



# Heteroaggregation of engineered nanoparticles and kaolin clays in aqueous environments



Hongtao Wang<sup>a,\*</sup>, Ya-nan Dong<sup>a</sup>, Miao Zhu<sup>a</sup>, Xiang Li<sup>a</sup>, Arturo A. Keller<sup>b</sup>, Tao Wang<sup>a</sup>, Fengting Li<sup>a</sup>

<sup>a</sup> State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China

<sup>b</sup> Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, 93106, United States

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## ABSTRACT

The increasing and wide use of nanoparticles (NPs), including TiO<sub>2</sub> and Ag NPs, have raised concerns due to their potential toxicity and environmental impacts. Kaolin is a very common mineral in aquatic systems, and there is a very high probability that nanoparticles (NPs) will interact with these clay minerals. We studied the effect of kaolin particles on the aggregation of NPs under different conditions, including the role of pH, ionic strength (IS), and humic acid (HA). We show that kaolin reduces the energy barrier and the Critical Coagulation Concentration (CCC) at pH 4. At pH 8, even though the energy barrier of the system without kaolin increases, kaolin promotes NP aggregation via heteroaggregation. When IS is equal to or greater than the CCC, on the one hand HA promotes aggregation of TiO<sub>2</sub> NPs, but on the other hand HA decreases the rate of Ag NP aggregation because the existence of a surface coating may limit the adsorption of HA on these Ag NPs. In addition, the presence of HA increases the energy barrier and the CCC of the binary system (kaolin + NPs). Thus, the complex interactions of clay, NPs, IS, pH, and HA concentration determine the colloidal stability of the NPs. We find that kaolin is a potential coagulant for removal of NPs that behave like Ag and TiO<sub>2</sub>.

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## 1. Introduction

The rapid growth of nanotechnology applications in consumer and industrial products in the past few years has increased the release of nanoparticles (NPs) to the environment (Keller et al., 2013; Theron et al., 2008). TiO<sub>2</sub> NPs are used in many products, including paints, pigments and personal care products, and Ag NPs are used in many consumer products that can result in transfer to the aqueous environment via wastewater treatment plants (WWTPs) (Keller et al., 2013; Lazareva and Keller, 2014). A recent study estimated that 10–30%, 3–17% and 4–19% NPs are discarded into water bodies in Asia, Europe and North America respectively and predicted release concentrations of engineered nanomaterials in WWTP effluent of 5–20 µg/L TiO<sub>2</sub> NPs and 0.05–0.2 µg/L Ag NPs (Keller and Lazareva, 2013). Westerhoff et al. found effluent concentrations of TiO<sub>2</sub> NPs in WWTPs were still 25 µg/L titanium, even though the WWTPs removed more than 96% of the influent

titanium (Westerhoff et al., 2011). The increasing understanding of the toxicity (Chen et al., 2006; Colvin, 2003; De Jong et al., 2013; Ghosh et al., 2013; Keller et al., 2010; Olmedo et al., 2005; Song et al., 2013; Trouiller et al., 2009; Zhang et al., 2007) of these NPs indicates that their potential risk can't be ignored, therefore, their fate, transport and removal need to be better understood.

Kaolin is an abundant clay material, found in many natural waters, and with high potential for wastewater treatment through adsorption due to its large surface area and pore volume (Ma and Wang, 2006; Ma et al., 2007). It should be noted that kaolinite is the clay mineral that characterizes/makes up most kaolin (Ross and Kerr, 1930). In this paper, we use kaolin to denote the clay material. Kaolin is divided into two kinds: a well-crystallized form (Zettlitz, with a Critical Coagulation Concentration (CCC) ≈ 3 mM NaCl at pH = 4, and CCC ≈ 100 mM NaCl at pH = 8) and a poorly-crystallized form (KGa-2, unstable at pH = 4, CCC ≈ 85 ± 5 mM NaCl at pH = 9.5). The cation exchange capacity (CEC) of well-crystallized kaolin (≈9 meq/100 g) has almost three times greater permanent charge than poorly-crystallized kaolin (3.3 meq/100 g) (Tombacz and Szekeres, 2006; Van Olphen and Fripiat, 1979).

\* Corresponding author.

E-mail address: [hongtao@tongji.edu.cn](mailto:hongtao@tongji.edu.cn) (H. Wang).

Kaolin has one Al–O face and one Si–O face. The Si–O face has a negative charge because of lattice ion replacement. In addition, kaolin has an edge which is around 10–120 nm (Brady et al., 1996; Wan and Tokunaga, 2002). Compared with the defective (poorly-crystallized) crystal face, the surface charge density of the pristine (original or untreated) crystal face is higher, and the electric double layer (EDL) is thicker (Wan and Tokunaga, 2002). At low IS (10 mmol/L NaCl) and  $\text{pH} < \text{pH}_{\text{pzc, edge}}$  (edge point of zero charge, pzc), the thickness of the EDL (Debye length  $\approx 3$  nm at 10 mmol/L) is larger than that of the thin lamella, and the dominant EDL extending from the face spills over the edge, screening the positive charge of the edge. This explains why at pH 4 poorly-crystallized kaolin is unstable at any IS, while well-crystallized kaolin is stable at low IS (Tombacz and Szekeres, 2004).

Humic substances represent an active and important fraction of natural organic matter (NOM) and they play important roles in the fate and transport of pollutants in the aqueous phase (Aiken, 1985; Buffle et al., 1998; Wang et al., 2011, 2010; Zheng et al., 2008). For example, humic acid (HA) affects the stability of NPs through electric forces, steric hindrances, and the bridging effect (Zhu et al., 2014). HA also reduces the removal of TiO<sub>2</sub> NPs by coagulation (Wang et al., 2014, 2013). The presence of NOM, and in particular HA, has been shown to contribute to the instability of Ag NPs at high ionic strength in divalent metallic cation solutions, most likely due to intermolecular bridging with the organic matter (Akaighe et al., 2012).

In recent years, the transport of NPs in natural systems, especially the interaction between NPs and clay particles has attracted much attention (Afrooz et al., 2013; Huynh et al., 2012; Labille et al., 2015; Praetorius et al., 2014; Zhao et al., 2015). For example, Liang et al. (2013) studied the transport of Ag NPs and their interaction with clay particles in soils, and Cai et al. (2014) discussed the combined effects of IS and clay particles on the transport of TiO<sub>2</sub> NPs in quartz sand. These studies mainly focused on the effect of pH, IS and clay particles, but some studies show that NOM also plays an important role in the stability of NPs, such as stabilization due to the adsorption of NOM, or enhanced coagulation due to the bridging effect of NOM (Chen and Elimelech, 2007a; Mohd Omar et al., 2014; Zhu et al., 2014). Furthermore, montmorillonite was shown to destabilize engineered NPs due to heteroaggregation (Zhou et al., 2012). Since kaolin is a widely available clay, its role in heteroaggregation should be studied.

The goal of this study was to evaluate the effects of kaolin particles and of NOM on the heteroaggregation of engineered nanoparticles in aqueous environments. In this study, the stability of NPs, NPs-kaolin, NPs-HA, and NPs-kaolin-HA systems were evaluated under different pH and IS conditions. CCC and aggregation rate were used to determine the stability of the NPs via DLS measurements.

## 2. Methods and materials

### 2.1. TiO<sub>2</sub> nanoparticles

TiO<sub>2</sub> Nanoparticles (rutile) were purchased from Sigma–Aldrich Trading Co., Ltd. (Shanghai), product number 53680-10G. According to the manufacturer, the transmission electron microscopy (TEM) size of the nanoparticles is 10 nm × 40 nm (diameter × length); their specific surface area is around 130–190 m<sup>2</sup>/g; their purity is around 99.5%. We used SEM and TEM images to characterize the size and shape of these nanoparticles (Fig. S1), and measured their  $\text{pH}_{\text{pzc}}$  with a Malvern Zetasizer (Fig. S2,  $\text{pH}_{\text{pzc}} \approx 6$ ). An appropriate amount of TiO<sub>2</sub> NPs was placed in Millipore water and sonicated for 20 min (Qi et al., 2013) to achieve

a 1 g/L TiO<sub>2</sub> NP stock suspension. Fresh stock suspensions were prepared daily.

### 2.2. Ag nanoparticles

A nanosilver dispersion (25 ml) was purchased from Sigma–Aldrich Trading Co., Ltd. (Shanghai), product number 730807. The diameter of these nanoparticles is around 40 nm (Fig. S4). These particles contain sodium citrate as stabilizer, thus they carry a negative charge at pH 4 and 8. The concentration of the suspension is 20 mg/L. For the experiments the suspension was diluted to 2 mg/L; this was the minimum concentration at which nanoparticles could be detected reliably via Dynamic Light Scattering (DLS).

### 2.3. Kaolin

Kaolin (K7375) was purchased from Sigma–Aldrich Trading Co., Ltd. (Shanghai). To produce an aqueous slurry, 200 g kaolin and 0.3 g Na<sub>2</sub>CO<sub>3</sub> were added to 100 ml Millipore water. To remove and replace the Ca<sup>2+</sup> contained in the kaolin with Na<sup>+</sup> so as to meet the requirement of the DLVO calculation (Zhou et al., 2012), the slurry was heated in a water bath at about 80 °C for 2 days then diluted using Millipore water to achieve a nominal concentration of 4 g clay in a 100 ml suspension, following Tombacz and Szekeres (2006). To obtain a fraction smaller than 2 μm, the larger particles were allowed to settle and then the supernatant was separated by decanting. Excess carbonate was eliminated by HCl addition. To obtain monocationic Na-kaolin, the suspension was treated with 1 M NaCl. After centrifuging the suspension at 3600 revolutions per minute (RPM), the supernatant was discarded and replaced with fresh solution (0.01 M NaCl). The procedure was repeated three times. The IS of the suspension was progressively lowered, first by washing with Millipore water and then by dialysis against 0.01 M NaCl. An MWCO 12–14K membrane (Spectrumlabs, USA) was used to dialyze the suspension. The progress of dialysis was controlled by measuring the conductivities of inner and outer phases daily. This procedure was repeated five times. The Na-kaolin suspension ( $\approx 200$  g/L) in the dialysis tubes reached an equilibrium state within 4 days (Tombacz and Szekeres, 2006). The stock Na-kaolin suspensions were stored at 4–5 °C. Before DLS measurements, the stock suspension was diluted using Millipore water to 3 g/L and then centrifuged at 4000 RPM for 3 min. DLS measurements were conducted on the supernatant. The Z-average size of the kaolin particles was around 263 nm, and the TEM images show that the size range of Kaolin can be as great as 500 nm (Fig. S3). As Fig. S5 shows, the kaolin crystal consists of alternating layers of silica tetrahedra and alumina octahedra and the unit cell of the kaolin lattice has the composition [Si<sub>2</sub>Al<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]. Each kaolin particle consists of a stack of about 50 sheets of twin-layers, held together with hydrogen bonds. The particles are plate-like and the aspect ratio (particle diameter: particle thickness) is about 5–15, depending on the mechanical treatment of kaolin (Nandi et al., 2009; Solomon and Hawthorne, 1983).

### 2.4. Humic acid preparation

Humic acid (53680-10G) was purchased from Sigma–Aldrich (Shanghai) Trading Co., Ltd. The HA stock solution was prepared by dissolving a certain amount of HA powder into deionized water, and adjusting the pH to 11 by adding 0.1 M NaOH, then stirring the solution at 600 RPM for 24 h to improve the solution stability. A 0.25 μm filter membrane was used to remove the insoluble fraction. The stock solution was preserved under 5 °C. The Total Organic Carbon (TOC) of the HA stock solution was measured using a

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