to the p*H*<sub>zpc</sub> or ionic strength increased. However, the presence of both SDS and NP-9 surfactants reduced the growth of aggregate size, and ionic SDS were found to be more pronounced in retarding the aggregation of TiO<sub>2</sub> and ZnO ENMs. In six different natural water sample, the key factor exerting impacts on the aggregation and sedimentation was attributed to ionic strength, and surfactant were proved to be effective in retarding the aggregation and sedimentation of the tested ENMs.

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## CHAPTER 5

### **Transport of TiO<sub>2</sub> nanoparticles in saturated porous media column with the presence of surfactants**

#### **Abstract**

In this chapter, the effect of surfactants on the transport of nano-TiO<sub>2</sub> in a saturated media was investigated. It was found that the introduction of surfactant can promote the transport of TiO<sub>2</sub> nanoparticles in porous media. At pH 6.0, the transport of TiO<sub>2</sub> was retarded because of the increased aggregation of TiO<sub>2</sub> nanoparticles near  $pH_{pzc}$ . As the pH rose to 9.0, the alkaline condition stabilized the nanoparticles and the transport of nano-TiO<sub>2</sub> increased. The high ionic strength significantly retarded the transport of nano TiO<sub>2</sub> because of the cations resulted compression of electrical double layer, a process that leads to the aggregation of nanoparticles. In environmental samples, the divalent cations further increased the aggregation of nanoparticles, therefore, significantly reduced transports of nano-TiO<sub>2</sub> were observed. However, the introduction of surfactants increased the transport of nano-TiO<sub>2</sub> in different extent. This is because nonionic NP-9 provided steric hindrance and SDS provided additional electrical repulsion to reduce the aggregation of nanoparticles.

#### **5.1. Introduction**

With the wide application of engineered nanomaterials (ENMs) and the environmental risk to the eco-system, the transport and fate of ENMs in the subsurface environment are arousing more and more scientific interest since soils and aquifers act as the primary

filter systems for the water resources (Nowack and Bucheli, 2007; Raychoudhury et al., 2012). Recently, more and more studies are focusing on revealing the ENMs' transport processes, the dominant mechanisms, and factors of some physicochemical conditions (Badawy et al., 2010; Cupi et al., 2016; Fatehah et al., 2014; French et al., 2009). An increasing number of researchers conducted laboratory-scale transport experiments and demonstrated that the ENMs have high mobility under environmental conditions, suggesting a potential risk of groundwater contamination (Klimkova et al., 2011; Lin et al., 2012; Majedi et al., 2014). The mobility of colloidal particles in the subsurface environment is generally considered to be determined by physico-chemical interactions and size-related processes (Lu et al., 2013; Petosa et al., 2012; Yechezkel et al., 2016). Researchers have proved the potential relationships between environmental factors (such as soil grain size, flow velocity, the physico-chemical properties of aqueous or solid phases, organic matter, ENMs concentration, etc.) and the environmental transport of ENMs (Cai et al., 2014; Fang et al., 2009; Liu et al., 2013; Qi et al., 2014; Sygouni and Chrysikopoulos, 2015; Yang et al., 2015).

Simplified simulation are widely applied to study the mechanisms and models for transport and deposition of colloid/ENMs in the real environment. Quartz sands or glass beads, for instance, are often used as idealized porous media. In addition, monovalent salts are usually used to prepare the electrolyte solutions. Most studies therefore frequently apply idealized systems consisting of repacked, homogeneous, coarse textured porous media and monovalent salts to minimize any disturbance from other physicochemical parameters (Cai et al., 2013; Chen et al., 2012; Goldberg et al., 2014;

Wang et al., 2015). This previous research has provided fundamental knowledge and understanding of the influence of many physicochemical factors on particle transport and retention. In this chapter, the effect of surfactant on the transport of a nano-TiO<sub>2</sub> were studied. Next, effect of water property factors such as ionic strength and pH on the transport of nano-TiO<sub>2</sub> had been investigated, and the effect of surfactants on the transport of nano-TiO<sub>2</sub> as functions of these factors were examined. Finally, two environmental water samples were used to flush the nano-TiO<sub>2</sub> in the porous media, and surfactants were introduced into to the eluent to examine the effect of surfactants on the transport of nanoparticle in realistic environmental waters.

## **5.2 Materials and methods**

### **5.2.1 Chemicals**

Aeroxide P25 TiO<sub>2</sub> (718467,  $\geq 99.5\%$  trace metals basis ) with a primary particle size of 21 nm (TEM) and surface area (BET) of 35–65 m<sup>2</sup> g<sup>-1</sup> was purchased from Sigma-Aldrich. ZnO ENM (351-34492,  $\geq 99.9\%$ ) with a primary particle size of 20 nm was obtained from WAKO Pure Chemical Industries. SDS (436143, ACS reagent,  $\geq 99.0\%$ ) and NPEO (521078, Tergitol NP-9,  $>97\%$ ) surfactants were obtained from Sigma-Aldrich. Glass beads (average size 0.6 mm) was purchased from Asahi Glass.

### **5.2.2 Column system**

Figure 5.1 shows the schematic overview of the saturated column experiment. Briefly, the TiO<sub>2</sub> dispersion was introduced into the saturated porous media column and rinsed by nanoparticle-free solution. The effluent was analyzed to obtain breakthrough curves

(BTCs). In particular, the glass beads were soaked in 10% (v:v) HNO<sub>3</sub> overnight, and washed repeatedly with Milli-Q water before the eluent becoming neutral, then the glass beads were dried in an oven before they were used for column packing. Fig.1 shows the experimental set-up: water saturated transport experiments were performed in acrylic columns (5 cm inner diameter, 10 cm length) that were dry-packed with glass beads (diameter 600 μm). A hydrophilic nylon net, which was supported by an acrylic plate, was used as a capillary barrier and filter at the bottom and the top of the column. During packing, the column was vibrated to minimize air entrapment and to ensure homogenous packing. A peristaltic pump was used to inject solutions at a flow rate of 10 mL min<sup>-1</sup> (Darcy velocity 0.51 cm min<sup>-1</sup>) through the column in an up-flow mode.



Fig.1 Experimental set-up of the column system

Before initiating a transport experiment, the packed column was conditioned with at least 10 pore volumes (PVs) of Milli-Q water. The weight of the packed column were

measured before and after saturation, and the pore volume of the column system was known by calculating the volume of water contained in the saturated column. Before injecting TiO<sub>2</sub> nanoparticle containing suspensions, the column was flushed continuously with the corresponding background solutions for at least 10 PVs. Then 4 PVs of TiO<sub>2</sub> nanoparticle containing suspensions were injected into the column, followed by flushing with 4 PVs of the corresponding background solution. The effluents were collected at a 0.25 PV interval in disposable centrifuge tubes by a fraction collector. The concentration of TiO<sub>2</sub> nanoparticle entering the column, C<sub>0</sub>, and in the effluent, C<sub>i</sub>, were measured as the absorbency by a UV-Vis spectrometer (wavelength 378 nm). And the BTCs were made by setting C<sub>i</sub>/C<sub>0</sub> as a function of PVs. The detailed experimental parameters of column system are listed in Table.1.

Table.1 The experimental parameters of column system

Column parameter	Value
Inner diameter of column	5 cm
Length of column	10 cm
Pore volume of column	72 mL
Porosity of media	36.7%
Collector diameter	600 μm
Initial concentration of nanoparticles	50 mg L <sup>-1</sup>
Darcy flow velocity	0.51 cm min <sup>-1</sup>

### ***5.2.3 Effect of surfactant on the transport of TiO<sub>2</sub> nanoparticle***

Since it was found that the presence of surfactant could significantly affect the particle size of TiO<sub>2</sub> nanoparticles, therefore in order to understand the effect of surfactant on the transport of nanoparticles in porous media, the nanoparticle transport was studied under the presence of different concentration of surfactants.

4 PVs of mixed suspensions containing 50 mg L<sup>-1</sup> nanoparticle and 0.010 or 0.020% SDS or NP-9 surfactant were prepared and injected into the surfactant solution saturated porous media, and then continuously flushed with 4 PVs of the same concentration of surfactant solutions. The UV absorbency of both the inflow and outflow were recorded in order to get the BTCs.

### ***5.2.4 Effect of surfactants on the transport of TiO<sub>2</sub> nanoparticle as the function of pH and ionic strength***

To investigate the effect of surfactant on the transport of TiO<sub>2</sub> nanoparticle as the function of pH and ionic strength, separated experiments were conducted. Firstly, the mixed suspensions containing 0.010% surfactant and 50 mg/L nanoparticle were prepared, the pH were adjust to 6.0 and 9.0 with 0.1 M HCl or NaOH solution. Then 4 pore volumes of the above-mentioned suspensions were injected into the column, following by the continuous injection of 4 PV corresponding surfactant solution with the same pH value in a constant flow rate. Secondly, mixed suspensions of surfactant and TiO<sub>2</sub> nanoparticle with the presence of 5 and 20 mM NaCl were prepared, followed by the same injection process described in former step, the effluent were collected and measured for plotting BTCs.

### 5.2.5 Effect of surfactant on the transport of TiO<sub>2</sub> nanoparticles in natural water matrices

Considering the significant difference between the laboratory solutions and real natural waters, the effect of surfactant on the transport of TiO<sub>2</sub> nanoparticles in natural water matrices were studied. The natural water were taken from Katsuragawa River (Kyoto) and tap water (Kyoto University Katsura campus), and the physico-chemical properties of the water samples were listed in the Table 2 in chapter 4.

## 5.3. Results and discussion

### 5.3.1 Effect of surfactant on the transport of TiO<sub>2</sub> nanoparticles

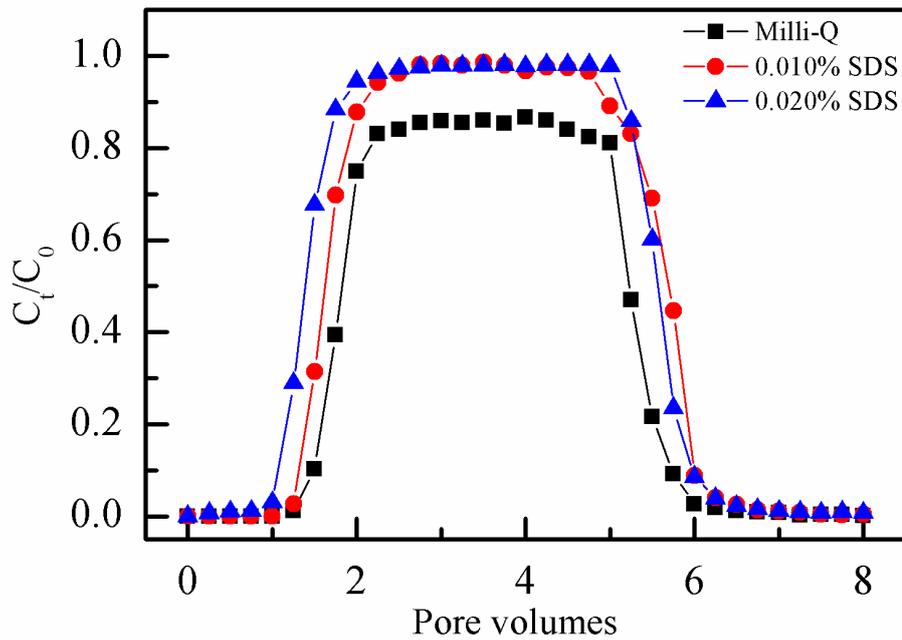


Fig.2 Breakthrough curves of TiO<sub>2</sub> with the presence of SDS

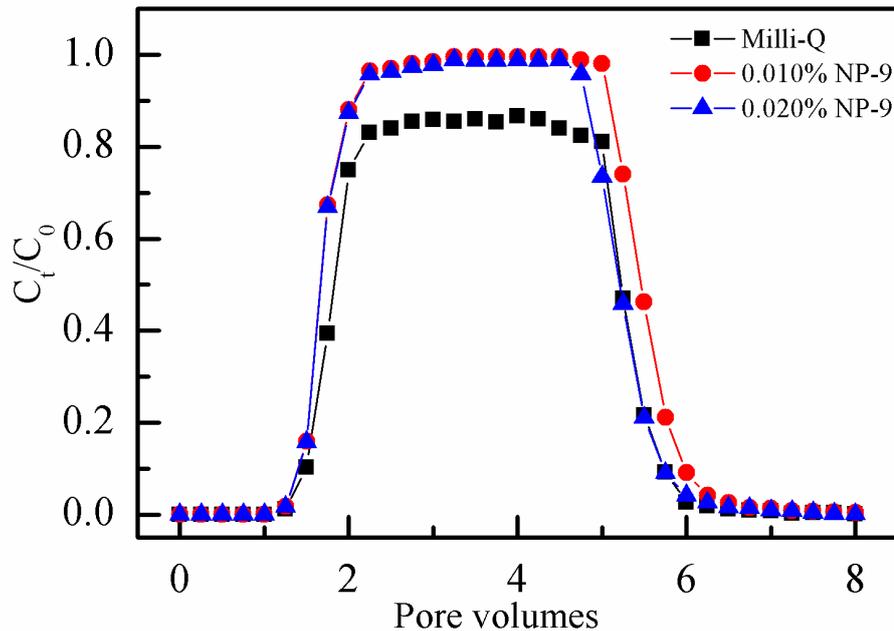


Fig.3 Breakthrough curves of TiO<sub>2</sub> with the presence of NP-9

To understand the effect of surfactants on the transport of TiO<sub>2</sub> nanoparticles in the saturated porous media, the transport of nano TiO<sub>2</sub> with the presence of ionic SDS and nonionic NP-9 surfactant were examined. As shown in Fig.2 and Fig.3, both the presence of SDS and NP-9 surfactants enhanced the transport of nano-TiO<sub>2</sub> in the saturated porous media systems. Fig. 1 describes the breakthrough curves of nano-TiO<sub>2</sub> in the cases of no surfactant, 0.010% and 0.030% SDS systems at a Darcy flow velocity of 5.01 cm min<sup>-1</sup>. During the flushing period, the maximum  $C_t/C_0$  effluent fraction concentration of nano-TiO<sub>2</sub> increased with the presence of surfactant. With the presence of 0.010% SDS, for example, a maximum  $C_t/C_0$  value of 0.986 was observed at the point of 3.5 PV, in comparison the highest  $C_t/C_0$  value in bare Milli-Q effluent was 0.867 which was observed at the point of 4 PV. Similarly, increased  $C_t/C_0$  values were also observed with the introduction of NP-9 surfactant according to Fig.2. When the

concentration of NP-9 was 0.010%, a maximum  $C_t/C_0$  value of 0.996 was calculated at the point of 3.25 PV. According to the results and discussions in chapter 1, it can be known that both SDS and NP-9 can be absorbed by the  $TiO_2$  nanoparticles, therefore inhibited the growth of particle size and attachment to the glass bead surface.

### ***5.3.2 Effect of surfactant on the transport of $TiO_2$ nanoparticles as the function of pH and ionic strength***

In chapter 4, it has been proved that pH and ionic strength are important factors that affect the aggregation and stability of nanoparticles in aqueous solution. To understand the transport of  $TiO_2$  nanoparticles in porous media, the factors of pH and ionic strength cannot be ignored.

Fig.4 and Fig.5 demonstrate the transport of  $TiO_2$  nanoparticles in the porous media under the pH value 6.0 and 9.0, respectively. It can be observed that the transport of  $TiO_2$  nanoparticles is enhanced as the pH increase from 6.0 to 9.0. At pH 9.0 in Milli-Q water, as it is reported in chapter 4, the aggregate size of  $TiO_2$  nanoparticle was found to be 47.2 % smaller than that observed at pH 6.0. Therefore, the transport of  $TiO_2$  nanoparticles in the column system at pH 9.0 is more significant than at pH 6.0. With the introduction of surfactants, the  $C_t/C_0$  value of was generally found increased, and the ionic SDS promoted the transport of  $TiO_2$  nanoparticles more than nonionic NP-9.

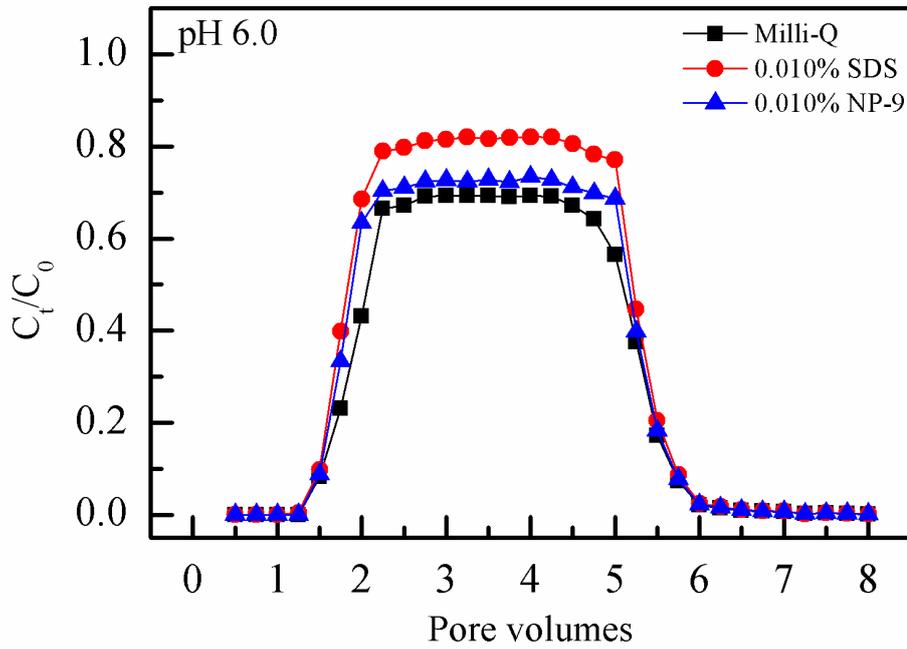


Fig. 4 Breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants at pH 6.0

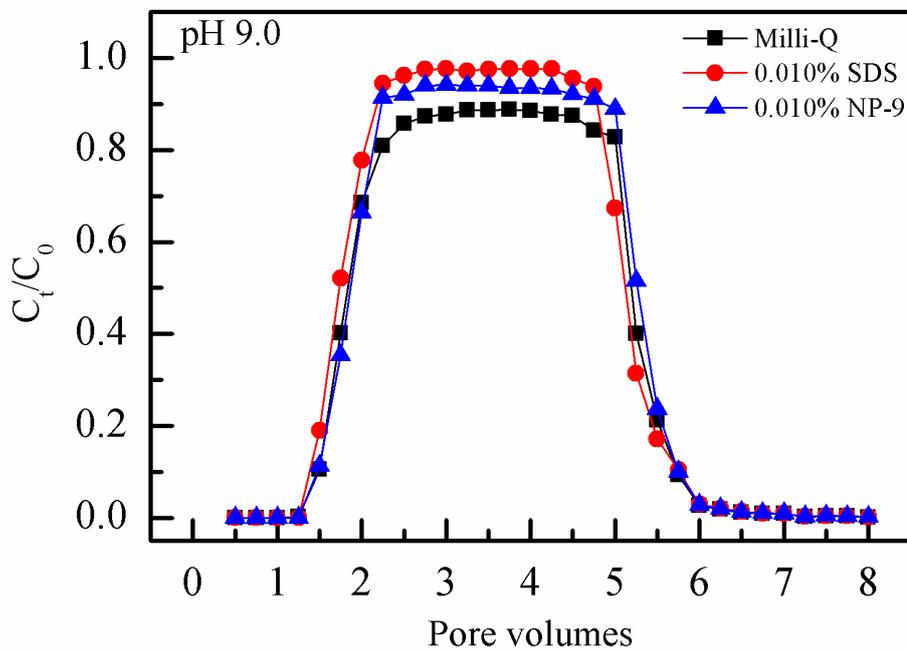


Fig. 5 Breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants at pH 9.0

Fig.6 and Fig.7 shows the breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants as a function of ionic strength. As the ionic strength increases, the

compression effect on the electrical double layer of nano TiO<sub>2</sub> also increases, leading to the increase of aggregation and interception of nanoparticles in the porous media. Hence, compared to Fig.2 and Fig.3, the transport of bare TiO<sub>2</sub> nanoparticles with the introduction of 5 mM and 10 mM NaCl was remarkably retarded. However, the presence of surfactant significantly promoted the transport of nano-TiO<sub>2</sub> and ionic SDS was more effective than nonionic NP-9, especially at high ionic strength. At a NaCl concentration of 20 mM, for instance, the presence of 0.010% SDS and NP-9 improved the peak  $C_t/C_0$  value for 15.40 and 4.20%, respectively.

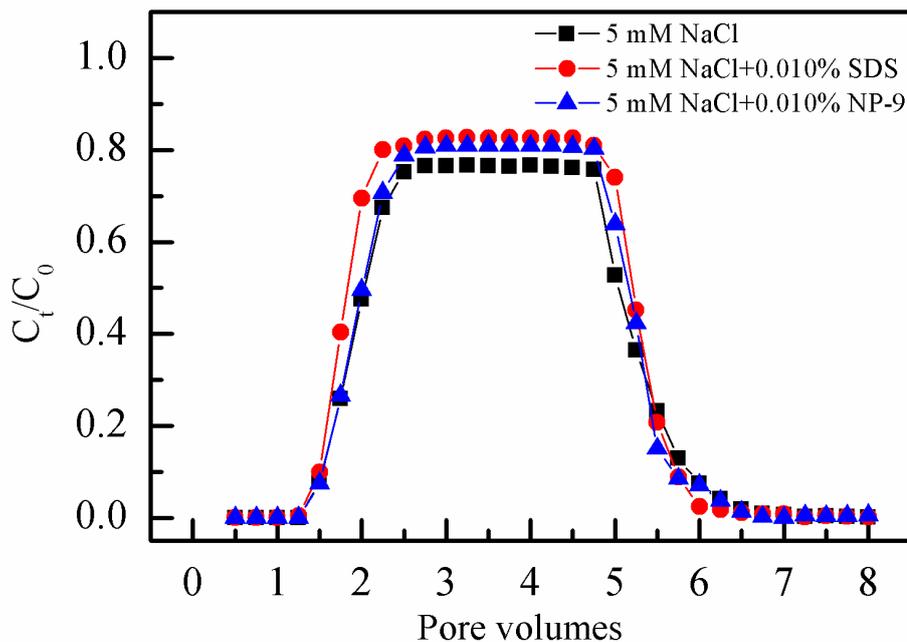


Fig. 6 Breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants at ionic strength of 5 mM

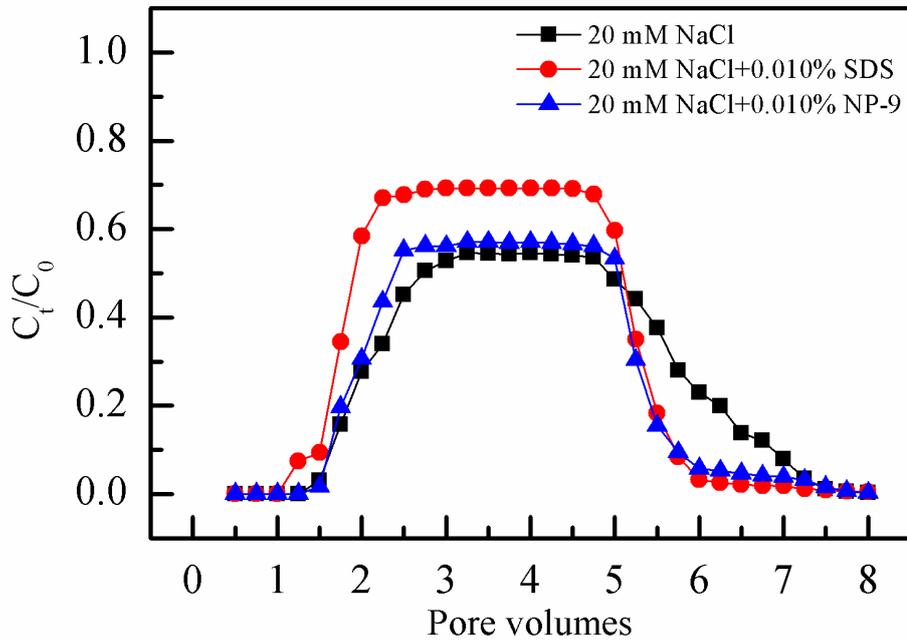


Fig. 7 Breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants at ionic strength of 20 mM

### 5.3.3 Effect of surfactant on the transport of TiO<sub>2</sub> nanoparticles with environmental water flushing

Considering the physico-chemical properties of environmental water is different from the artificial solution, it is important and constructive to study the transport of nanoparticles in porous media with the flushing of realistic environmental water. Therefore, followed Chapter 4, two water samples which were from the tap and Katsuragawa river were selected to conduct the experiment.

Fig.8 and Fig.9 demonstrates the breakthrough curves of TiO<sub>2</sub> nanoparticles with the presence of surfactants and flushing of two environmental waters. It can be observed that the transport of bare nano-TiO<sub>2</sub> in both tap water and river water is not as profound as in Milli-Q water. When flushed by tap and river water, the maximum  $C_t/C_0$  values

are 20.91% and 25.00% smaller than that flushed by Milli-Q water, respectively. The retarded transports flushed by environmental waters are in accordance with the retarded stability observed in chapter 4. The ions especially the divalent cations compressed the electro double layers and bridged the nanoparticles, causing the increase in aggregate size of particles and decrease in transport. However, with the presence of both SDS and NP-9 surfactant, the transport of nano-TiO<sub>2</sub> increased, and ionic SDS exerted more pronounced effect than nonionic NP-9. As an ionic surfactant, the SDS not only provided steric hindrance, but also provided electrical repulsion to stabilize the nanoparticles. In comparison, the NP-9 surfactant can only provide steric hindrance to reduce the aggregation. Therefore, ionic SDS exerted more significant effect on increasing the transport of nanoparticles under all the experimental conditions.

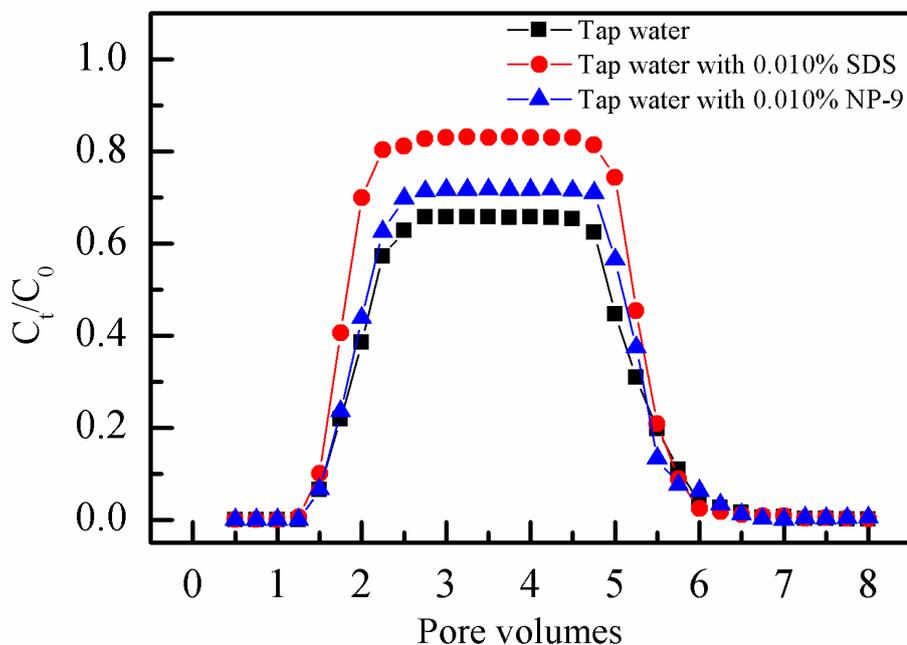


Fig. 8 Breakthrough curves of TiO<sub>2</sub> nanoparticles flushed by tap water with the presence of surfactants

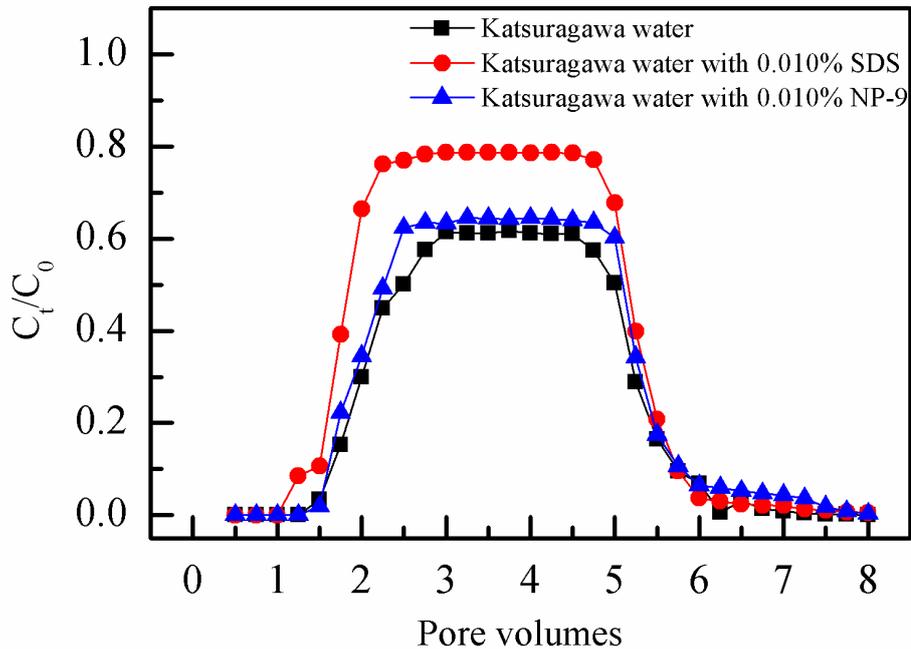


Fig. 9 Breakthrough curves of TiO<sub>2</sub> nanoparticles flushed by Katsuragawa river water with the presence of surfactants

## 5.4 Conclusions

In this chapter, effect of surfactants on the transport of TiO<sub>2</sub> nanoparticles in saturated porous media was investigated as a function of anionic and nonionic surfactant concentration, pH and ionic strength of solutions. Besides, the transport of TiO<sub>2</sub> nanoparticles with the co-presence of surfactants were also investigated in natural water samples. It was found surfactants enhanced the transport of TiO<sub>2</sub> ENMs in saturated porous media while a pH approaching the point of zero charge (6.2) of nano-TiO<sub>2</sub> limited its transport. The deposition process, a retention mechanism of TiO<sub>2</sub> ENMs saturated porous media was impacted by surfactant, pH and ionic strength. And the presence of both SDS and NP-9 further increased the transport distances of TiO<sub>2</sub> and ZnO ENMs in porous sand media.

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## CHAPTER 6

### Conclusions

Currently, engineered nanomaterials (ENMs) are being widely applied to a plenty of industrial and consumer products. However, the large-scale industrial production and application of ENMs will inevitable result in their release into environment and generate potential environmental risks. Surfactants are commonly used in both industry and household, which can usually be detected in the wastewater with high concentration. The dispersive effect of surfactants on ENMs make it necessary to study the effect of surfactant on the environmental behaviors and transports of ENMs. Considering the wide application of ENMs and surfactant in the industries and households, it is reasonable to assume the co-existence of ENMs and surfactant in natural environment may happen. In this study an ionic sodium dodecyl sulfate (SDS) and nonionic nonylphenol ethoxylates (NPEO, Tergitol NP-9), two surfactants widely used in industries, were selected to study the effect of surfactants on the behaviors and transport of TiO<sub>2</sub> and ZnO ENMs in aqueous matrices and porous media.

In the first part of research (Chapter 3), the adsorption of surfactants and the resulted effect on the behaviors of TiO<sub>2</sub> and ZnO ENMs were studied after a 24-h batch reactor experiment, and then the sedimentation of the aggregates of TiO<sub>2</sub> and ZnO ENMs were observed with a UV-spectrophotometer at a wavelength of 378 nm. It was found that both SDS and NP-9 surfactant can be apparently adsorbed by TiO<sub>2</sub> and ZnO ENMs, and Langmuir model can be well applied to the fitting of the adsorption isotherms. Next, the presence of both surfactants effectively reduced the aggregation of two ENMs when

surfactant concentration exceeded 0.015% as observed by both dynamic scattering lightening (DSL) and scanning electronic microscopy (SEM). The SDS surfactant remarkably affected the zeta potential of TiO<sub>2</sub> and ZnO nanomaterials, and the absolute value of nanomaterials' zeta potential decreased at first and then significantly increased with growth of SDS concentration. This process remarkably increased the electrical repulsive forces between nanoparticles, and hence reduced the aggregation and increased the stabilities of the aggregates of both TiO<sub>2</sub> and ZnO nanomaterials. As for the non-ionic NP-9 surfactant, the surfactant covered the surface of nanomaterials, hence reduced the aggregation and increased the stability of both nanomaterials. In a 24-h sedimentation observation, it was found the presence of both surfactants significantly retarded the sedimentation of TiO<sub>2</sub> and ZnO aggregate, and the increase of concentration of surfactants resulted stronger retardation on the sedimentation of the aggregate of ENMs.

In the second part of this work (chapter 4), the effect of surfactants on the behaviors of TiO<sub>2</sub> and ZnO ENMs in environmental conditions and six realistic water samples were explored. It was found that as pH increase from 6.0 to 9.0, the aggregate size of TiO<sub>2</sub> and ZnO ENMs varied significantly after 24-h batch reactor experiment. In addition, as the ionic strength increased to 50 mM, the aggregation of ENMs increased significantly. However, the introduction of surfactants reduced the aggregate size of both TiO<sub>2</sub> and ZnO ENMs as the function of pH and ionic strength. In six natural water matrices, the aggregation of both TiO<sub>2</sub> and ZnO ENMs were found most significant in Yangtze river water, and the ionic strength were thought to be a major reason for the increased

aggregation of ENMs. With the presence of surfactant, however, both aggregation and sedimentation of ENMs were found to be retarded, and the ionic SDS were found more effective than nonionic NP-9 surfactant.

In the third part of this study (Chapter 5), effect of surfactants on the transport of TiO<sub>2</sub> ENMs in saturated porous media was investigated as a function of anionic and nonionic surfactant concentration, pH, ionic strength of solutions and the environmental water flushing. It was found that the introduction of surfactant can promote the transport of TiO<sub>2</sub> nanoparticles in porous media. At pH 6.0, the transport of TiO<sub>2</sub> was retarded because of the increased aggregation of TiO<sub>2</sub> nanoparticles near  $pH_{pzc}$ . As the pH rose to 9.0, the alkaline condition stabilized the nanoparticles and the transport of nano-TiO<sub>2</sub> increased. The high ionic strength significantly retarded the transport of nano TiO<sub>2</sub> because of the cations resulted compression of electrical double layer, a process that leads to the aggregation of nanoparticles. In environmental samples, the divalent cations further increased the aggregation of nanoparticles, therefore, significantly reduced transports of nano-TiO<sub>2</sub> were observed. However, the introduction of surfactants increased the transport of nano-TiO<sub>2</sub> in different extent. This is because nonionic NP-9 provided steric hindrance and SDS provided additional electrical repulsion to reduce the aggregation of nanoparticles.

This study provides an insight into the effect of surfactants on the aggregation, sedimentation, and transport of metal oxide ENMs as a function of different water matrices, which are contributive to the environmental risk assessment of the engineered nanomaterials.