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Acute and chronic responses of macrophyte and microorganisms in constructed wetlands to cerium dioxide nanoparticles: Implications for wastewater treatment

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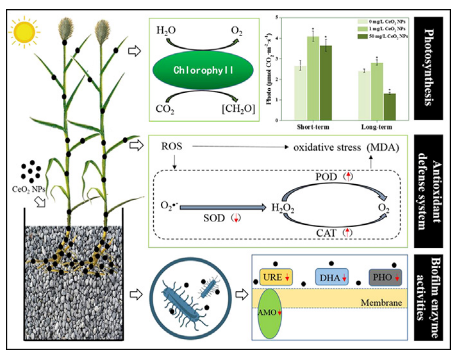
HIGHLIGHTS

- The CW substrate was the main sink of CeO_2 NPs.
- 1 and 50 mg/L CeO_2 NPs promoted and inhibited plant photosynthesis, respectively.
- CeO_2 NPs induced acute oxidative stress to plants, with no obvious chronic effect.
- CeO_2 NPs inhibited microbial enzyme activities and changed the microbial community.
- CeO_2 NPs lowered contaminant removal efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

The extensive release of cerium dioxide nanoparticles (CeO_2 NPs) causes increasing potential health and environmental risks. In this study, acute and chronic responses of macrophyte and microorganisms were evaluated following exposure to CeO_2 NPs in constructed wetlands (CWs). It was found that most of the CeO_2 NPs were retained in the CW substrate, with minor amounts accumulated in plant tissues. Photosynthetic activity experiment indicated that environmentally relevant concentration (1 mg/L) of CeO_2 NPs enhanced the net photosynthesis rate of plants, while chronic exposure to a high concentration (50 mg/L) of CeO_2 NPs inhibited photosynthesis. The variations of the malondialdehyde (MDA) content and antioxidant enzyme activities in plant tissues revealed that acute exposure to CeO_2 NPs induced oxidative stress to plants, while there was no obvious chronic effect. Moreover, the biomass increased marginally under exposure to 1 mg/L CeO_2 NPs, whereas exposure to 50 mg/L CeO_2 NPs reduced the total biomass of plants by 29%. The release of lactate dehydrogenase (LDH) suggested that chronic exposure to CeO_2 NPs inhibited microbial viability. Metagenome and enzymatic activities analyses further revealed that CeO_2 NPs significantly changed the microbial community structure and inhibited the activities of dehydrogenase, urease, ammonia monooxygenase, and phosphatase. This resulted in the decline of contaminant removal efficiency. Overall, acute and chronic exposure to CeO_2 NPs had multiple effects on macrophyte and microorganisms in CWs, which significantly impacted the treatment performance of the ecological system.

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1. Introduction

With the rapid development of nanotechnology, engineered nanomaterials (ENMs) with specific physical and chemical characteristics have been increasingly manufactured into commercial and industrial products over the past decade [1]. Among these ENMs, cerium dioxide nanoparticles (CeO_2 NPs) have been widely applied in catalysts, physicochemical polishing agents, coatings, and fuel additives [2]. The direct or indirect utilization of these products will inevitably result in the release of CeO_2 NPs into soil, sewage sludge, wastewater, surface water, and even ocean [3–6], which have raised great concerns concerning their potential adverse impacts on human beings and environment [7].

Due to the existence of CeO_2 NPs in sludge and soil, the impacts of CeO_2 NPs on plants have been an essential field of environmental impact assessment. Previous studies have found that the effects of CeO_2 NPs on plants depend on the plant species and treatment conditions. For instance, Gui et al. [8] showed that lettuce grew obviously faster than the control under a 30-day exposure to 100 mg/kg CeO_2 NPs, while 1000 mg/kg CeO_2 NPs inhibited plant growth and decreased biomass production. Cao et al. [9] reported that exposure to 100 mg/kg CeO_2 NPs (uncoated and polyvinylpyrrolidone (PVP) coated) for three weeks facilitated soybean plant growth and enhanced the photosynthesis rate, whereas the photosynthesis rate decreased in a treatment with 500 mg/kg CeO_2 NPs. It has been reported that CeO_2 NPs could protect plants from abiotic stress by relieving the oxidative stresses [10,11]. While, a large accumulation of CeO_2 NPs in plant tissues could induce adverse effects on plants by means of DNA damage and oxidative stresses [8,12]. Currently, the phyto-impact of CeO_2 NPs is mostly focused on terrestrial plants. However, the impacts of CeO_2 NPs on aquatic macrophytes are still unclear.

In recent years, there have been an increasing number of studies concerning the influences of CeO_2 NPs on microorganisms. Pelletier et al. [13] observed that exposure to CeO_2 NPs inhibited the growth and viability of model bacteria-*Escherichia coli* and *Shewanella oneidensis*, whereas it had no obvious impact on *Bacillus subtilis*. Similarly, Roh et al. [14] found that the application of CeO_2 NPs induced ecotoxicity on *Caenorhabditis elegans* in terms of both fertility and survival. To the best of our knowledge, the inhibition of microbial viability and activity will undoubtedly induce adverse influences on the treatment performance of biological wastewater treatment systems. It has been reported that exposure to 30 mg/L CeO_2 NPs had no significant influence on the ammonia nitrogen (NH_4^+-N) removal, whereas it reduced the chemical oxygen demand (COD) removal efficiency and slightly enhanced the soluble orthophosphate (SOP) removal efficiency in a sequencing batch reactor (SBR) [15]. Xu et al. [16] reported that 0.1 mg/L CeO_2 NPs had no obvious impact on the total nitrogen (TN) removal, while the treatment efficiency was reduced to 53% under exposure to 10 mg/L NPs in a sequencing batch biofilm reactor (SBBR). Xu et al. [17] further found that 0.1 mg/L CeO_2 NPs had no obvious impact on the total phosphorus (TP) removal after an 8 h of operation, whereas it was reduced by 30% under exposure to 20 mg/L CeO_2 NPs in an SBBR. With regard to the effects of CeO_2 NPs on wastewater treatments, previous studies mainly focused on biological treatment processes, such as SBR and SBBR, in which the nutrient removal mainly attributed to the role of microorganisms. However, research concerning the impacts of CeO_2 NPs on ecological wastewater treatment technologies is still in its infancy.

As a decentralized and cost-effective ecological wastewater treatment technology [18], constructed wetlands (CWs) are widely used to dispose of wastewater that potentially contains NPs [19,20]. Contaminants can be removed under the cooperation of microorganisms, plants, and substrate according to physicochemical and biological processes [21,22]. As an inorganic pollutant, NPs can be adsorbed on the biofilm covering the gravel and the surface of plant roots or even be absorbed by plants, and finally be efficiently removed from wastewater [23,24]. Meanwhile, the accumulation of NPs in wetlands may induce toxicological impacts [25]. Thus, previous studies regarding the effects of NPs on biological wastewater treatment systems are quite difficult to extrapolate to CWs. A previous study reported that a three-month exposure to Ag NPs had no effect on COD removal, whereas it reduced the removal efficiencies of TN, NH_4^+-N, and TP. Furthermore, the microbial community structure was shown to be significantly changed in vertical subsurface flow CWs [26]. Previous studies mainly focused on the impacts of Ag NPs on treatment performance and microbial community in CWs. However, as far as can be ascertained, there have not been any studies on the fate of CeO_2 NPs in CWs, and the time effects of CeO_2 NPs on functionalities of CWs are not known. Furthermore, very few studies have investigated the acute and chronic responses of physiological functions of wetland plants and microorganisms to CeO_2 NPs in CWs.

The present predicted environmental concentration of CeO_2 NPs in wastewater is at the level of μg/L [27], whereas the actual CeO_2 NPs concentration may reach mg/L level, because industrial effluent containing high concentration of CeO_2 NPs may flow to wastewater treatment systems. Additionally, owing to the increasing manufacture and massive usage of CeO_2 NPs, the concentration of CeO_2 NPs will be inevitably higher in the future. Meanwhile, due to the accumulative effect of NPs on the biofilm of CWs, the actual concentration of CeO_2 NPs is higher than that of influent. Thus, in this study, environmentally relevant concentration (1 mg/L) and a possible high concentration (50 mg/L) of CeO_2 NPs are used to investigate: (a) distribution and translocation of CeO_2 NPs in CWs; (b) physiological and growth impacts of CeO_2 NPs on plants; (c) acute and chronic effects of CeO_2 NPs on microbial community and activity; and (d) acute and chronic effects of CeO_2 NPs on the wastewater treatment performance of CWs.

2. Materials and methods

2.1. NP suspension and synthetic wastewater

Commercial CeO_2 NPs (powder, purity: > 99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The primary particle size of CeO_2 NPs is < 25 nm (BET data). To obtain a 400 mg/L CeO_2 NP stock suspension, 400 mg of CeO_2 NPs was added into 1 L of synthetic wastewater by ultrasonication (1h, 25 °C, 250 W, 40 kHz) before the experiment, based on a method used in a previous study [28]. According to a dynamic light scattering (DLS) analysis via a Malvern Autosizer 4700 (Malvern Instruments, Malvern, UK), the particle size measured in the stock suspension was in the range of 70–100 nm. The synthetic wastewater was simulated to represent the influent of wastewater treatment plants (WWTPs), with the composition provided in the text S1 of Supporting Information (SI). The initial concentrations of COD, TN, NH_4^+-N, and TP in the synthetic wastewater were approximately 200, 45, 35, and 10 mg/L, respectively.

2.2. Set-up of CW microcosms and sample collection

Nine sequencing batch CW microcosms (length: 0.3 m, width: 0.3 m, height: 0.5 m), with a pore volume of 12 L, were situated on Chongqing University campus, Chongqing, China. Three types of CWs, each in triplicate, were set as follows: W0 (0 mg/L NPs), W1 (1 mg/L NPs), and W2 (50 mg/L NPs). Each of the wetland microcosms was planted with *Phragmites australis* (*P. australis*). All the microcosms were saturated - with gravel (*Φ*: 8–10 mm, porosity: 0.4, height: 0.4 m). The water surface was 5 cm below the gravel bed. The wetland microcosms were seated in an air-conditioned greenhouse, ensuring a temperature of 25 ± 1 °C. Details of the microcosm design were reported in our previous study [29].

Prior to the beginning of the experiment, wetland microcosms were fed with synthetic wastewater without NPs for 6 months until the operation reached steady state. The formal experiment started on 15 July