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Looking for engineered nanoparticles (ENPs) in wastewater treatment systems: Qualification and quantification aspects

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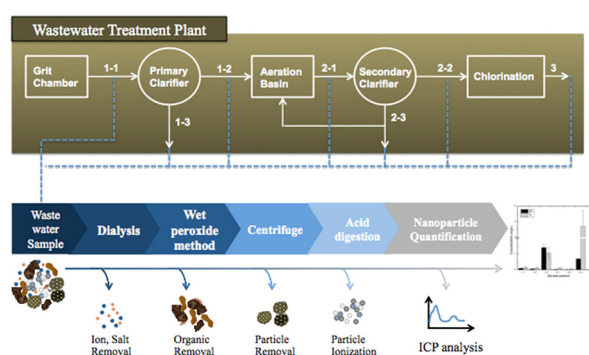[b] Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19711, United States
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HIGHLIGHTS

- A method was developed to quantify ENPs in wastewater samples.
- The method detects ENPs in samples of high organic loadings.
- About 80% Ti and 83% Zn ENPs were lost during sedimentation.
- Mass flux describes the distribution of ENPs in wastewater system effectively.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The current study developed a rationalized method for the quantification and identification of engineered nanoparticles (ENPs) in wastewaters. A review of current literature revealed that overall, presently available methods focused on single ENP mostly and were applicable mainly to samples of low organic loadings or under well-controlled laboratory conditions. In the present research, procedures including dialysis for desalting and low-temperature oxidation for organic removal were used to pretreat samples of high organic loadings, specifically, municipal wastewater and sludge. SEM mapping technique identified the presence of nanoparticles, which was followed by ICP-OES quantification of different engineering nanoparticles in wastewater and sludge samples collected from two major regional municipal wastewater treatment plants. Results showed successful identification and quantification of nano-size titanium and zinc oxides from wastewater treatment plants studied. Concentration profile was mapped out for the wastewater treatment plants (WWTPs) using the method developed in this research. Results also showed an overall 80% and 68% removal of titanium and zinc by primary and secondary sludge particulates, respectively. Mass flux of engineered nanoparticles (ENPs) was also calculated to estimate the daily flow of engineered nanoparticles in the system.

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1. Introduction

Due to its novel behavior and large specific surface area, nanomaterials have been synthesized and used at exponential rate

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(Chen et al., 2013). For the past two decades, the average growth of journal publications and patents in nanotechnology has increased steadily from 23 to 35% annually. Accordingly, the global market of nanotechnology related products has been estimated to reach US$3 trillion by the year 2020 (Roco et al., 2011).

Nanoparticles have been used in making a long list of consumer products, from semiconductors and microelectronics to everyday products such as foods, personal care products, textiles, coatings, paints, and pigments (Benn and Westerhoff, 2008; Windler et al., 2012; Weir et al., 2012; Nowack et al., 2011). Due to these excessive uses, the daily human exposure to TiO_2 alone is estimated at 0.2–0.7 and 1–2 mg-TiO_2/kg-bw/day for adults and toddlers, respectively, in the U.S. (Weir et al., 2012). Foods and personal care products appear to the major exposure sources of nanoparticles. For example, TiO_2 can be found in food products at concentration higher than 3 µgTiO_2/mg-food (Nowack et al., 2011). However not all such products are accurately labeled with the type and content of nanoparticles present. Nowack et al., reported that 53% of registered biocidal silver products likely contained silver nanoparticles, however only 7% of them were labeled as silver containing materials (Nowack et al., 2011). Although engineered nanoparticles are becoming a large part of our everyday lives, there is scarce information on the fate and transport of engineered nanoparticles in the environment after consumer usage.

Ultimately, all products made with engineered nanoparticles will escape to the environment, particularly via the municipal wastewater streams, after usage (Lazareva and Keller, 2014; Keller and Lazareva, 2014; Hendren et al., 2013; Westerhoff et al., 2012). There are reports on the release of titanium and silver into the aquatic system (Benn et al., 2011; Botta et al., 2011; Kaegi et al., 2008). Textiles imbedded with nano-silver particles can release significant amounts of silver into laundry water upon repeated washing. The amount of functional nanoparticles in textile products was estimated in the range of 20 to 100% of total particle content (Benn and Westerhoff, 2008; Nowack et al., 2011). Personal care products, such as sunscreen and functional cosmetics, containing titanium are discharged directly into municipal waste streams, where TiO_2 at concentration of 300–400 µg/L in the runoff from exterior paints has also been detected (Windler et al., 2012). The nanoparticles that were discharged to wastewater treatment plants, which served as redistribution points, and ultimately transferred to the aquifer was estimated at 26–39% of the total nanoparticles used (Lazareva and Keller, 2014).

Various attempts have been made to measure the actual material mass flow of ENPs in WWTPs. Westerhoff et al. quantified the concentration of TiO_2 in an Arizona wastewater treatment plant using acid digestion as pretreatment followed by the analysis of Ti element using inductively coupled plasma (ICP) technique and reported an average 843 µg/L of total Ti in the inflow and a maximum 8.46 mg/L of total Ti in the secondary sludge particulates of the wastewater treatment plant studied (Westerhoff et al., 2009). Li et al. quantified silver nanoparticles in nine wastewater treatment plants in Germany, with ion exchange resins and cloud point extraction to separate particulates from ionic silver species followed by graphite furnace atomic adsorption spectrometry to quantify the silver content in the particulates and reported a maximum daily load of 4.4 g-Ag/d and, >95% of the particles were removed in the primary and secondary sedimentation tanks (Li et al., 2013). Various attempts have been made to study the distribution of engineered nanoparticles such as cerium, silica, and carbon materials in laboratory scale wastewater treatment units. All results showed similar trends that biological sorption dominated the removal of nanoparticles from the liquid phase.

It is noted that most past studies involved well-controlled laboratory batch reactors, low organic loadings and single nanoparticles. There are needs to investigate the distribution and transport of engineered nanoparticles in wastewater systems using field samples.

The aim of this research was to seek a comprehensive methodology for identifying and quantifying different engineered nanoparticles in wastewater systems by improving the pre-treatment processes and subsequent enumeration techniques. Samples of high organic loadings were collected from various points of two typical municipal wastewater treatment plants as to study the identity and distribution of engineered nanoparticles in the entire system. Pre-treatment procedures were designed and refined to separate engineered nanoparticles, coarse particles, and ionic matters from wastewater and sludge particulates. The concentration and mass flux of selected nanoparticles at different points were determined and analyzed as to understand the fate and distribution of engineered nanoparticles in the wastewater treatment plants.

2. .0 Materials and methods

2.1. Sample collection

Samples were collected from wastewater treatment plants B and W. These two plants were selected based on the location and the population served. Both cities have population ranked among the top 30 in the USA and have a continuous increase in population indicating a thriving economy. Both facilities are conventional biological treatment plants for organic BOD removal with plant W being equipped with an anaerobic treatment system and tertiary sedimentation tanks. The average flow capacity was 400 MGD (or 1514 m^3/d) and 384 (or 1453 m^3/d) MGD for plant B and W, respectively.

Samples were collected at different locations of the treatment system including the inflow, outflow, and waste sludge from the sedimentation basins as seen in Fig. 1. The samples were labeled with a first digit of "1" and "2" for the primary and the secondary sedimentation basin, separately and a second digit for the direction of flow into or out of the reaction chamber, "1" for influent, "2" for effluent and "3" for return or waste flow. Wastewater or sludge samples were collected in plastic containers without head space, firmly caped and stored in a refrigerator at 4 °C before experiments. Experiments were conducted within three days after sampling. The MLSS, conductivity, and pH of the sludge or wastewater samples were measured immediately after collection.

2.2. Removal of inorganic salts and ions

A seamless cellulose dialysis tube with a molecular weight cut-off of 1 kDa (Fisher Scientific) was used to remove inorganic slats and ions from the wastewater sample. Wastewater sample was placed in dialysis tube and sealed with a plastic clip at both ends. The dialysis tube was submerged in a two-liter tank receiving continuous flow of deionized water (18 mΩ) at 0.1 mL/min for 12 h under constant stir with a magnetic stirrer. A conductivity meter (YSI model 35) was used to monitor continuously the salt content of submerging water. Results showed an exponential rate of salt removal, where the conductivity dropped from 3.7 to 0.26 m-Ω in 12 h.

2.3. Removal of organic matrices

The organic matrix of waste sample was removed by low-temperature oxidation. The deionized sample was transferred from the dialysis tube to a glass beaker for the removal of organic matrix. Ten mL of 30% H_2O_2 were added to the deionized sample and autoclaved for 1 h at 105 °C. Different amounts of H_2O_2 were added to the deionized sample and autoclaved (Yuamato SM52) two times. Sample containing high concentration of organic matter (i.e., sludge) was initially digested with 5 mL of H_2O_2 over a hot plate before wet oxidation experiment as described above. After autoclave, the beaker was sonicated to detach particles adhered to the beaker wall.

2.4. Separation of coarse particles

The oxidized sample after sonication with a high intensity ultra sound processor (Ultrasonic Homogenizer 4710 series, Cole-Parmer