Adsorption of cadmium on cerium oxide nanoparticles and oyster shells

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Abstract. This study investigated the adsorption of cadmium (Cd(II)) by cerium oxide nanoparticles (CeO₂ NPs) and oyster shells in seawater. The results showed that the addition of Cd(II) significantly inhibited the agglomeration of CeO₂ NPs both in DI water and seawater, increased the positive charges of CeO₂ NPs in DI water and neutralized the negative charges of CeO₂ NPs in seawater. Additionally, CeO₂ NPs could adsorb Cd and the bioavailability of Cd was reduced in the presence of oyster shells. This study demonstrated that the adsorption of metals on shells should not be neglected for the accumulation of metals by shellfish.

1. Introduction
With the rapid development of nanotechnology, nanoparticles (NPs) will be inevitably released into environment [1], and eventually converge to the sea. Therefore, the evaluation of the impact of NPs on marine organisms is particularly important [2]. Metal oxides NPs, such as ferric oxides, aluminum oxides, titanium oxides, and cerium oxides NPs, provide high surface area and specific affinity for heavy metals adsorption from aqueous systems [3]. Among them, cerium oxide (CeO₂) NPs are widely applied in energy, medical, catalysis, cosmetics, lubricants, building glass, and electronics fields due to their excellent photochemical properties, catalytic activity and unique mechanical properties [4, 5]. It is reported that the concentration of CeO₂ NPs in the sediments was about 10³ μg/L [6]. Studies showed that CeO₂ NPs could adsorb metal ions mainly by electrostatic attraction [7, 8], thus affecting the transport and fate of metal ions.

Shellfish are often used as indicators of marine metal pollution because of their strong accumulation of metals. Some studies noted that metal oxides NPs could adsorb heavy metals, and thus induced different accumulation and toxicity compared with single pollutant exposure [9-11]. But the shellfish shells may also adsorb metals in the sea, which will have a negative impact on the bioavailability of metals to shellfish [12]. Therefore, it is very important to investigate the effect of shells on the accumulation of heavy metals.

2. Materials and methods

2.1 Materials
Oysters were purchased from Xiaogang Fisheries Market, Qingdao, China, then the soft tissues were removed to clean the shell with tap water. CeO₂ NPs with particle diameter of 25 nm were purchased...
from Sigma-Aldrich. The morphology of CeO$_2$ NPs was characterized by transmission electron microscopy (TEM, H-7650, Hitachi, Japan). Seawater used in this experiment was collected from Stone old beach, Qingdao, then filtered through mixed fiber membrane (0.45 μm). 4 mg/L Cd(II) stock solution was prepared from CdCl$_2$·2.5H$_2$O, then diluted to a range of concentrations. The hydrodynamic diameter and zeta potential of CeO$_2$ NPs were measured by Zetasizer (Nano ZS90, Malvern, UK).

2.2 Adsorption of Cd on CeO$_2$ NPs
400 μg/L Cd(II) was prepared by diluting the stock solution with seawater. 0.20 mg CeO$_2$ NPs was added in glass vials, and then mixed with 40 mL of 400 μg/L Cd(II). The solutions were sonicated for 30 min (100 W, 40 kHz) and then placed on a shaker (150 rpm, 25°C). At 0.5, 1, 3, 6, 12, 24, and 48 h, the vials were centrifuged at 4000 rpm for 20 min, and the supernatants were pipetted to determine Cd(II) concentration by ICP-MS (NexION 350).

2.3 Oyster shells exposure experiment
Oyster shells were exposed 400 μg/L Cd(II) tanks containing 6 L seawater in the presence and absence of 5 mg/L CeO$_2$ NPs. Eight oyster shells of similar size were placed in each tank (Fig. 1a). Under full aeration condition, the upper surface seawater was pipetted from the tank at 0, 1, 3, 5, and 7 d to determine the concentration of free Cd(II) in seawater.

2.4 Statistical analysis
Results were analyzed statistically by Data Processing System (DPS). When analyzing the variance treatment effect (p < 0.05), the least standard deviation (LSD) test was applied to make comparison between means at the 0.05 levels of significance.

3. Results and discussion
The morphology of CeO$_2$ NPs was observed by TEM (Fig. 1b). It showed irregular diamond shapes and spheres with particle size of 25 nm, which was consistent with the manufacturer. But CeO$_2$ NPs showed significant aggregation and the hydrodynamic diameter increased to 500 nm and 2000 nm within 120 min in DI water and seawater, respectively (Fig. 2a). This indicated that CeO$_2$ NPs was easy to generate large agglomerates, especially in the seawater because of the high ionic strength. However, the addition of Cd(II) significantly reduced the hydrodynamic diameter of CeO$_2$ NPs both in DI water and seawater, and inhibited the agglomeration, especially in DI water (Fig. 2a). It was supposed that CeO$_2$ NPs adsorbed Cd(II) and occupied the agglomeration sites of CeO$_2$ NPs, thus inhibiting the formation of large agglomerates.

![Fig. 1](image-url) (a) Picture of oyster shells during adsorption experiments; (b) TEM image of CeO$_2$ NPs
As shown in Fig. 2b, the zeta potential of CeO$_2$ NPs was significantly increased after the addition of Cd(II) in DI water, and this may be due to the increase of the positive charges caused by the Cd(II) adsorption. CeO$_2$ NPs was negatively charged in seawater and the zeta potential was significantly decreased after the addition of Cd(II) resulted from charge neutralization.
Fig. 2 The hydrodynamic diameter (a) and zeta potential (b) of CeO₂ NPs. The concentrations of CeO₂ NPs and Cd(II) were 5 mg/L and 400 μg/L, respectively. DW: DI water; SW: seawater. DW and SW were in the same pH condition at 8.1. ‘*’ and ‘a-b’ represent significant difference of zeta potential in DI water and seawater, respectively (P < 0.05).

Fig. 3 Adsorption of Cd(II) on CeO₂ NPs (a) and oyster shells (b). The concentrations of CeO₂ NPs and Cd(II) were 5 mg/L and 400 μg/L, respectively.

The adsorption of Cd(II) by CeO₂ NPs reached equilibrium at 24 h, and the adsorption rate was 21% (Fig. 3a). In the exposure experiment, as shown in Fig. 3b, the concentration of free Cd(II) in seawater gradually decreased with time in the absence of CeO₂ NPs, indicating Cd(II) was adsorbed by the shells. The adsorption rate of Cd(II) by oyster shells was about 20% in 7 d, and CeO₂ NPs addition decreased Cd(II) concentration further, leading to the bioavailability of Cd(II) reduce significantly in seawater.

4. Conclusions
CeO₂ NPs could adsorb Cd(II), inhibiting the agglomeration of CeO₂ NPs. Meanwhile, the addition of Cd(II) increased the positive charges of CeO₂ NPs in DI water and neutralized the negative charges of CeO₂ NPs in seawater. Additionally, oyster shells showed strong adsorption capacity toward Cd(II) and reduced the bioavailability of Cd(II) in seawater. This study highlights the significant effect of shells during the accumulation of metals by shellfish.

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