



# Accelerated effects of nano-ZnO on phosphorus removal by *Chlorella vulgaris*: Formation of zinc phosphate crystallites

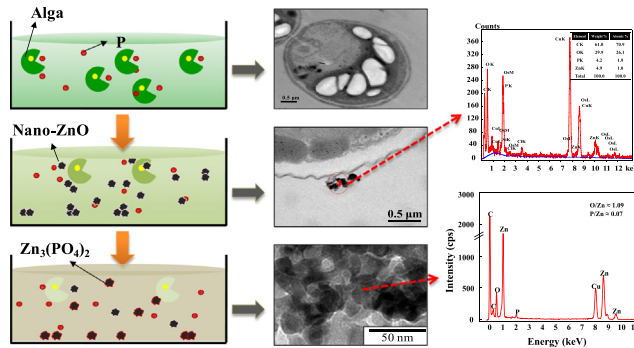
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## HIGHLIGHTS

- High concentrations of nano-ZnO accelerated phosphorous removal by algae.
- Formation of  $Zn_3(PO_4)_2$  crystallite was the main reason for phosphorous removal.
- Interaction of  $PO_4^{3-}$  with nano-ZnO promoted  $Zn_3(PO_4)_2$  crystallite formation.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 1 February 2018  
Received in revised form 25 March 2018  
Accepted 1 April 2018  
Available online 24 April 2018

Editor: Baoliang Chen

### Keywords:

Nano-ZnO  
Phosphorus removal  
Crystallites  
Algae

## ABSTRACT

Nanoparticles have been reported to induce toxicity to aquatic organisms, however, their potential impacts on phosphorus removal from wastewater by algae are unclear. In this study, the effects of nanoparticle ZnO (nano-ZnO) on phosphate ( $PO_4^{3-}$ ) removal by a green alga *Chlorella vulgaris* were investigated. We found that  $PO_4^{3-}$  removal efficiency was accelerated with high concentrations of nano-ZnO (0.04–0.15 mM) but reduced with low concentrations of nano-ZnO (0.005–0.04 mM) compared to the control (without nano-ZnO), suggesting that  $PO_4^{3-}$  removal efficiency by *C. vulgaris* was related to nano-ZnO concentrations. Moreover, we observed changes of nano-ZnO morphology and detected element P on the surface of nano-ZnO by using transmission electronic microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX), indicating that  $PO_4^{3-}$  was interacted with nano-ZnO or the dissolved  $Zn^{2+}$  from nano-ZnO. Furthermore, we confirmed this interaction induced the formation of  $Zn_3(PO_4)_2$  crystallites sedimentation by employing X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS), which finally accelerates the removal of  $PO_4^{3-}$ .

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## 1. Introduction

Human activities have increased the input of phosphorus into aquatic ecosystem, which potentially causing eutrophication in natural water bodies and disturbing of ecological balance (De-Bashan and

Bashan, 2004; Karageorgiou et al., 2007). For these reasons, China issued the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB 18918-2002) which limits the phosphorus concentration allowable in treated municipal wastewater (Grade I-A: <0.5 mg/L) (Li et al., 2012). In order to avoid irreversible ecological problems, various efforts such as chemical precipitation, adsorption, biological treatment etc. have been carried out to remove phosphorus (Beuckels et al., 2015; Galvagno et al., 2016; Wang et al., 2016). Among these treatments, algae-based biotechnology is considered to

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be an environment-friendly approach to wastewater treatment due to its high phosphorus removal efficiency, low operational cost, lack of organic carbon requirement, potential for recycling assimilated P into algal biomass as fertilizer, etc. (Aslan and Kapdan, 2006). The main mechanisms of phosphorus removal by algae are considered as a combination of biological assimilation and abiotic precipitation owing to the elevated of pH (Wang and Lan, 2011). Besides, phosphorus adsorption by algal extracellular polymeric substances (EPS) is another mechanism for the phosphorus removal (Chen et al., 2015).

Recently, nanoparticles, such as nano-ZnO, nano-Al<sub>2</sub>O<sub>3</sub>, nano-TiO<sub>2</sub> etc., have been extensively used. They are frequently detected in sewage and wastewater treatment plants (WWTPs), which affects wastewater biological nutrient removal efficiency (Chen et al., 2012a; Ma et al., 2013; Zheng et al., 2011a). Among these nanoparticles, nano-ZnO particles have aroused much attention because of their dissolution behavior and potential toxicity to aquatic organisms (Manzo et al., 2013; Odzak et al., 2014; Suman et al., 2015). For example, nano-ZnO can depress algal growth even at a low concentration of 60 µg Zn/L (72-h IC<sub>50</sub> value) (Franklin et al., 2007). In fact, the zinc ion (Zn<sup>2+</sup>) released from nano-ZnO has been considered to be the main reason to induce the toxicity to aquatic organisms (Franklin et al., 2007; Miller et al., 2010). These studies mainly focused on the toxicity of nano-ZnO to cell growth (Bhuvaneshwari et al., 2015; Suman et al., 2015), however, the potential effects of nano-ZnO or the dissolved Zn<sup>2+</sup> on phosphorus removal by algae are unknown. Several researchers have investigated the effects of nanoparticles on phosphorus removal by activated sludge (Chen et al., 2012a; Zheng et al., 2011a; Zheng et al., 2011b). For example, Zheng et al. (2011b) found that concentration of phosphorus increased from nondetectable to 10.3 and 16.5 mg/L in effluent with high concentrations of nano-ZnO (10 and 50 mg/L, respectively), which were higher than that in influent (9.8 mg/L), indicating nano-ZnO induced the loss of normal phosphorus removal. However, studies revealed that after long-term exposure to nano-Cu (Chen et al., 2012b) or nano-TiO<sub>2</sub> (Zheng et al., 2011a), biological phosphorus removal by activated sludge was unaffected. Up to date, although the effects of several nanoparticles on phosphorus removal by activated sludge have been studied, the potential effects of nanoparticles on phosphorus removal by algae in waste water treatment remain unknown.

When coexisting with other contaminants in the practical wastewater, there is no doubt that nano-ZnO causes a significant change in Zn speciation. For example, Lombi et al. (2012) discovered that zinc, including native Zn in “fresh” biosolid and added nano-ZnO, converted to ZnS, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and cysteine-bound Zn during anaerobic digestion of wastewater by means of X-ray absorption near edge structure spectroscopy technology. Lv et al. (2012) found nano-ZnO partly transformed into Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in presence of phosphate by employing X-ray diffraction analysis and transmission electronic microscopy method. For natural nano-materials, Fe-(hydr)oxides in soil play an important role in the adsorption of nutrient anions such as phosphate (Theng and Yuan, 2007). Since the  $k_{sp}$  of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is extremely low ( $k_{sp} = 9.1 \times 10^{-33}$ ), it is prone to form Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> precipitation when Zn and phosphate coexisted. Thus, phosphorus removal in the presence of nano-ZnO will be different from that in absence of nano-ZnO. This indicates that besides adsorption of EPS and biological assimilation, Zn and phosphate would generate chemical precipitation to accelerate phosphate removal in algal system.

Based on the above background, by choosing a green alga *C. vulgaris* as the tested target, we investigated the effects of nano-ZnO on phosphate removal efficiency by the algae. First, removal efficiency of PO<sub>4</sub><sup>3-</sup> by the algae under different concentrations of nano-ZnO was compared. To elucidate the possible mechanism of the interaction between Zn<sup>2+</sup> dissolved from nano-ZnO and PO<sub>4</sub><sup>3-</sup> in the algal system, we employed the Fourier transform infrared spectroscopy (FTIR), TEM-EDX, XRD, and XPS to analyze the micromorphology and structural composition of possible Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> crystallite. Results of this work are expected to evaluate the effects of nano-ZnO on phosphorus removal by algae.

## 2. Materials and methods

### 2.1. Nano-ZnO particles and their dispersion

In the present study, nano-ZnO was purchased from Aladdin Industrial Corporation (particle size: 30 ± 10 nm, purity: 99.9%). Stock solutions of nano-ZnO were prepared by dispersing 0.16 g dry powders into 100 mL ultrapure water to the final concentration of 0.02 M, and then sonication for 20 min at 300 W. It is noteworthy that sonication should be carried out in an ice bath to prevent the temperature rising. The stock solutions were properly diluted to 0.005, 0.01, 0.02, 0.04, 0.08, and 0.15 mM. The suspensions were vortexed briefly before the test.

The primary particle size and morphology were observed by TEM (JEM-2100, JEOL, Japan). The crystallinity and purity of the particles were assessed using an XRD (D/max-2550VK/PC, Rigaku, Japan). The specific surface area of nano-ZnO was analyzed by method of Brunauer, Emmett and Teller (BET, NOVA2200e, Quantachrome Ins, U.S.). In fact, it's possible to calculate what is called the 'BET radius' (r) through the following equation (Roelofs and Vogelsberger, 2004).

$$r = 3/S_{BET} \cdot \rho$$

Here, S<sub>BET</sub> is the specific surface area of particles measured by the BET method, ρ is the particle density.

Hydrodynamic diameters of the particles after being sonicated in ultrapure water with the particle concentration of 1 mM were measured using dynamic light scattering (DLS) method. Samples were measured at a temperature of 25 °C, and the size distribution of ZnO particles was measured every 24 h in 7 days. All the characterization results of nano-ZnO are presented in supplementary material.

### 2.2. Dissolution behavior of nano-ZnO

The modified OECD medium (OECD, 2006) used in this study was prepared. Because phosphorus occurs in wastewater mainly as phosphate, including organic phosphate, inorganic phosphate (orthophosphate) and polyphosphate (particulate P) (Biswas et al., 2007; Huang et al., 2013; Zeng et al., 2004). Thus, KH<sub>2</sub>PO<sub>4</sub> was used as the sole phosphate source in this study. Additionally, NH<sub>4</sub>Cl was used as the sole nitrogen source. Here, the concentration of ammonia nitrogen (NH<sub>4</sub><sup>+</sup>) and the orthophosphate (PO<sub>4</sub><sup>3-</sup>) of standard OECD medium was turned into 10 and 2 mg/L using NH<sub>4</sub>Cl and KH<sub>2</sub>PO<sub>4</sub>, respectively, and other components were the same as the standard OECD medium. Since nano-ZnO particles can partially dissolve, the solubility of nano-ZnO in ultrapure water and modified OECD medium were evaluated by analyzing the Zn<sup>2+</sup> content using atomic absorption spectrophotometer (AAS, AA-6300C, SHIMADZU, Japan). Different concentrations of nano-ZnO suspensions were obtained by diluting the stock suspensions with ultrapure water and modified OECD, respectively. Next, the samples at different time intervals were centrifuged at 10000g for 30 min. After that, the supernatants were filtered with a 0.22 µm mixed cellulose ester membrane. Finally, the filtrate was determined using AAS at 213.7 nm. Zinc remaining in the supernatants was considered as dissolved Zn<sup>2+</sup> from nano-ZnO (Jiang et al., 2009; Lin and Xing, 2008; Wu et al., 2010a). Besides, the concentrations of Zn<sup>2+</sup> from Zn(NO<sub>3</sub>)<sub>2</sub> in ultrapure water and modified OECD medium were also determined.

### 2.3. Algal culture and growth

The green alga *C. vulgaris* F1068 used in present study was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences. The *C. vulgaris* cells were cultured at pH 7.1 in sterile standard OECD medium. All glasswares were acid-washed, rinsed with ultrapure water, and then autoclaved at 120 °C for 30 min. Algal cells in the exponential growth phase (on the 4th day) were inoculated in Erlenmeyer flasks (250 mL) containing 100 mL the standard OECD medium. All cultures

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