

# The distribution of engineered nanoparticles (ENPs) in municipal wastewater treatment systems

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## ABSTRACT

The goal of this research was to quantify the distribution of engineered nanoparticles (ENP) in wastewater treatment systems. Sludge samples were pretreated with electro dialysis for salt removal followed by oxidation for removal of organic detritus and acid digestion before measuring the metal concentration using ICP-OES analysis. The hydraulic flow rate and ENP concentration were used to calculate the flux of ENPs of the wastewater treatment plant (WWTP). Results showed that 80% of the ENP inflow was adsorbed onto the primary and secondary sludge particulates. Elemental mapping was also conducted to evaluate the elemental compositions of sludge particulates effectively. Sedimentation experiments were conducted to evaluate the interaction of TiO<sub>2</sub> and sludge constituents. Results showed that DOM alone does not influence the settlement of ENP. However it is shown that DOM plays an important role in the interaction and adsorption of ENP on sludge.

**Keywords:** Engineered nanoparticle, Wastewater, Adsorption, Elemental mapping, Sedimentation

## 1 INTRODUCTION

The increasing use of nanomaterials will result in their eventual escape into the environment, namely, atmosphere, soil, and water. Municipal and industrial wastewaters are expected to be the major transport routes for ENPs in the environment due mostly to the inefficiency in the removal of nano-materials at modern wastewater treatments, in spite that the major function of modern wastewater treatment systems is to remove “solids”, both soluble and insoluble, from the waste streams, using a series of unit physical, biological and chemical processes. Studies on the removal and release of titanium nanomaterial from wastewater treatment plant have reported that the average overall removal of Ti from an activated sludge WWTP was 82% and the removal of filterable Ti (GF/F-grade glass microfiber filter) was only about 42% leaving 10-50 µg/L

Ti in the effluent [1]. The study of the recovery of silver nanoparticles from surface water and wastewater samples using cloud point extraction pre-concentration treatment reported a recovery efficiency of 57-116% for spike concentration of 0.1-146 µg/L Ag [2]. There are laboratory studies on the removal of nanoparticles from industrial wastewater using electrocoagulation and magnetic seeding aggregation processes [3-6]. However these studies only measure the removal in terms of turbidity, not nanoparticles per se. The removal of nanoparticles from industrial wastewater by coagulation using polyaluminum chloride reported that chemical coagulation contributed to only 9% removal [7]. Reports have shown that Fe-salts may yield better removal of nanoparticles than Al-salts [8]. Studies with cerium oxide nanoparticles in a model wastewater treatment plant have reported a high removal efficiency of over 95% [9]. However there was still a very high concentration of 2-5 mg/L nanoparticles remaining in the effluent. Based on limited published results, it is expected that nanoparticles are likely to be present in the effluent treated by conventional activated sludge process. From a pollution control point of view, further treatment of the effluents of conventional wastewater treatment plants may be necessary. Before developing new technologies for the removal of nanoparticles from wastewater treatment effluents, it is necessary to understand the distribution of engineered nanoparticles (ENP) in the system.

## 2 MATERIAL AND METHODS

### 2.1 Sample preparation

Dialysis tubes were used to remove the salts of the sludge. Seamless cellulose dialysis tube with a molecular weight cut-off of 1 kDa (Fisher Scientific) was used. Figure 2 shows a continuous batch unit constructed for the dialysis experiments. Deionized water (18 µΩ) was circulated into a reservoir containing 2 L of water. Water was pumped into the unit at a flow rate of 0.1 mL/min for 12 h. The reservoir was stirred with a magnetic stirrer throughout the process. A conductivity meter (YSI model 35) was used to monitor the salt content of both samples.

After 12 h of water circulation the conductivity dropped from 3.7 to 0.26  $\mu\text{-}\Omega$  where the run without water circulation showed a conductivity of 0.52  $\mu\text{-}\Omega$ .

## 2.2 Sludge Oxidation

For sludge oxidation experiments sludge after removal of the salt content using the dialysis method was transferred to glass beakers. For the wet hydrogen peroxide method, 10 mL of 30%  $\text{H}_2\text{O}_2$  were added to the sludge and the mixture was autoclaved for 1 h. Different amounts of  $\text{H}_2\text{O}_2$  were introduced into the sludge sample and autoclaved (Yuamoto SM52) up to two times to assess the maximum effect of sludge oxidation. To prevent the overflow of sludge due to the rapid oxidation of wastewaters with  $\text{H}_2\text{O}_2$ , samples containing high concentrations of organic matter were initially digested using 5 mL of 30%  $\text{H}_2\text{O}_2$  on a hot plate before the wet hydrogen peroxide method.

## 2.3 Acid digestion

The purpose of acid digestion was to dissolve any existing metallic ENP including  $\text{TiO}_2$  due to its low solubility. Liquid and solid samples were digested using  $\text{HNO}_3/\text{H}_2\text{SO}_4$  method as described by Standard Method 3030G for water and wastewater analysis. After the oxidation process 20 mL of well mixed samples were transferred to a flask. Then 5 mL of  $\text{HNO}_3$  (Analytical grade, Fisher Scientific, US) was added to the flask and slowly boiled on a hot plate and evaporated to 15 mL. 5 mL of  $\text{HNO}_3$  and 10 mL of  $\text{H}_2\text{SO}_4$  was added to the sample and evaporated until fumes of  $\text{SO}_3$  start to show. The samples were heated additionally until the  $\text{HNO}_3$  was all removed as well. After the heating process the samples were cooled and diluted with water to its original volume. Samples were also filtered after the acid digestion, before the ICP-OES analysis.

## 2.4 ICP-OES analysis

Inorganic material collected from the sludge was sonicated to prevent the ENP within the samples to attach to the clay particles. Samples were contained in a 50 mL centrifuge tube with an addition of 5% nitric acid. A quality control standard (Perkin Elmer, 21 Elements, Matrix per Volume 5%  $\text{HNO}_3$  per 100 mL) was used for a standard calibration of the selected elements to be detected. Standard curves were constructed with five different concentrations ranging from 0.01 to 1 ppm. All the samples were filtered with a 0.45- $\mu\text{m}$  filter (Fisher Scientific, US) to prevent clogging the ICP tubes. Additional filtration with 1.2  $\mu\text{m}$  and 0.2  $\mu\text{m}$  cellulose acetate filters (Fisher Scientific, US) were used to filter the sample for particle size evaluation. ICP-OES measurements were conducted on a Perkin Elmer Optima 7300. The following ICP-OES parameters were used: nebulizer flow, 0.80  $\text{L min}^{-1}$ ; radio frequency power,

1450; sample introduction, 1.50  $\text{mL min}^{-1}$ ; flush time, 15 sec; delay time, 20 sec; read time, 10 sec; wash time, 60 sec.

## 3 RESULTS AND DISCUSSION

### 3.1 Quantification of ENP in WWTPs

Figure 1 presents the results of the ENP concentration analysis conducted on the B-WWTP samples. Concentrations of the titanium inflow to the plant were 0.15 ppm with a 0.02 ppm outflow indicating an 80% decrease of  $\text{TiO}_2$  prior to discharge.  $\text{ZnO}$  also showed the same percentage of concentration drop from the plant inflow to the final discharge. The removal of ENPs was due to the accumulation in plant solids. This can be confirmed through the elevated concentrations in the waste sludge of the primary sedimentation basin (sample 1-3 in Figure 1) and the return sludge from the secondary basin (sample 2-3 in Figure 1). In these elevated values we can also see that there is a higher concentration of  $\text{ZnO}$  in the primary sludge compared to the secondary sludge and an opposite trend with  $\text{TiO}_2$ . From the different concentration distributions of the two ENPs it can be conjectured that the chemical composition of the particles influence the amount of adsorption but the type of sludge (or organic matter) also influences the adsorption as well.

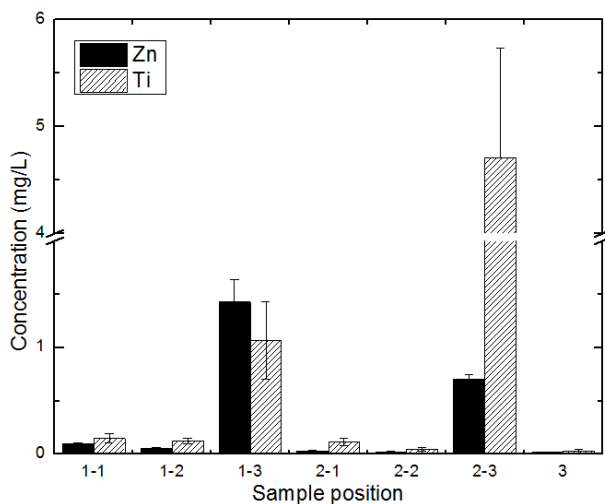


Figure 1. Concentration profile of  $\text{TiO}_2$  and  $\text{ZnO}$  nanoparticles in B-WWTP. Samples were collected at 6 different positions; 1-1: Primary inflow, 1-2: Primary outflow, 1-3 Primary waste sludge, 2-1 Secondary inflow, 2-2 Secondary outflow, 2-3 Secondary return sludge, 3 final outflow.

Figure 2 shows the mass flow of the ENP through the WWTP where the hydraulic flow was incorporated into the concentration values giving the total mass of ENP that flow through the plant per day. Due to the capacity of the plant (131 MGD) the total inflow is 50kg for  $\text{ZnO}$  and 75kg for  $\text{TiO}_2$  per day. As seen in Figure 2, 80% of this amount is adsorbed to the sludge with 20% discharged from the plant. The mass balance was checked with each sediment basin

and with the total inflow and outflow to show a 10~20% error. Compared to Figure 1, Sample 2-1 in Figure 2 showed highly elevated levels of both particles which are due to two different phenomena. The first is the accumulation of Ti with the biomass of the sludge and the second being the recirculation of the secondary biomass as return sludge where particles are adsorbed to the sludge until steady state is reached.

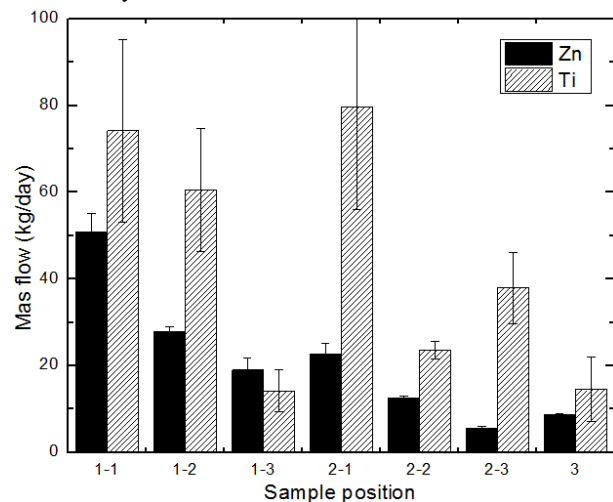


Figure 2. Mass flow of  $\text{TiO}_2$  and ZnO in B-WWTP.

### 3.2 Elemental mapping as a spectroscopic analysis method

Elemental mapping was conducted on dried wastewater samples to verify the chemical distribution of titanium nanoparticles of interest. In the course of using the elemental mapping technique areas containing any number of elements can be highlighted simultaneously. The distribution of elements will show based on the chemical composition. Through this method various numbers of particles can be analyzed to verify the particle composition and whether additional metal species are adsorbed as well. Figure 3 shows an example of the elemental mapping applied to the Baltimore secondary sludge sample. Figure 3-(a) shows an area including 6 or 7 particles of interest. With the conventional EDS results (Figure 3-(d)) both iron and titanium can be seen in the spectrum which was also evident when the particles were scanned individually. However each elemental results showed the layout of the composition individually as shown in Figure 3-(b),(c). Figure 3-(b) shows the results of titanium where a perfect overlap of the elemental readings and particle shapes can be observed. Oxygen also showed a good overlap with the particles indicating the particles being  $\text{TiO}_2$ . However the results of iron showed highly scattered distribution without overlapping of the particles indicating that most of the iron is exogenous. As seen with the analysis above elemental mapping can help find various different ENP simultaneously with the capability to distinguish additional background noise caused by different metal species. Additional analysis using this method aided in the

discovery of  $\text{TiO}_2$  particles with a size range of 80 to 250 nm in diameter.

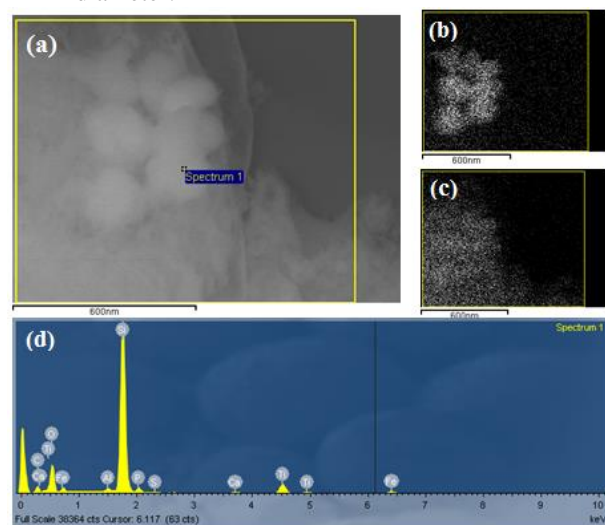


Figure 3. Elemental analysis of  $\text{TiO}_2$  in secondary return sludge. (a) SEM image of sludge, (b) Titanium distribution of selected image, (c) Oxygen distribution of selected image, (d) EDS results of the selected area

### 3.3 Interaction of ENP with sludge constituents

Sludge was separated into four different samples based on the constituents. DOM was separated from the sludge by centrifuging the sludge at 10,000G for 10 min. DOM and small organic particles ( $<1 \mu\text{m}$ ) were separated with gravimetric settling, where the sludge was settled for 4hr and the supernatant was collected. Large organic particles ( $<1 \mu\text{m}$ ) were collected from the settled matter of the gravimetric settling. To assess only the influence of large particulate matter the DOM was washed out by continuously refilling the samples with deionized water, steeling the organic matter and pouring out the supernatant. The last sample was the original sludge without additional pretreatments. Experiments were conducted with both primary and secondary sludge. All of the samples pH and ionic strength were matched to the original sludge samples. Figure 4 shows the results of sediment experiment results with different sludge constituents. Based on the results of the  $\text{TiO}_2$  and DOM it can be observed that minimal to no change of the turbidity occurs. Based on the sediment experiment the free concentration of  $\text{TiO}_2$  was calculated. Results showed that the original concentration of the NP did not change throughout the experiment. The same results were shown with the DOM and small organic materials (supernatant). It can be conjectured from these results that DOM alone does not influence the sedimentation of the particles. The free  $\text{TiO}_2$  concentration after the large organic particles and sludge were each 53.6 ppm and 45 ppm, respectively. Considering the fact that the free particle concentration after the sediment of each of the sludge constituent do not measure up to the removal of sludge it can be inferred that DOM may not solely influence the

sediment of the ENP but aids in the adsorption process. This indicates that the adsorption process is a complex interaction of each of the sludge constituents. Also the free concentration after the sediment experiments resulted in the same concentrations in both sludges. This showed that the high titanium concentration in the secondary return sludge was due to the longer retention time of  $\text{TiO}_2$ .

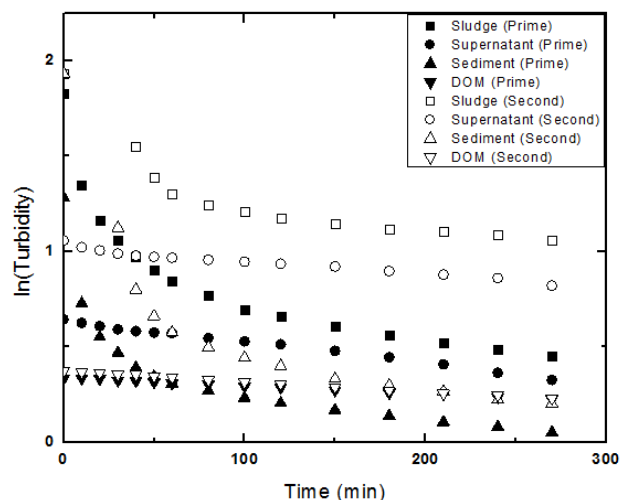


Figure 4. Sedimentation results of  $\text{TiO}_2$  in primary and secondary sludge.

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#### REFERENCES

[1] Keiser MA, Westerhof P, Benn T, Wang Y, Perez-Rivera J, Hristovski K, "Titanium nanomaterial removal and release from wastewater treatment plants." *Environ Sci Technol*, 2009, 43, 6757-6763  
 [2] Liu JF, Chao JB, Liu R, Tan ZQ, Yin YG, Wu Y Jang GB, "Cloud point extraction as an

advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters." *Anal Chem*, 2009, 81, 6496-6502

[3] Lai CL, Lin SH, "Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics." *Chemosphere*, 2004, 54, 235-242  
 [4] Den W, Huang CP, "Electrocoagulation for removal of silica nano-particles from chemical-medical-planarization wastewater." *Colloids Surf A*, 2005, 254, 81-89  
 [5] Chin CJM, Chen PW, Wang LJ, "Removal of nanoparticles from CMP wastewater by magnetic seeding aggregation." *Chemosphere*, 2006a, 63, 1809-1813  
 [6] Den W, Huang CP, Ke HC. "Mechanistic study on the continuous flow electrocoagulation of silica nanoparticles from polishing wastewater." *Ind Eng Chem Res*, 2006, 45, 3644-3651  
 [7] Chang MR, Lee DJ, Lai JY, "Nanoparticles in wastewater from a science-based industrial park coagulation using polyaluminum chloride." *J Environ Manage*, 2007, 85, 1009-1014  
 [8] Shon HK, Phintsho S, Vigneswaran S. "Effect of photocatalysis on the membrane hybrid system for wastewater treatment." *Desalination*, 2008, 225, 235-248  
 [9] Limbach LK, Bereiter R, Muller E, Krebs R, Galli R, Stark WJ, "Removal of oxide nanoparticles in a model wastewater treatment plant: influence of agglomeration and surfactants on clearing efficiency." *Environ Sci Technol*, 2008, 42, 5828-5833