



# Coagulation of TiO<sub>2</sub> nanoparticles-natural organic matter composite contaminants in various aquatic media: Fluorescence characteristics, flocs properties and membrane fouling abilities

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## ABSTRACT

The presence of TiO<sub>2</sub> nanoparticles (NPs) influences the efficiency of water and wastewater treatment because of the composite contaminants formed due to the interaction between TiO<sub>2</sub> NPs and Natural Organic Matter (NOM). In this study, the coagulation of TiO<sub>2</sub> NPs and NOM composite contaminants (TiO<sub>2</sub> NPs-NOM) was explored by comparing their fluorescence characteristics, flocs properties, and membrane fouling abilities in different aquatic media (i.e., humic acid synthetic water: WATER<sub>HA</sub>, surface water: WATER<sub>XQ</sub>; and municipal wastewater: WATER<sub>MW</sub>). Results showed that the TiO<sub>2</sub> NPs-NOM removal efficiency depended on the characteristics of NOM in various aquatic media. TiO<sub>2</sub> NPs improved the removal efficiency for fluorescent substances from WATER<sub>HA</sub> and WATER<sub>XQ</sub> when the solution pH was 5. However, this removal efficiency declined as the pH was increased to 9. In comparison, the removal efficiency for fluorescent substances from WATER<sub>MW</sub> increased as the TiO<sub>2</sub> NPs concentration was increased to 5 mg/L, and then decreased gradually as the TiO<sub>2</sub> concentration was increased to 20 mg/L. This is due to the competing adsorption and precipitation reactions between aromatic proteins and NPs. The different TiO<sub>2</sub> NPs-NOM in the tested water showed different flocs structures. The fractal dimensions of the flocs in WATER<sub>HA</sub> decreased with increasing TiO<sub>2</sub> NPs concentration until it exceeded 10 mg/L, while the fractal dimensions of WATER<sub>MW</sub> flocs increased with increasing TiO<sub>2</sub> NPs concentration. This was due to the formation of more loose flocs in the presence of aromatic proteins and soluble microbial byproducts. Total membrane resistance showed little change with increasing TiO<sub>2</sub> NPs concentration in the coagulation-ultrafiltration membrane process. The percentages of strongly attached external fouling resistance (Ref-s) and internal fouling resistance (R<sub>if</sub>) increased with increasing TiO<sub>2</sub> NPs concentration.

## 1. Introduction

Since TiO<sub>2</sub> nanoparticles (NPs) are extensively used in a variety of applications, they are inevitably released into aqueous environments and pose potential risk to human health and ecosystems [1]. TiO<sub>2</sub> NPs could penetrate cell membranes, and cause cell injury by damaging DNA, proteins, and membranes [2,3]. After exposure of animals to TiO<sub>2</sub> NPs, the NPs were demonstrated to accumulate in a wide range of organs, and to induce hepatic injury, myocardial damage, renal fibrosis, dysfunction of reproductive systems, and inflammatory response in both the lungs and the brain [4].

To control the health and ecological risks from NPs, many treatment

technologies, such as coagulation, adsorption, and membrane filtration, have been explored to remove them from aqueous environments [5–7]. Coagulation is considered a good option for removing nanoparticles from water or wastewater because of its low cost and wide applicability. Chen et al. reported that alum coagulation could remove 80% of the total mass of commercial nanoparticles, including TiO<sub>2</sub> NPs [8]. Qi et al. found that TiO<sub>2</sub> NPs could be aggregated and separated from water through hydrolysis and polymerization with polyferric sulfate (PFS) and FeCl<sub>3</sub> [9]. In addition, application of ultrafiltration (UF) after coagulation (coagulation-UF process) would achieve greater removal of NPs than either coagulation or ultrafiltration [10]. Our previous studies reported almost complete capture of nanoparticles by the coagulation-

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UF process, wherein a combination of two coagulants (polyaluminum chloride (PAC) and sodium alginate) was used [11].

As TiO<sub>2</sub> NPs enter aqueous environments, Natural Organic Matter (NOM) can interact with them and form TiO<sub>2</sub> NPs and NOM composite contaminants (TiO<sub>2</sub> NPs - NOM) due to the electrostatic attractive and repulsive interactions, along with steric and van der Waals interactions [12]. These interactions would significantly change the fate and transport of TiO<sub>2</sub> NPs [13,14]. NOM is a complex mixture of organic components, such as humic and fulvic acids, low molecular weight acids, proteins and amino acids, and carbohydrates. Previous studies indicated that the physicochemical properties of NOM, such as molecular weight distribution and hydrophobic or hydrophilic property, significantly affect its interaction with NPs [15]. Due to the steric hindrance effect, the influence of macromolecular NOM on nanoparticles is much larger than that of low molecular weight NOM [16]. Highly hydrophobic humic acid was much easier to transfer from water to the surface of TiO<sub>2</sub> NPs, than was hydrophilic fulvic acid [17].

The different organic components in various aquatic media would be expected to form TiO<sub>2</sub> NPs-NOM with different properties, which would inevitably influence the removal of NPs from water or wastewater. Sun et al. used four regular coagulants (aluminum sulfate, ferric chloride, PFS, and PAC) to remove NPs from synthetic/natural water samples and achieved high removal rates. However, when PAC and PFS were used as coagulants, the removal of NPs was greatly reduced due to increase in NOM concentration (humic acid) [18]. In contrast, Chang et al. observed low nanoparticle removal from high-technology manufacturing-hub wastewater by PAC [19]. To achieve better control over the release of nanoparticles to the environment, it is necessary to study NP removal behavior in coagulation or coagulation-UF processes in waters of different quality.

The objectives of this study were: (1) to explore the capture of TiO<sub>2</sub> NPs-NOM by polyaluminum chloride (PAC) in different aquatic media; (2) to characterize the effect of TiO<sub>2</sub> NPs on the flocs properties of different NOM species; and (3) to evaluate the impact of TiO<sub>2</sub> NPs on membrane fouling during the coagulation-UF process.

## 2. Materials and methods

### 2.1. Water samples

Three types of water samples, including HA synthetic water (WATER<sub>HA</sub>), surface water (WATER<sub>XQ</sub>), municipal wastewater (WATER<sub>MW</sub>), were used to investigate the effect of TiO<sub>2</sub> NPs on the removal and aggregation of NOM. The TiO<sub>2</sub> NPs were in the form of hydrophilic nano TiO<sub>2</sub> powder (rutile), purchased from Aladdin Co. (China). According to the manufacturer, it was composed of 99.8% TiO<sub>2</sub>, with an average particle size of 40 nm, a specific surface area of 50 m<sup>2</sup>/L, and a density of 5.6 g/cm<sup>3</sup>.

WATER<sub>HA</sub> was prepared by dispersing TiO<sub>2</sub> NP powder in 1 L of tap water in an ultrasonic bath (BaoDexing Ultrasonic Co., Ltd.) for two cycles of ultrasonication (60 min). During the two ultrasonication intervals, humic acid (10 mg) was added and mixed using a magnetic stirrer for 15 min. WATER<sub>XQ</sub> was prepared by dispersing TiO<sub>2</sub> NP powder into 1 L Xiaoqing River water, which was passed through a 0.45 μm filter membrane before being placed in an ultrasonic bath (BaoDexing Ultrasonic Co., Ltd.) for 60 min. The Xiaoqing River is an urban stream in Jinan (China) that receives some effluent from municipal wastewater treatment plants (MWTPs). WATER<sub>MW</sub> was prepared from the secondary effluent of the Jinan MWTP by the same method as for WATER<sub>XQ</sub>. The characterizations of WATER<sub>HA</sub>, WATER<sub>XQ</sub>, and WATER<sub>MW</sub> are shown in Table 1.

### 2.2. Coagulation experiments

In this study, polyaluminum chloride (PAC) was chosen as the coagulant. It was prepared in our lab as follows: AlCl<sub>3</sub>·6H<sub>2</sub>O (8.942 g)

was dissolved in 100 mL distilled water and then mixed with 3.925 g Na<sub>2</sub>CO<sub>3</sub> powder to obtain the desired [OH<sup>-</sup>]/[Al] (B) value [11]. The target PAC had the following characteristics: C<sub>Al</sub> = 5.3 g L<sup>-1</sup>, B = 2.0, and pH = 3.56.

The coagulation test was conducted in 1.0 L Plexiglas beakers using a conventional ZR4-6 laboratory stirrer jar-test apparatus (Zhongrun Water Industry Technology Development Co., China). The TiO<sub>2</sub> NPs test water (500 mL) was coagulated with rapid-stirring at 200 rpm for 2 min, followed by slow-stirring at 40 rpm for 20 min, and then allowed to settle for 30 min. PAC was added during the rapid-stirring period. The optimal dosage of WATER<sub>HA</sub>, WATER<sub>XQ</sub>, and WATER<sub>MW</sub> was 12 mg/L, which was determined in preliminary experiments (Supplemental Fig. S1).

The coagulation dynamics was measured using a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) as the coagulation proceeded. Floc size and fractal dimension (D<sub>f</sub>) were calculated according to data from a Malvern Mastersizer 2000. The details about the calculation of floc size and D<sub>f</sub> can be found in the supporting information (S1) [20–22]. After settling, the supernatants were collected to determine the residual concentration of TiO<sub>2</sub> NPs and dissolved organic carbon (DOC). The DOC was tested using a TOC analyzer (TOC-VCPH, Shimadzu Co., Ltd.). The concentration of TiO<sub>2</sub> NPs was replaced by the total concentration of Ti, which was determined using an ICP mass spectrometer (IRIS INTREPID IIXSP, Thermo Electrom, USA).

### 2.3. Organic components of NOM

Excitation-emission matrix (EEM) fluorescence spectra of NOM were used to analyze the organic components of the water samples via luminescence spectrometry (F-7000 FL spectrophotometer, Hitachi, Japan). According to the emission spectra and excitation wavelength, the excitation-emission matrix (EEM) spectra could be divided into five regions: aromatic protein I, aromatic protein II, fulvic-acid-like, soluble microbial-byproduct-like, and humic-acid-like substances (Supplemental Fig. S2) [23]. The normalized excitation-emission area volumes of the various EEM regions, which represented the content of fluorescent substances, were quantified using equation (1) according to the method reported by Li et al. [24].

$$\Phi_{i,n} = MF_i \sum_{ex} \sum_{em} I(\lambda_{ex}, \lambda_{em}) \Delta\lambda_{ex} \Delta\lambda_{em} \quad (1)$$

where MF<sub>i</sub> is a factor for region i, equal to the inverse of the fractional projected excitation-emission area, Δλ<sub>ex</sub> is the excitation wavelength interval (taken as 5 nm), Δλ<sub>em</sub> is the emission wavelength interval (taken as 5 nm), and I(λ<sub>ex</sub>, λ<sub>em</sub>) is the fluorescence intensity for each excitation-emission wavelength pair.

### 2.4. Ultrafiltration fouling analysis

After coagulation, the coagulated water with flocs was transferred into a 0.3 L cylindrical filtration cell and passed through an ultrafiltration membrane under constant pressure (0.08 MPa). A dead-end batch ultrafiltration unit, and ultrafiltration membranes (Mosu, China) with molecular weight cutoff (MWCO) of 100 kDa, was used in this study. The membrane was modified by regenerated cellulose with an effective membrane area of 50.24 cm<sup>2</sup>. A fresh piece of membrane was used in each experiment.

Membrane fouling was determined by calculating fouling resistance from the flux variation during the filtration process [25]. The fouling resistance included both external and internal fouling resistance. The external fouling resistance (R<sub>ef</sub>) was divided into the loosely attached external fouling resistance (R<sub>ef-1</sub>) and the strongly attached external fouling resistance (R<sub>ef-s</sub>). The internal fouling resistance was divided into the reversible internal fouling resistance (R<sub>if-r</sub>) and the irreversible internal fouling resistance (R<sub>if-ir</sub>). Details about the ultrafiltration fouling analysis can be found in the supporting information (S2).

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