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Characterization of titanium dioxide nanoparticle removal in simulated drinking water treatment processes

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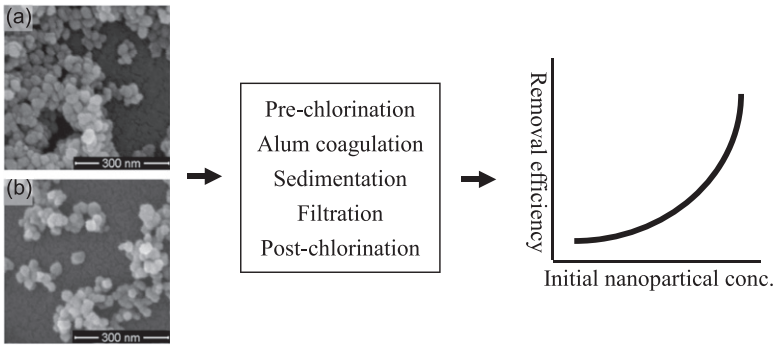
HIGHLIGHTS

- Fates of nano-TiO_2 particles in conventional water treatments were assessed.
- Treatment efficiency was characterized at different nano-TiO_2 concentrations.
- SEM showed that the nano-particles were covered by foreign substances after coagulation.
- Sedimentation and filtration were the most important processes for removal of nano-TiO_2.
- Removal efficiencies were higher for the groups of nano-TiO_2 with higher concentrations.

GRAPHICAL ABSTRACT



Treatment efficiencies of nano-TiO_2 in powder (a) and suspension (b) forms after conventional water treatments.

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ABSTRACT

This study characterized the fate of nano-TiO_2 in both powder (TiO_2(P)) and suspension (TiO_2(S)) forms in simulated drinking water treatments. Nano-TiO_2 solutions of 0.1, 1.0, and 10 mg/L were prepared with deionized water and raw waters from the Changxing and Fengshan Water Treatment Plants in Taiwan to assess the effects of water matrices on nano-TiO_2 behavior during water treatment. After the laboratory simulated water treatment, including pre-chlorination, coagulation, sedimentation, filtration and post-chlorination, the residual Ti concentration ranged from 2.7 to 47.4% in different treatment units and overall removal efficiency was between 52.6% and 97.3% in all cases except for nano-TiO_2 at concentration of 0.1 mg/L. Overall removal efficiency for the TiO_2 at 10 mg/L concentration ranged from 9.3 to 53.5%. Sedimentation (after coagulation) and filtration were the most important processes for removing nano-TiO_2 due in part to particle agglomeration, which was confirmed by size distribution and zeta potential measurements. The size of nano-TiO_2 increased from 21–36 nm to 4490 nm in the supernatant after sedimentation, and subsequent filtration treatment further removed all agglomerates at size >1 μm. Zeta potential revealed interactions between nano-TiO_2 particles and anionic functional groups or negatively-charged natural organic matters, leading to a decrease in surface charge. After sedimentation and filtration, the zeta potential of supernatants and filtrates were close to zero, meaning the absence of nanoparticles. The highest Ti removal after sedimentation occurred in Fengshan raw water due to higher ionic strength and coagulant dosage applied. On the other hand, the surfactant additives in TiO_2(S) promoted dispersion of nano-TiO_2

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particles, which in turn led to lower particle removal. SEM images of nanoparticles after chlorination or coagulation revealed the coverage of nano-TiO_2 particles by viscous substances and formation of colloidal structures.

1. Introduction

Over the past decade, the increasing environmental presence of emerging contaminants, including engineered nanoparticles especially metal oxide nanoparticles, has received global attention (Colvin, 2003; Maynard et al., 2006; NNI, 2008; Naidu et al., 2016). Metal oxide nanoparticles are widely used for a variety of applications, including catalysis, sensors, environmental remediation, and commercial products. There are many potential applications in water treatment processes, such as controlling toxic metals (Simeonidis et al., 2015), as catalytic media for the photolysis of organic pollutants (Alvarez et al., 2016), and as water disinfection agents (Hossain et al., 2014). An estimated 7800–38,000 tons of titanium dioxide nanoparticles (nano-TiO_2) are produced every year in the US (Hendren et al., 2011). Nano-TiO_2 has been found in the natural environment in larger quantities than ZnO, Ag, carbon nanotubes, and fullerenes (Gottschalk et al., 2009).

Nano-TiO_2 is the most commonly used as an ultraviolet (UV)-absorber in sunscreens and within photocatalytic coatings (USEPA, 2010). Results of dermal exposure studies have consistently found evidence that nano-TiO_2 does not penetrate life skin nor cross the skin barrier (Schulz et al., 2002; Mavon et al., 2007; Wu et al., 2009; Jonaitis et al., 2010). In contrast, inhaled nano-TiO_2 may cross the air-blood barrier and be distributed all over the body via the blood stream (Geiser et al., 2005; Kapp et al., 2004). Nano-TiO_2 may also induce a much greater pulmonary-inflammatory neutrophil response in rats and mice (Oberdörster, 2000, 2001). Furthermore, uncoated nano-TiO_2 exposed to solar-simulated UV radiation may generate reactive oxygen species that induce in vitro photo-cytotoxic effects (Spielmann et al., 1998; Spielmann et al., 2008). DNA and cell assays have also confirmed that nano-TiO_2 augments the UV-induced damage of DNA and cells (Oberdorster et al., 2005; Hidaka et al., 2006; Rampaul et al., 2007).

Several transport modeling studies have indicated that, once in the environment, nano-TiO_2 had the highest expected environmental concentrations in water, soil, and sediments relative to other nanoparticles (Gottschalk et al., 2009, 2011; Mueller and Nowack, 2008). Rivers and wastewater treatment plants are reservoirs most likely to receive these substances due to the use of sunscreen and cosmetic products. If the nanoparticles in wastewater are directly discharged into rivers or pass through wastewater treatment processes, they may potentially affect human health through tap water consumption. Various carbon-based nanomaterial, zero-valent iron nanoparticles and have been shown effective for treatments of groundwater contaminants including nitrate, chlorinated organic solvents and some persistent organic pollutants (Zhang and Elliott, 2006; Rajan, 2011; Matlochová et al., 2013). After their applications, nanomaterial and nanoparticles can then be released into surface and groundwater environments either accidently or intentionally (Baumann, 2010). However, the fate of nano-TiO_2 in environment media and water treatment processes has not been fully investigated.

Kim et al. (2012) found nano-TiO_2 as well as larger particles in sewage sludge samples. These faceted TiO_2 particles were in rutile form and were clustered as small, loosely-packed aggregates with sizes ranging from 40 to 300 nm. Kaegi et al. (2008) reported that nano-TiO_2 (20–300 nm) from industrial building facades were released into surface runoff waters, and showed an estimated TiO_2 particle concentration of 3.5×10^7 particles/L for particles smaller than 100 nm in diameter, and Ti concentrations of 16 μg/L in the runoff waters. Kiser et al. (2009) demonstrated the occurrence, characterization, and removal of nano- and larger-sized Ti in wastewater treatment plants (WWTPs). Influent Ti concentrations in the WWTPs ranged from 181 to 1233 μg/L (Nowack and Bucheli, 2007). The majority of Ti particles were larger than 0.7 μm, of which 95% were removed through water treatment steps. Although most of the Ti was sorbed to biomass, the Ti levels in the effluents remained between 10 and 100 μg/L. Johnson et al. (2011) reported a decrease in mean Ti concentration from 30 to 3.2 μg/L between influent and effluent streams for particles smaller than 0.45 μm, which corresponds to a removal efficiency of approximately 90%. Here, the activated sludge process accounted for the greatest decline in mean Ti concentration. In addition, the Ti-containing particles evaluated by these investigators were not in the nanometer size range and not specified as TiO_2 particles.

Zhang et al. (2008) performed a simulated jar test for nano-TiO_2 added to de-ionized (DI) water and tap water. The authors found that coagulation followed by sedimentation removed 20–60% of the total TiO_2 mass, and subsequent filtration with a 0.45 μm filter removed >90% of the total TiO_2 mass. However, this study characterized nano-TiO_2 in jar tests and used much higher doses (10 mg/L or higher) than the typical concentrations found in aquatic environments. Moreover, variations in nanoparticle morphology and characteristics were not discussed. Ma et al. (2016) stated that conventional treatments may be inadequate in effectively removing engineered nanoparticles from aquatic environments. Troester et al. (2016) assessed the vulnerability of drinking water supplies to engineered nanoparticles, concluding that the potential risk caused by engineered nanoparticles in surface water resources is limited. However, conventional treatment plants without suitable flocculation units may be ineffective against raw water contaminated by engineered nanoparticles.

The objective of this study was to determine the fate of commercial nano-TiO_2, in both powder (TiO_2(P)) and suspension (TiO_2(S)) forms, after simulated drinking water treatments. We prepared nano-TiO_2 solutions at concentration of 0.1, 1.0, and 10 mg/L in deionized (DI) water along with raw water from the Changxing and Fengshan water treatment plants (WTPs) in Taiwan to assess the effects of water matrix on the fate of nano-TiO_2. Disinfection, coagulation, flocculation, sedimentation, and filtration processes were performed to elucidate the fate of nano-TiO_2 during conventional drinking water treatment processes. In addition, we determined the characteristics of nano-TiO_2 using traditional water quality parameters, Ti concentrations, and nanoparticle characteristics, including crystal structures, size distributions, zeta potentials, and scanning electron microscope (SEM) images.

2. Materials and methods

2.1. Water matrices

In order to determine the impact of raw water quality on characteristics of nanoparticles in water treatment processes, we collected raw waters (RWs) from the Changxing and Fengshan WTPs in Taiwan. We selected Changxing RW to represent good quality source water with low levels of pollution. For comparison, Fengshan RW, which has been impacted by industrial wastewater, animal husbandry wastewater, domestic sewage, and eutrophication (TWEPA, 2011), was selected to represent source water with poor water quality. After sampling, water samples were prefiltered by a 5-μm glass fiber filter (ADVANTEC). Table 1 summarizes measured water quality parameters. Detail description of the two WTPs selected was provided in Supplemental information (SI).