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# Fate of fluorescent core-shell silica nanoparticles during simulated secondary wastewater treatment



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## ABSTRACT

Increasing use of silica nanoparticles (SiO<sub>2</sub> NPs) in consumer products and industrial processes leads to SiO<sub>2</sub> NP discharge into wastewater. Thus, there is a need to understand the fate of SiO<sub>2</sub> NPs during wastewater treatment. However, the detection of SiO<sub>2</sub> NPs in environmental systems is hindered by the elevated background levels of natural silicon. In this work, laboratory-synthesized fluorescent core-shell SiO<sub>2</sub> NPs were used to study the fate of these NPs during secondary wastewater treatment. Fluorescent measurements provided an easy and fast method for SiO<sub>2</sub> NP tracking. A laboratory-scale activated sludge system consisting of an aeration tank and a settler was fed with synthetic wastewater containing ca. 7.5 mg L<sup>-1</sup> of fluorescent SiO<sub>2</sub> NPs for 30 days. SiO<sub>2</sub> NPs were effectively removed from the wastewater (>96%) during the first 6 days, however the concentration of SiO<sub>2</sub> NPs in the effluent gradually increased afterwards and the NP discharge was as high as 65% of the input after 30 days of NP dosing. The poor removal of the SiO<sub>2</sub> NPs was related to the high colloidal stability of the NPs in the wastewater and their limited propensity to biosorption. Although some degree of NP adsorption on the biomass was observed using fluorescence microscopy, the affinity of SiO<sub>2</sub> NPs for the activated sludge was not enough for a sustained and effective removal of the SiO<sub>2</sub> NPs from the wastewater.

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## 1. Introduction

The increased use of engineered nanomaterials in industrial applications and consumer products has raised concerns about their health and environmental safety. Nano-sized silica (SiO<sub>2</sub>) is among the most common nanomaterials used, with an estimated annual production worldwide exceeding

1.5 million metric tons (Holden et al., 2014). SiO<sub>2</sub> nanoparticles (NPs) are used in construction materials such as concrete and ceramics, in biomedical applications as drug and label carriers, or as filler materials in food packaging. SiO<sub>2</sub> NPs are also utilized in large quantities as abrasives in polishing slurries that are applied in chemical-mechanical planarization (CMP) processes during the manufacturing of semiconductor materials (Singh et al., 2002). CMP operations are a major source of

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wastewater in semiconductor manufacturing plants and it has been estimated that the SiO<sub>2</sub> NP concentration in CMP effluents may range from 1.3 to 8.5 g L<sup>-1</sup> (Liu et al., 2014). SiO<sub>2</sub> NPs have shown adverse effects in a number of *in vitro* and *in vivo* toxicity studies performed in mammal cells, mice and aquatic organisms (e.g. algae, mussels) (Canesi et al., 2010; Karlsson et al., 2014; Napierska et al., 2010; Van Hoecke et al., 2008). Consequently there is great interest to understand the fate and behavior of SiO<sub>2</sub> NPs from the source point to the environment.

Industrial and municipal wastewater discharges are considered primary sources of NPs to the environment (Boxall et al., 2007). However, there are not specific water regulations limiting the release of NPs to sewers or the environment. Although release of some NPs may be limited by regulations that control other water quality parameters (e.g. turbidity), it is unclear if those are enough to prevent potential risks associated with NPs. Likewise, the capacity of current wastewater treatment plants (WWTPs) to deal with NP contaminants is uncertain. Despite the high utilization of SiO<sub>2</sub> NPs, very little is known about the fate of these engineered NPs during municipal wastewater treatment. Only a few studies have addressed this question. For example, Jarvie et al. (2009) investigated the fate of SiO<sub>2</sub> NPs during simulated primary wastewater treatment, while other studies explored the interaction of SiO<sub>2</sub> NPs with heterotrophic biomass in short-term batch assays (Grass et al., 2014; Kiser et al., 2010; Rottman et al., 2012). These investigations provide valuable information about the interactions of SiO<sub>2</sub> NPs with wastewater and biosolids, however they are insufficient to predict the fate of SiO<sub>2</sub> NPs during biological wastewater treatment that involves long-term operation of continuous-flow bioreactor systems.

Research on the fate of SiO<sub>2</sub> NPs during wastewater treatment is complicated by interference of the background silicon (Si) with the measurements of SiO<sub>2</sub> NPs. Dissolved Si is present in natural water and wastewater at relatively high and quite variable concentrations. For example, the range of dissolved Si concentration in different natural waters measured in several countries ranged from 0.9 to 23 mg Si L<sup>-1</sup> (Georg et al., 2006; Jansen et al., 2010). These high background Si concentrations complicate the monitoring of SiO<sub>2</sub> NPs by means of elemental analysis. Thus, to avoid interferences with SiO<sub>2</sub> NP measurement we propose the use of fluorescent-labeled SiO<sub>2</sub> NPs. Fluorescent-doped NPs are commonly used in biomedical applications for imaging purpose (Senarath-Yapa et al., 2007) since these NPs provide an easy approach to follow the path of NPs into the cell. However, few studies have used fluorescent labeled NPs to monitor their fate in environmental systems. One exception is a recent study that effectively used three types of labeled SiO<sub>2</sub> NPs, including fluorescent-labeled NPs, to evaluate their transport in saturated sand (Vitorge et al., 2014).

The aim of this work was to investigate the fate of SiO<sub>2</sub> NPs during secondary wastewater treatment in a laboratory-scale activated sludge unit. Fluorescent core-shell SiO<sub>2</sub> NPs were synthesized and used in the study to facilitate the traceability of the NPs. These NPs contain a core of fluorescent dye covalently bound to SiO<sub>2</sub> and an outer shell of pure SiO<sub>2</sub>, so the

surface chemistry of the NPs is not modified by the organic functional groups of the dye.

## 2. Materials and methods

### 2.1. Synthesis of fluorescent core-shell SiO<sub>2</sub> NPs

Fluorescent core-shell SiO<sub>2</sub> (f-SiO<sub>2</sub>) NPs were synthesized using a reverse microemulsion method adapted from a previously described protocol (Jin et al., 2012; Senarath-Yapa et al., 2007). First, rhodamine B isothiocyanate (Rh-B ITC) was linked to (3-aminopropyl)triethoxysilane (APTES) by mixing 15 mg Rh-B ITC and 0.15 mL APTES in 7.5 mL of n-hexanol. The mixture was stirred for 12 h at room temperature (25 ± 1 °C). Next, 5.0 mL of the resulting Rh-B ITC/APTES conjugate was added to a microemulsion solution containing 75 mL of cyclohexane, 13 mL of n-hexanol, 17.7 mL of Triton X-100, and 5.46 mL of deionized (DI) water, and stirred for 15 min. Then, 0.9 mL of tetraethyl orthosilicate (TEOS) was added and stirred for another 30 min. Finally, 0.6 mL of NH<sub>4</sub>OH (28–30%) was added to initiate the hydrolysis of TEOS and Rh-B ITC/APTES. The reaction mixture was stirred for 12 h at room temperature followed by the addition of 80 mL of acetone to disrupt the inverse micelles. NPs were recovered by centrifugation (10,000 g for 10 min) and washed once with DI water. Then, NPs were suspended in 5.46 mL of DI water and sonicated to improve the dispersion of the particles. This NP suspension was subjected to a capping step where a shell of pure SiO<sub>2</sub> was added to the surface of the NPs. For that, the NP suspension was added to the microemulsion solution previously described, except for the DI water that now was added together with the particles. After stirring for 14 h, the capped f-SiO<sub>2</sub> NPs were separated and washed 3 times each with ethanol and DI water, as describe before. Finally, the NPs were resuspended in 6 mL of DI water and this suspension was utilized as stock dispersion in further experiments. A total of 4 batches of f-SiO<sub>2</sub> NPs were used during the study.

### 2.2. Size and surface characterization of f-SiO<sub>2</sub> NPs

Transmission electron microscopy (TEM) was used to analyze the morphology and primary particle size of f-SiO<sub>2</sub> NPs. TEM images were acquired on a Hitachi H-8100 TEM instrument (Hitachi, Tokyo, Japan) at 200 kV. NPs were suspended in isopropanol and sonicated in an ultrasonic bath for 5 min before analysis.

The hydrodynamic particle size distribution (PSD) of f-SiO<sub>2</sub> NP suspensions in DI water (100 mg L<sup>-1</sup>) and synthetic wastewater (7.5 mg L<sup>-1</sup>) was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments, Westborough, MA, US). The unit employs a 4 mW He-Ne laser with a wavelength of 633 nm, and a measurement angle of 173°.

The zeta potential ( $\zeta$ -potential) of f-SiO<sub>2</sub> NPs dispersions was measured with the same instrument using laser Doppler velocimetry and the Smoluchowski equation to correlate particle electrophoretic mobility to  $\zeta$ -potential. Additionally, the surface charge of f-SiO<sub>2</sub> NPs was characterized by

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