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Simultaneous removal of nanosilver and fullerene in sequencing batch reactors for biological wastewater treatment

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HIGHLIGHTS

- Biological SBR treatment removed 83–96% of nC_{60} dosed daily at 0.07–2 mg L^{-1}.
- Adding functionalized nano Ag at 2 mg L^{-1} for 30-d led to lower COD removal rate.
- The COD removal was re-established within 1 SRT when loading *fn*-Ag for 30 d.
- A distribution model of nC_{60} on biomass simulated well the removal of nC_{60} in SBRs.

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ABSTRACT

Increasing use of engineered nanomaterials (ENMs) inevitably leads to their potential release to the sewer system. The co-removal of nano fullerenes (nC_{60}) and nanosilver as well as their impact on COD removal were studied in biological sequencing batch reactors (SBR) for a year. When dosing nC_{60} at 0.07–2 mg L^{-1}, the SBR removed greater than 95% of nC_{60} except for short-term interruptions occurred (i.e., dysfunction of bioreactor by nanosilver addition) when nC_{60} and nanosilver were dosed simultaneously. During repeated 30-d periods of adding both 2 mg L^{-1} nC_{60} and 2 mg L^{-1} nanosilver, short-term interruption of SBRs for 4 d was observed and accompanied by (1) reduced total suspended solids in the reactor, (2) poor COD removal rate as low as 22%, and (3) decreased nC_{60} removal to 0%. After the short-term interruption, COD removal gradually returned to normal within one solids retention time. Except for during these "short-term interruptions", the silver removal rate was above 90%. A series of bottle-point batch experiments was conducted to determine the distribution coefficients of nC_{60} between liquid and biomass phases. A linear distribution model on nC_{60} combined with a mass balance equation simulated well its removal rate at a range of 0.07–0.76 mg L^{-1} in SBRs. This paper illustrates the effect of "pulse" inputs (i.e., addition for a short period of time) of ENMs into biological reactors, demonstrates long-term capability of SBRs to remove ENMs and COD, and provides an example to predict the removal of ENMs in SBRs upon batch experiments.

1. Introduction

Engineered nanomaterials (ENMs) including nanosilver (nano Ag) and nano fullerenes (nC_{60}) are used in consumer products (Jensen et al., 1996; Meyer et al., 2009; Li and Chen, 2011; Ripp and Henry Theodore, 2011; Yang and Westerhoff, 2014). When released from these consumer products, the ENMs are at risk of entering sewers and wastewater treatment plants (WWTPs) (Mueller and Nowack, 2008; Westerhoff, 2013). Batch studies, limited pilot tests, and full scale WWTP monitoring suggest that WWTPs employing activated sludge treatment can remove released ENMs from the sewage, resulting in accumulation in settled biomass (Kiser et al., 2010; Kaegi et al., 2011). However, the removal and the impact of ENM in activated sludge processes differ, depending on the properties of ENMs. Nano fullerene is hydrophobic and demonstrates little impact to microorganism activity (Gharbi et al., 2005; Nyberg et al., 2008; Johnson et al., 2011). For example, introducing 2.5 mg L^{-1} of nC_{60} to the activated sludge reactor has negligible effect on COD removal (Wang et al., 2012). In contrast, nano Ag has the potential to act as a inhibitor or toxic agent for a variety of microbes involved in wastewater treatment (Choi et al., 2008; Kim et al., 2008). Nano Ag at 0.5 mg L^{-1} exhibits inhibitory effects on the nitrification efficiency

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of nitrifying bacteria (Choi and Hu, 2008). Shock loading of nano Ag at 1 mg Ag L^{-1} for 12 h can reduce nitrification efficiency as much as 46.5% for a month in a Modified Ludzacke Ettinger reactor with mixed liquor suspended solids of 2000 mg L^{-1} (Liang et al., 2010). Very little is known, however, about the long-term effects of combination addition of ENMs on the performance of biological wastewater treatment reactors, because the majority of studies that examine these effects are conducted in batch or a short term experiments.

Many research groups have studied the biosorption and removal of ENMs in the activated sludge system (Benn and Westerhoff, 2008; Mueller and Nowack, 2008; Kiser et al., 2009), with removal of ENMs often explored in batch study (Kiser et al., 2010). One of the most popular life cycle model for ENMs in the environment applies a constant removal rate of ENMs in wastewater treatment processes based on results from batch studies (Mueller and Nowack, 2008). However, it is unknown whether the distribution coefficients of ENMs obtained in batch studies can be applied to predict the ENM removal in a continuous bioreactor. To answer this question and to provide better information on the fate of ENMs in WWTPs, the distribution coefficients obtained from batch tests need to be compared and validated with data from a long-term bioreactor study.

The objectives of this research are to explore the long-term impact of ENM addition on biological organic matter removal in a sequencing batch reactor (SBR). The nC_{60} was added daily at 0.07–2 mg L^{-1} to assess dose–response relations for a year, with total suspended solids (TSS) concentration from 500 to 2000 mg L^{-1}. To explore synergistic impacts of the nanomaterials, nC_{60} was continuous applied to SBR with one-month intervals of nano Ag co-addition with an influent concentration of 2 mg Ag L^{-1}. During periods of dosing of both nC_{60} and nano Ag, the concentrations of total Ag and dissolved Ag in the biomass and effluent were monitored to assess changes. To develop a model for nC_{60} removal in SBRs, the distribution coefficients of ENMs between biomass solids and liquid phase were measured using separate bottle-point-distribution batch tests of nC_{60} on biomass. A mass-balance model was developed to predict the removal efficiency of nC_{60} in SBRs using the distribution coefficients determined in the bottle-point batch tests.

2. Methodology

2.1. Sources and characterization of the engineered nanomaterials

Concentrated suspensions of functionalized (carboxyl terminated polymer coating) silver nanoparticles (*fn*-Ag) were obtained from the manufacturer (Northern Nanotechnologies, Ontario, Canada). The *fn*-Ag stock solution contained between 8% and 10% ionic silver, which was determined by ion-specific electrode (ISE) (Accumet® Silver/Sulfide, Fisher, U.S.) and further confirmed by centrifugal ultrafiltration with a 10 kDa membrane (Amicon, U.S.) followed by ICP-AES analysis. The mean hydrodynamic diameter measured by phase analysis light scattering (PALS, ZetaPALS, Brookhaven Instruments Corporation, U.S.) was 5 nm and 30 nm in Nanopure water and SBR feed solutions, respectively. The zeta potential was −6 mV at pH 7 in the feed solution of SBR.

Nano fullerene (nC_{60}) was purchased from MER Corporation (Arizona, U.S.). Aqueous nC_{60} was prepared by adding ~500 mg of nC_{60} dry powder to 1 L nanopure water and sonicating at 200 W L^{-1} for 6 h. The solution was filtered (Whatman GFF, U.S.), and permeate was used as the stock solution. The mean diameter determined by PALS was 88 nm and 130 nm in nanopure water and SBR feed solutions, respectively. The zeta potential of nC_{60} was −52 mV at pH 7 in the feed solution.

2.2. Sequencing batch reactor and spiking of nanomaterials

Laboratory-scale SBRs were inoculated with return activated sludge from a full-scale nitrification/denitrification WWTP in the metro-Phoenix area (Arizona, U.S.). The SBRs consisted of 3.75 L-amber glass bottles wrapped in aluminum foil and had a working-volume of 2.5 L. SBR aeration was conducted via an air pump and ceramic diffusion stones (1.2 cm × 2.5 cm). During the aeration stage, the sludge was also stirred with a magnetic stir bar for better mixing. The synthetic feed solution, which contained monosodium glutamate ($C_5H_8NO_4Na$) as carbon and nitrogen sources, was described in previous publication (Moussa et al., 2005; Wang et al., 2010). The feed solution had a conductivity of 0.5 mS cm^{-1}, COD of 750 mg L^{-1}, and total dissolved nitrogen of 150 mg N L^{-1}. Nanomaterials were added to the feed solution and then introduced into the SBR. A control SBR was maintained without any ENM addition.

SBRs were operated in a 10-h cycle mode that consisted of 8 h of aeration, 90 min of sludge settling, and 30 min of feed solution replacement. The feed solution replacement included discharge of settled supernatant followed by addition of 2 L fresh synthetic feed solution. Before the sludge settling step, a varied amount of the mixed liquor suspended solid was removed to control the solids retention time (SRT, varied during experiments and based on the TSS level) and stored for analysis at 4 °C. In the first 50 d, SBRs were maintained to obtain a stable MLSS concentration. To explore the effect of SRT on nanomaterial removal, the SRT was maintained at 4.4 d from day 50 to day 270, and was adjusted to 12 d from day 270 to the end of a year.

Influent concentration of nC_{60} was changed to examine the effect of different loading rate on SBR performance (Table 1). During the first 80 d, SBRs were continually dosed with fullerene at 0.76 mg L^{-1}. From day 81 to day 120, the fullerene concentration in the feed solution was maintained at 0.07–0.1 mg L^{-1}. From day 121 until the end of the study, the influent fullerene concentration was maintained at 2.0 mg L^{-1}. To explore the potential combination effects of fullerene and *fn*-Ag, co-addition of *fn*-Ag was performed at 2 mg L^{-1} in the feed solution during three 30-d intervals: day 151–180 (Phase 5), day 211–240 (Phase 7), and day 301–330 (Phase 10). Phase 5 was also used to explore the silver accumulation and depletion in the SBR biomass.

2.3. Kinetics and distribution of fullerene to biomass

A bottle-point batch study on kinetics and distribution of nC_{60} to biomass provides the equilibrium time to achieve stable distribution and the distribution coefficients of nC_{60} in the water and biomass phases. The distribution experiments were conducted with clean activated sludge biomass sampled from the control SBR (i.e., without nanomaterial dosing). The experiments followed procedures detailed elsewhere (Kiser et al., 2010). Briefly, activated sludge was rinsed three times with a carbonate buffer solution (10 mM NaCl and 4 mM $NaHCO_3$). After centrifugation ($F = 350$ G) for 15 min, the supernatant was discarded and dewatered sludge was re-suspended with 1 mM $NaHCO_3$ buffer solution. The pH of mixed sludge and buffer solution was adjusted to pH 7 with HCl and NaOH.

In order to determine the distribution kinetics of nC_{60} to biomass, two concentrations (i.e., 600 and 1600 mg TSS L^{-1}) of biomass were used, representing biomass concentrations observed in the SBRs. After dosing the biomass with nC_{60} in amber glass vials, the mixtures of nC_{60} and biomass were placed on a shaker with continuous mixing for 4 h. For the loading rate of 2.5 mg nC_{60} g^{-1} TSS (1.5 mg nC_{60} L^{-1} on the biomass of 600 mg TSS L^{-1}), aliquots of 5 mL were sampled at time 0, 0.5, 1, 2, 3, 5, and 8 h. After 30-min settling, the concentration of nC_{60} in supernatant was further determined. A similar study was conducted with a loading rate of 1.19 mg nC_{60} g^{-1} TSS (1.9 mg