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Technical Note

Removal of silver nanoparticles in simulated wastewater treatment processes and its impact on COD and NH_4 reduction

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ABSTRACT

The increasing utilization of silver nanoparticles in industrial and consumer products has raised concern to wastewater treatment utilities due to its antimicrobial activity. In this work, the removal of citrate stabilized silver nanoparticles (Ag-NPs) during the wastewater treatment processes and its impact on treatment performance were examined. During simulated primary clarification, over 90% of the Ag-NPs remained in the wastewater, indicating that the majority of silver nanoparticles in sewage would enter the subsequent treatment units. During sequencing batch reactor processes, silver nanoparticles were effectively removed in each cycle throughout the 15-d experimental duration. Continuous input of silver nanoparticles into the wastewater did not significantly alter chemical oxygen demand (COD) removal. NH_4 removal was reduced at the beginning of the SBR experiment but quickly recovered at the later stage of the experiment. This study demonstrated that in the near future it is unlikely that citrate-stabilized Ag-NPs released into sewage will cause significant adversary effects on the COD and NH_4 removal of activated sludge processes in municipal wastewater treatment plants.

1. Introduction

Large increases in the production and application of engineered nanoparticles inevitably result in the release of these materials into the natural environment (Nowack and Bucheli, 2007; Kaegi et al., 2010). For many engineered nanoparticles, sewage and industrial discharges are the primary pathways of release (Boxall et al., 2007). Thus wastewater treatment plays an important role in controlling the release of engineered nanoparticles into the environments, e.g., into surface waters via effluent discharges and to land via sewage sludge disposal (Colvin, 2003; Evans, 2006; Wiesner et al., 2006). However, reports on the fate of engineered nanoparticles during wastewater treatment processes are scarce (Chang et al., 2007; Limbach et al., 2008; Jarvie et al., 2009; Kiser et al., 2009; Ganesh et al., 2010; Kaegi et al., 2011). The behavior of engineered nanoparticles in wastewater treatment plants is largely unknown and has been identified as one of the major knowledge gaps for accurate environmental risk assessments of nanomaterials (Scheringer, 2008). As a result of such a knowledge gap, when estimating environmental concentrations of nanoparticles, researchers had to make highly simplified assumptions on the removal of these materials in treatment plants (Mueller and Nowack, 2008; Gottschalk et al., 2009).

Due to its antimicrobial properties (Sondi and Salopek-Sondi, 2004; Elechiguerra et al., 2005; Kim et al., 2007), silver nanoparticles (Ag-NPs) are incorporated into many consumer products, such as clothing, paints, bandages, and food containers. In fact, over 20% of the consumer products that claim to include some forms of engineered nanoparticles contain Ag-NPs (Maynard and Michelson, 2006; Liu and Hurt, 2010). The widespread use of products containing Ag-NPs would certainly release Ag-NPs into sewer systems and subsequently into municipal wastewater treatment plants. For example, significant fractions of Ag-NPs contained in nanotextiles and socks were found to be released during washing (Benn and Westerhoff, 2008; Geranio et al., 2009). However, reports on the fate of Ag-NPs during wastewater treatment process have been scarce in the literature. Benn and Westerhoff (2008) examined adsorption of Ag-NPs onto wastewater biomass and concluded that typical activated sludge reactors would remove over 99% of Ag-NPs in wastewater influent. Recently, Kaegi et al. (2011) confirmed that Ag-NPs were sorbed to wastewater biosolids both in the sludge and in the effluent.

Given the antimicrobial activity of Ag-NPs, the possible effects of Ag-NPs on the bacteria in the environment cannot be overlooked (Neal, 2008; Bradford et al., 2009). Of particular concern is the potential impact of Ag-NPs on the microbial community in the wastewater treatment processes, since inhibition and loss of bacteria that are essential for chemical oxygen demand (COD) reduction and nitrogen removal would comprise treatment efficiencies. Using extant respirometry, Choi et al. (2008) demonstrated that

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Ag-NPs at a concentration of 1 mg L^{-1} greatly inhibited respiration of autotrophic nitrifying organisms (by >85%) from a continuously operated bioreactor. However, whether Ag-NPs have detrimental effects on microbes in real wastewater treatment plants has not been studied.

The objective of this work was to examine the fate and impact of Ag-NPs during simulated wastewater treatment processes. Sewage was collected from a wastewater treatment plant and Ag-NPs removal during primary clarification was determined. Simulated sequencing batch reactor (SBR) experiments were conducted continuously for half a month to examine Ag-NP release following simulated aeration and secondary clarification. COD reduction and NH_4 removal were monitored throughout the experiments to examine the potential adverse effects of Ag-NPs on wastewater treatment. In addition, oxygen uptake rates during SBR processes were measured to corroborate the variations of NH_4 removal in the presence of Ag-NPs.

2. Materials and methods

2.1. Silver nanoparticles

The silver nanoparticles used in this study were prepared by chemical reduction of $AgNO_3$ (Šileikaitė et al., 2006). First, 0.3 g $AgNO_3$ was dissolved in a beaker containing 1 L ultra-pure water. After the solution was heated to boiling, 6 mL of 1% sodium citrate was added in drops under agitation. After the solution was re-boiled for 2 min, 44 mL sodium citrate was added in drops. Agitation was continued for additional 20 min, during which the solution turned into a gray-yellow suspension. The suspension was transferred into a 1 L flask and the volume was adjusted to 1 L. Measurement using a flame atomic adsorption spectrophotometer indicated that the total Ag concentration in the stock suspension was 161 mg L^{-1}.

An aliquot of the prepared Ag-NPs stock suspension was scanned from 190 to 1100 nm to obtain adsorption spectra using a Lambda 35 UV–Vis spectrophotometer (Perkin Elmer, Walthem, MA). The sizes of Ag-NPs were characterized using a Tecnai F30 transmission electron spectroscopy (TEM, FEI, Hillsboro, OR) at 300 kV. To determine the maximum concentrations of Ag^+ in the stock suspension, 15 mL of the stock suspension was added into a 15 mL Amicon centrifugal ultrafilter with a molecular weight cutoff of 3000 (Millipore, Billerica, MA). The centrifugal filter was centrifuged at 4000 rpm for 20 min and the Ag concentration in the filtrate was determined using graphite-furnace atomic adsorption spectroscopy.

2.2. Simulated primary clarification

The wastewater and biosolids used in this study were collected from the Xiaojiahe Municipal Wastewater Treatment Plant in Beijing. The plant uses an activated sludge process that involves primary clarification, aeration, secondary clarification, and further treatment. The influent of the plant was collected to determine Ag-NPs removal by the primary clarification process. The influent contained 269 mg L^{-1} of suspended solids (SS) and had a pH of 7.3. The Ag-NPs were added into 1 L collected influent in three replicate 1-L beakers to each reach a concentration of 1 mg L^{-1}. Following the Ag-NPs addition, the mixtures were stirred using an agitator at a rate of 300 rpm (Model TJ6, Hengling Technology, Wuhan, China) for 60 min to allow complete mixing. Upper layer aliquots (10 mL) in the beakers were collected using a pipette at about 1 cm beneath the water surface, at the beginning of the settling ($t = 0$) and periodically up to 150 min after the settling commenced. The silver concentrations in the aliquots were analyzed using flame atomic adsorption spectrometry. Additional aliquots were sampled at 30 min and immediately centrifuged using the Amicon filters to determine dissolved Ag concentrations.

The SS content in the influent to the Xiaojiahe Plant occasionally exceeds 500 mg L^{-1}. To simulate these extreme situations, the collected influent was allowed to settle for 3 h and the wastewater at the upper part of the container were decanted. An additional experiment was performed following the same procedure using the "concentrated" influent to examine the impact of SS content on Ag-NPs removal. The "concentrated" influent used in the second experiment contained 730 mg L^{-1} SS.

2.3. Simulated aeration and secondary clarification

Sequence batch reactors were used to simulate the full-scale operations of aeration and secondary clarification. To examine Ag-NPs removal by the SBR process, an experiment was performed using 1 L beakers as reactors. The reactors were continuously operated for 15 d at a volume of 0.9 L, with a hydraulic residence time of 12 h (i.e., 2 cycles per day). The SBR cycle involved 10 h of aeration using a mini-aerator (Risheng Electric Products, Guangdong, China), followed by 2 h of settling. The returned sludge from the Xiaojiahe plant was collected and adjusted to a biomass concentration of 2.4 g L^{-1}, using the effluent from the primary clarifier at the same plant. The experiment included three treatments (each with three replicates) which involved adding 0, 0.55, 2.75 mL of Ag-NPs stock suspension into the reactors, respectively. The treatment without Ag-NPs addition served as a control. The lower and higher Ag dosage corresponded to 0.1 and 0.5 mg L^{-1}, respectively. In each cycle, supernatants (about 650 mL) following settling were replaced with the effluent from the primary clarifier to start the next cycle. Upon replacement of the supernatants, Ag-NPs were added with the amounts identical to what were added in the first cycle. Aliquots (10 mL) of supernatants were collected every day at the end of settling of the day time cycle (9 AM–9 PM). Silver concentrations in the supernatants collected on selected dates were analyzed using graphite furnace atomic adsorption spectroscopy.

To examine the effects of Ag-NPs on COD and NH_4 removal by the simulated SBR process, another experiment was conducted following the same procedure (2 cycles per day for 15 d). In this experiment, the sludge concentration was 2.5 g L^{-1}. The experiment also included three treatments (control, low and high Ag-NPs dosage). The low and high Ag-NPS dosage in each cycle corresponded to added silver concentrations of 0.1 and 0.5 mg L^{-1}, respectively. Measurements in selected cycles indicated that the average dissolved oxygen (DO) concentration during aeration was around 7.2 mg L^{-1}. In each cycle, aliquots of completely mixed suspensions (50 mL) and supernatants (10 mL) were collected every day at the beginning of the aeration and the end of settling of the daytime cycle. The aliquots were filtered using filter papers. COD and NH_4 in the filtrates on selected dates were determined.

2.4. Analytical methods

The aliquots (10 mL) taken during the experiments were digested by mixing with 10 mL HNO_3 (32.5% w/w), 1 mL H_2SO_4, 1 mL H_2O_2 (30%). The Ag concentrations in the digested aliquots from the simulated primary clarification were determined using a flame atomic adsorption spectrometer (Hitachi Z-5000, Hitachi High-Tech, Tokyo) at a wavelength of 328.1 nm. The lamp current was set at 9.0 mA. The Ag concentrations in the digested samples from the simulated SBR experiment were determined using a graphite furnace atomic adsorption spectrophotometer (Hitachi Z-5000). The temperature for drying, ashing, atomization, and cleaning were 80–140, 500, 2200, 2500 °C, respectively. The holding time for the four steps was 40, 20, 5, and 4 s, respectively. The CODs of the samples collected at the beginning and end of each cycle were determined using the potassium dichromate method. The NH_4 concentrations in the samples were determined using