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Facilitated bioaccumulation of perfluorooctanesulfonate in zebrafish by nano-TiO_2 in two crystalline phases

Liwen Qiang [a], Xiaomei Shi [a], Xiaoyu Pan [b], Lingyan Zhu [a, *], Meng Chen [a], Yuwei Han [a]

[a] College of Environmental Science and Engineering, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Key Laboratory of Pollution Processes and Environmental Criteria, Ministry of Education, Nankai University, Tianjin, 300071, PR China
[b] College of Marine Science of Engineering, Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin, 300457, PR China

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ABSTRACT

Zebrafish were placed in the upper layer of aquariums to investigate the impacts of anatase and rutile nano-TiO_2 on perfluorooctanesulfonate (PFOS) bioaccumulation in zebrafish. Both variations of particle hydrodynamic size and concentration in water column suggest that anatase was better dispersed than rutile. PFOS could be significantly adsorbed on nano-TiO_2 to form TiO_2-PFOS complexes, leading to reduced concentration of PFOS in upper layer. Due to enhanced exposure to PFOS by ingestion and adhesion of TiO_2-PFOS complexes, the whole-body PFOS concentration in zebrafish was enhanced by 59.0% (95% CI: 55.9%, 61.9%) and 25.4% (95% CI: 24.8%, 25.6%) in the presence of anatase and rutile nano-TiO_2 after equilibrium compared with the control with PFOS alone. The bioaccumulation of PFOS was much more promoted by anatase, which was attributed by greater adsorption capacity of PFOS to anatase, slower migration of their complex in water column, and slower elimination rate of anatase from fish.

1. Introduction

Applications of titanium dioxide (TiO_2) are numerous and well-documented, including photo-catalysis, dye-sensitized solar cells, pigments, optical coatings, and gas sensing (Domingos et al., 2009). Given the small size, high mobility, and high reactivity of the nano-TiO_2 and its potential to be released to the natural environment, the environmental fate and safety has been receiving increasing attention (Menard et al., 2011; Tedja et al., 2012). Many studies suggested that nano-TiO_2 could pose adverse effects to aquatic organisms including microbes, algae, invertebrates, and fish (Chen et al., 2012). Moreover, the nano-TiO_2 particles could also affect the bioavailability of some toxic pollutants such as heavy metals and organic chemicals (Hu et al., 2011). Due to the high surface area and surface functional groups of nano-TiO_2, ubiquitous pollutants in the aquatic environment could be adsorbed on the surface of nano-TiO_2 through physical or chemical interactions (Pettibone et al., 2008; Tan et al., 2011). This will finally affect the behaviors, such as transport, bioaccumulation, toxicities, and fate of the pollutants in the aquatic environment. Several studies demonstrated that nano-TiO_2 could enhance the toxicities of heavy metals (Fan et al., 2011; Tan et al., 2011; Yang et al., 2014; Zhang et al., 2007) (such as Cd, Cu, Zn) and organic pollutants (Zheng et al., 2012; Zhu et al., 2011) (tributyltin, bisphenol A) in organisms.

It was reported the toxicity of nanometric TiO_2 particles is correlated to the crystalline structure, morphology, suspension state and other factors (Clement et al., 2013). Rutile and anatase are the two major allotropic forms of TiO_2 (Menard et al., 2011), which display quite different physicochemical properties (Grinter et al., 2012). Some studies investigated the effects of the crystalline structure on the toxicities of nano-TiO_2 (Federici et al., 2007; Warheit et al., 2007). The anatase was reported to be more active than rutile to generate reactive species (Warheit et al., 2007), which could induce DNA damage, lipid peroxidation, and micronuclei formation (Federici et al., 2007). As a result, anatase displayed a greater toxic effect than rutile. However, these toxicity studies on nano-TiO_2 did not consider the aggregation and precipitation behaviors of nano-TiO_2 in different crystal phases. Sparse information is available on the impact of the aggregation and deposition of nano-TiO_2 in different crystal phases to contaminants present in aquatic environment. In the present work, we hypothesize that the nanoparticle crystal phase (anatase or rutile) will affect the

* Corresponding author.
E-mail address: zhuly@nankai.edu.cn (L. Zhu).

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environmental behavior of pollutants in different ways due to different sorption and aggregation behavior.

Perfluoroalkyl acids are a group of chemicals that have been used in various industrial and household commercial products (Asher et al., 2012). Among them, perfluorooctanesulfonate (PFOS) is one of the most detected in different environmental matrices and humans (Martin et al., 2003; Zhang et al., 2013). It is associated with adverse effects to wildlife and humans (Zhang et al., 2013), and was listed as a new member of persistent organic pollutants (POPs) (Asher et al., 2012; Martin et al., 2004). Although PFOS is more soluble in water than typical hydrophobic pollutants, many studies demonstrated that it could be significantly accumulated and biomagnified in aquatic organisms (Fang et al., 2014). Since PFOS has a hydrophobic fluorinated carbon chain and a sulfonate group, it can be adsorbed on the surface of adsorbents by various interactions, such as electrostatic interaction, hydrogen bonding, hydrophobic interaction, and ligand exchange (the sulfonate groups of PFOS molecules could act as the paired groups for functionalities on adsorbents) (Deng et al., 2012; Du et al., 2014; Yan et al., 2014). Theoretical calculation studies on the interactions between PFOS and nano-TiO_2 indicated that PFOS could be adsorbed on both anatase and rutile nano-TiO_2 (He et al., 2013; Xue et al., 2013), implying TiO_2-PFOS complexes could be formed in water medium. Thus, the accumulation behavior of PFOS could be affected by nano-TiO_2 released in the aquatic system.

The present study aimed to investigate: 1) the agglomeration and deposition of anatase and rutile nano-TiO_2 in water; 2) the adsorption and desorption of PFOS on anatase and rutile nano-TiO_2; 3) the impacts of aggregation and deposition of anatase and rutile nano-TiO_2 on the accumulation of PFOS in zebrafish. The results are beneficial to understand the impacts of engineered nano-TiO_2 particles with different crystal structures on the environmental behaviors of organic chemicals in natural aquatic environment.

2. Materials and methods

2.1. Chemicals and reagents

The main chemicals and reagents used in the experiment are listed in Supporting Information (SI). Detailed information about chemicals and reagents can be found in SI.

2.2. Characterization of TiO_2 nanoparticles

The morphologies and microstructures of the anatase and rutile powder were characterized. The aggregation behavior was investigated by measuring the particle size distribution using dynamic light scattering (DLS), and the deposition behavior was examined by determining the concentrations of anatase and rutile in water column. These details are provided in SI.

2.3. Sorption and desorption experiments

PFOS adsorption. All PFOS sorption isotherms were obtained using batch experiments in 50 mL vials at 25 °C and pH 6.6 ± 0.3. The PFOS stock solution was diluted sequentially to a series of solutions with the concentration varying over five orders of magnitude. Forty mL of PFOS solution was added in a polypropylene (PP) centrifuge tube (50 mL, CNW, China) which contained 0.02 mg of nano-TiO_2 (anatase or rutile). The PP centrifuge tubes were sealed and shaken at 25 °C on a temperature-controlled shaker (IncuShaker, Crystal Technology & Industries, Inc. USA) at 200 rpm for 3 d to reach apparent equilibrium (a preliminary experiment suggested that 3 d was enough for adsorption equilibrium). The PP centrifuge tubes were centrifuged at 3512 g for 30 min. One mL of the supernatant was used for measuring PFOS concentration via an ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS). The supernatant was filtered through a 0.22-μm Teflon membrane (Agela Technologies, China) and collected in an auto sampler vial with internal standard mass labeled MPFOS. The Teflon membrane could separate dissolved PFOS and particles effectively. Parallel control experiments without addition of nano-TiO_2 were also performed to assess the loss of PFOS due to the adsorption on the wall of PP tubes. The results indicated that the loss was less than 3.0% of the initial mass (Su et al., 2013).

PFOS desorption. Desorption of higher concentration PFOS from nano-TiO_2 was conducted by successively replacing (75.0 ± 1.0) % of the supernatant with water or simulated intestinal fluids (SIF) at 37 °C. The tubes were resealed and placed on the shaker for another 3 d to reach desorption equilibrium. After centrifugation at 3512 g for 30 min, one mL of the supernatant was used for PFOS determination, and water (or SIF) was added to initiate the next desorption step. All the adsorption and desorption experiments were repeated twice, and all desorption steps were conducted at 37 °C.

2.4. Accumulation of PFOS in zebrafish

Exposure tests were conducted in a series of self-made glass aquariums of 12 L. The aquariums were separated by nylon sieve (mesh size of the nylon net was 1.40 mm) as upper (water depth was 10 cm) and bottom layers (water depth was 20 cm). Zebrafish was obtained from local fish market and were acclimated in aerated and dechlorinated tap water (pH 7.1–7.5) at 25 ± 1 °C (14:10 h light/dark photoperiod) for at least one month and were fed with fish feed twice a day. After acclimatization, the zebrafish were put in the upper layer of the aquariums which was 20 cm high from the bottom. The fish were acclimatized for another week in the aquariums before exposure.

A certain amount of PFOS stock solution and nano-TiO_2 powder (anatase/rutile) were added in the aquariums with 9 L water and dispersed with ultrasonication (KQ-500DA, Kunshan Ultrasonic Instruments Co., Ltd, China) and mechanical stirring (constant speed electric mixer, HD2004W, Shanghai Sile Instruments Co., Ltd, China) for 30 min. The aquariums were lightly aerated (Oxygen aeration pump ACO-002, 35 W, 40 L/min) throughout the experiment. The pH of the water was 7.3 ± 0.2. The temperature was maintained at 25 ± 1 °C, dissolved oxygen was 7.8 ± 0.3 mg/L and turbidity was 0.35 ± 0.06 NTU. Each aquarium contained five zebrafish. The nominal PFOS concentration in all test groups was 600 ng/L, except for the control group in which TiO_2 and PFOS were not added. The concentration of PFOS and nano-TiO_2 were set to be as close as possible to potential environmental levels near source area (Kaegi et al., 2008; Pan and You, 2010), while allowing for detectable levels in the fish tissues. Four exposure groups were designed: (1) Control group (no PFOS or nano-TiO_2); (2) P group (PFOS only without TiO_2); (3) AT-P group (PFOS and 0.5 mg/L anatase nano-TiO_2); (4) RT-P group (PFOS and 0.5 mg/L rutile nano-TiO_2). The tests lasted 58 d during which the exposure solution was completely renewed every two days (48 h). To eliminate the influence of the fish feed, fish were fed with fish feed in clean water when solution was renewed every other day. At each sampling time, one aquarium of each group was sacrificed and four fish were sampled on 0, 1, 2, 6, 12, 18, 24, 32, 40, 48 and 58 d. There were 12 aquariums for each group (11 aquariums were for sampling, the other one was for tissue analysis and backup in case of fish death). Twenty five mL of water was sampled at upper layer at each sampling time. Two of the fish were used for PFOS analysis and the other two were used for TiO_2 analysis. The fish were euthanized by given over dose of