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Insights into the short-term effects of CeO_2 nanoparticles on sludge dewatering and related mechanism

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ABSTRACT

As CeO_2 nanoparticles (NPs) are used in many applications, the released particles eventually enter wastewater treatment plants, influencing sludge dewatering and increasing the disposal costs. We conducted tests to gain insight into the sludge dewatering performance and the potential mechanism related to the distribution and production of extracellular polymeric substances (EPS). In addition, we conducted single-factor tests with six concentrations of CeO_2 NPs in sequencing batch reactors containing matured activated sludge. Overall, the specific resistance to filtration (SRF) improved with an increase in the CeO_2 NPs dosage. The SRF significantly increased from 1.460×10^{12} to 1.632×10^{12} m/kg after the addition of 5 mg/L CeO_2 NPs ($p < 0.05$). The bound water content was enhanced from 2.43 to 2.75 kg/kg dry solid, indicating a deteriorated dewaterability. We found that the increased EPS production, especially the dominant protein ($r = 0.987$, $p < 0.01$), was correlated significantly with the SRF. This is ascribed to the inhibited activity of leucyl aminopeptidase and the reduced adenosine 5′-triphosphate concentrations after exposure to CeO_2 NPs. The fluorescence region integration technique and protein secondary structures revealed the reasons for the poor dewatering performance in the presence of CeO_2 NPs. These are the enhanced amount of soluble microbial by-product-like material and the low value of the α-helix/(β-sheet + random coil). These results could potentially expand the knowledge on sludge dewatering in the presence of NPs.

1. Introduction

With the rapid commercialization and broad application of nanotechnology, the engineered nanoparticles (NPs) have been widely used in commercial and industrial products, such as sunscreens, textiles, antibacterial and antifungal agents, food additives, and medical devices (Brunetti et al., 2015; Robichaud et al., 2009; Xu et al., 2016). Inevitably, nanoparticles are released into wastewater systems and natural waters in their production, utilization, and disposal processes (You et al., 2016; Wagner et al., 2014), causing toxicity toward microorganisms and bacteria (Li et al., 2012; Hou et al., 2016a). As wastewater treatment plants (WWTPs) are the main exposure sites and the final destination of nanomaterials, such plants have become important research objects in the environmental risk assessment of NPs (Brunetti et al., 2015; Wagner et al., 2014). It has been demonstrated that NPs could have negative effects on the surface physicochemical properties of sludge and biofilms, leading to a reduction in the performance of wastewater treatment (Xu et al., 2016; You et al., 2016; Hou et al., 2016a, 2016b).

Sludge is a heterogeneous colloidal system, in which small sludge aggregates, containing microorganisms and organic/inorganic compounds, form a stable suspension in water (Qi et al., 2011). Sludge commonly contains more than 95% water and the separation of biosolids and liquid is extremely difficult (Liang et al., 2015). The treatment and disposal of sludge account for 40–50% of the costs of the wastewater treatment process (Liu et al., 2016). Enhancing the dewaterability and reducing the solid content of sludge production have proven to be effective methods to reduce

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the water content and volume of sludge (Qi et al., 2011; Liang et al., 2015; Liu et al., 2016). Therefore, the characteristic of sludge dewatering and the volume of the sludge are extremely important factors in the activated sludge process. In previous studies, we have demonstrated that the flocculation and aggregation ability of microaggregates are affected by NPs (You et al., 2016; Hou et al., 2016b). Generally, the dewaterability of microbial aggregates is related positively to their flocculation and aggregation ability. In addition, a number of researches have focused on pretreatment methods (e.g., the Fenton-like process, microwave-acid, enzymatic lysis, and advanced oxidation processes) to improve sludge dewaterability (Liu et al., 2016; He et al., 2015; Chen et al., 2015; Li et al., 2016). However, few studies have investigated the effects of NPs on the dewaterability of the sludge.

Reports have indicated that mainly three limiting factors affect the dewatering of biosludge, namely, low settleability of microbial aggregates, high compressibility of the sludge solid particles, and the high affinity of extracellular polymeric substances (EPS) to trapping the water molecules they contain (Mowla et al., 2013). Among these factors, EPS, which acts as a gel-like matrix that binds the cells together and accounts for 80% of the total sludge mass (You et al., 2015; Zhang et al., 2016), is the most significant factor in sludge dewatering (Chen et al., 2015; Mikkelsen and Keiding, 2002). The EPS substances can be divided into soluble EPS (S-EPS) and bound EPS (Yu et al., 2008), of which the latter has a dynamic double-layered structure, with an outer region of loosely bound EPS (LB-EPS) and an inner region of tightly bound EPS (TB-EPS) (Hou et al., 2016b). Yu et al. (2008) and Liu and Fang (2003) pointed out that the chemical composition and distribution of EPS significantly affected sludge dewaterability. Moreover, the EPS content is closely related to sludge dewatering; therefore, optimal EPS content facilitates maximum dewaterability for each type of sludge (Chen et al., 2015; Zhang et al., 2015). According to Li and Yang (2007), the role of LB-EPS in sludge dewaterability is more important than is that of TB-EPS, and excessive LB-EPS could affect dewaterability negatively. As regards the main components in EPS, the protein (PRO) is more strongly related to sludge dewatering than is polysaccharide (PS) (Liu and Fang, 2003; Zhang et al., 2015). This is ascribed to PRO being a major contributor to the sludge structure and the entrapment of water (Mikkelsen and Keiding, 2002). In addition, the release of bound water (BW) retained in the EPS structure is important in enhancing dewaterability due to the degradation mechanism of EPS (Liang et al., 2015). Therefore, mechanistic study on sludge dewatering, especially of the characteristics of EPS, could be beneficial in the treatment of sludge. Different concentrations of NPs could probably affect the production and composition of EPS differently (Hou et al., 2016b; You et al., 2015). However, to the best of our knowledge, scarcely any research has been conducted on the potential mechanism of dewatering of sludge in terms of EPS in the presence of NPs.

Here, as in our previous studies (Xu et al., 2016; You et al., 2015, 2016), CeO_2 NPs were chosen as the model NPs. Single-factor tests, containing different levels of CeO_2 NPs, were conducted to explore the effects of CeO_2 NPs on sludge dewatering in a series of parent sequencing batch reactors (SBRs). The objectives of this study are (1) to investigate the effects of CeO_2 NPs on the sludge dewatering performance and the BW content; (2) gain comprehensive insight into the dynamic variations in distribution and composition of EPS conditioned with CeO_2 NPs; (3) gain a deep understanding of the dewatering mechanism in terms of the activity of hydrolytic enzymes in sludge, key organic matters in EPS, and floc morphology; and (4) explore further the potential relationship between sludge dewaterability and EPS properties.

2. Materials and methods

2.1. CeO_2 NPs and sludge culturing

We purchased CeO_2 nanopowder from Sigma-Aldrich (St. Louis, MO, USA) for use in our experiments. The CeO_2 NPs used here are similar to those used in our previous studies (You et al., 2015, 2016). Detail information on the properties of the NPs is provided in the Supplementary Material. The activated sludge was collected from a second sedimentation tank of the Jiangning Municipal Wastewater Treatment Plant in Nanjing, China. The activated sludge was cultured in a parent SBR, and six laboratory-scale parent SBRs with a working volume of 2 L were employed in the experiments. The SBRs were uniformly operated daily in 8-h cycles, including a 3.5-h aeration period and a 1.5-h anaerobic period, 1-h of settling, 10-min of effluent withdrawal, and a 110-min idle period (You et al., 2016). Additional details on the sludge culturing methods and the SBR operation are provided in the Supplementary Material. After acclimatization lasting approximately 90 days, the chemical oxygen demand, total nitrogen, and total phosphorus removal efficiency reached the steady state at averages of 90.63%, 78.42%, and 93.15%, respectively. Before proceeding to the exposure experiment, the mature sludge was washed through 0.4-mm sieves to remove large particles.

2.2. Exposure experiment and EPS extraction

To explore the effects of the CeO_2 NPs on sludge dewatering, six concentrations of CeO_2 NPs were employed. A suspension of 0.1 mg/L CeO_2 NPs was designed as the lowest concentration. In view of the rapid development and growth in the use of NPs and some other models of entry (i.e., accidental release from a production facility), a concentration of 50 mg/L CeO_2 NPs was prepared also (You et al., 2016). To conduct the experiment, 1 L of the synthetic wastewater (double the culturing concentration) was fed into each reactor. Thereafter, a stock solution of 500 mg/L CeO_2 NP was prepared, and subsequently stock solution volumes of 0, 0.4, 4, 20, 80, and 200 mL were injected into the reactors. Deionized water was added to yield a final volume of 2 L in the SBRs. The test solutions for short-term exposure included the following concentrations, namely, control (received no CeO_2 NPs), 0.1, 1, 5, 20, and 50 mg/L. The time was recorded after the addition of the CeO_2 NPs. The short-term exposure experiment lasted 24 h (three cycles). The volume of synthetic wastewater added in each cycle was calculated based on the residual concentrations of C, N, and P in the liquid at the end of each previous cycle in accordance with Fang et al. (2012). After the exposure experiment, the sludge samples in each reactor were collected and prepared for further measurements.

The S-EPS, LB-EPS, and TB-EPS were extracted using a process that included centrifugation, sonication, and thermal extraction (You et al., 2015; Zhang et al., 2016). Approximately 25 mL of sludge samples were placed in 50-mL centrifuge tubes, mixed with distilled water to form a 50-mL suspension, and subsequently centrifuged at 3000 g for 10 min. The supernatant was collected as S-EPS. The sediments at the bottom of the centrifuge tubes were re-suspended in a 0.05% (w/w) NaCl solution, and then sonicated at 20 kHz for 2 min. Afterwards, the suspensions were horizontally vibrated in a thermostat incubator at 150 rpm for 15 min. The liquid was centrifuged at 8000 g for 10 min and the supernatant was collected as the LB-EPS. The residual sediments were re-suspended at their initial volume, again using a 0.05% (w/w) NaCl solution, sonicated at 20 kHz for 2 min, and subsequently heated at 60 °C for 30 min. The suspension was centrifuged at 12 000 g for 20 min, and the supernatant was collected as the TB-EPS. Finally, all the EPS fractions were filtered through 0.45-μm acetate cellulose