



Effects of Fe(II) on Cd(II) immobilization by Mn(III)-rich δ -MnO₂

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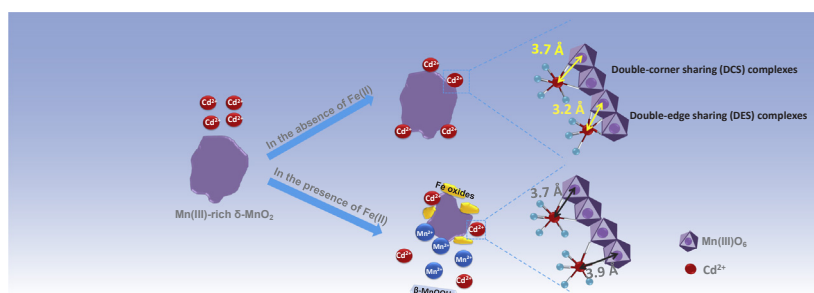
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HIGHLIGHTS

- Fe(II) decreased Cd(II) retention on Mn(III)-rich δ -MnO₂ at pH 5.5.
- Cd(II) was mainly adsorbed on Mn(III)-rich δ -MnO₂ rather than the newly formed Fe oxides and β -MnOOH.
- Fe(II) addition promoted Cd(II) desorption by altering the surface complexes Cd(II) formed on Mn(III)-rich δ -MnO₂.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese (Mn) oxides have high Cd(II) sorption affinities and could effectively immobilize Cd(II) in soil and aquatic systems. However, coexisting Fe(II) can react with Mn oxides at oxic-suboxic interfaces, thereby affecting Cd(II) immobilization by Mn oxides. Mn(IV)-rich Mn oxides in the environment are readily to be reduced to Mn(III)-rich Mn oxides by natural organic matter. Herein, we determined the effects of Fe(II) on Cd(II) immobilization by Mn(III)-rich δ -MnO₂ (denoted as HE-MnO₂) at pH 5.5 and 7.5. Results show that Fe(II) decreased Cd(II) retention on HE-MnO₂ at pH 5.5 but had no effects at pH 7.5 due to the high Cd(II) adsorption affinity of HE-MnO₂ at high pH. Poorly crystalline Fe oxides, likely ferrihydrite, uniformly precipitated on HE-MnO₂ surfaces upon Fe(II) addition at both pHs. β -MnOOH formed at the high initial Fe(II) concentration at pH 7.5. Cd(II) was mainly adsorbed on HE-MnO₂ rather than the newly formed Fe oxides and β -MnOOH which had low Cd(II) adsorption capacities. The decrease of Cd(II) sorption in the presence of Fe(II) could be explained by the reduction of HE-MnO₂, the precipitation of Fe oxides on HE-MnO₂, and the competition of generated Mn(II) for the sorption sites. Cd(II) formed double-corner sharing (DCS) and double-edge sharing (DES) complexes with Mn(III) edge sites on HE-MnO₂. After the addition of Fe(II), Cd(II) formed only DCS complexes with Mn(III) edge sites. The alternation of the surface complexes caused by Fe(II) promoted Cd(II) desorption from HE-MnO₂. This work suggests that Fe(II) can decrease the removal efficiency of Cd(II) by Mn(III)-rich δ -MnO₂ at oxic-suboxic interfaces in the environment.

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1. Introduction

As a nonessential element for human beings, cadmium (Cd) exposure from contaminated soils through food chain and dust would do harm to the liver and kidney, posing great threat to human health [1–3]. Mining wastes and industrial discharge are the main sources of Cd in soils [4–6]. Although the total Cd concentration is low in contaminated soils, the bioavailability of Cd(II) tends to be high because of its weak sorption to common components. However, Mn oxides have high sorption affinity for Cd(II) because of their large amount of negative charges and abundant structural defects [7,8]. Attempts have been made to use Mn oxides to mitigate Cd pollution [1]. Mn oxides effectively reduced Cd solubility and Cd accumulation in wheat [9].

Mn oxides play an important role in controlling the migration and transformation of trace elements and pollutants in the environment [10]. They are strong oxidants and readily reduced by redox-sensitive compounds, such as As(III), Fe(II), Mn(II) and S(II) in the environment [10–12]. The redox reactions can affect metal immobilization by Mn oxides [10,13–15]. Hinkle et al. [15] observed that Mn(II) decreased both Zn(II) and Ni(II) uptake by δ -MnO₂ at pH 4 and that both ions migrated from the interlayer to the edge sites. The effects of Mn(II) on Zn(II) and Ni(II) sorption correlated with Mn(II)-induced structural changes and the competition of Mn(II) for surface sites. Lefkowitz et al. [10] found that Mn(II) led to the desorption of Zn(II) from acid birnessite at pH 6.5, but enhanced Zn(II) sorption at pH 7.5 by the reaction with structural Mn(IV), generating Mn(III) which coprecipitated with Zn(II) and Mn(II) to form Zn-substituted hausmannite.

At oxidic-suboxic interfaces in the environment, Fe(II) is a common species and an important reductant for Mn oxides [11,12].

Both Fe(III) and Mn(II) ions, derived from partial reduction of Mn oxides by Fe(II), were adsorbed by Mn oxides [13] or precipitated as ferrihydrite, jacobsonite, lepidocrocite and goethite [13,14], depending on the reaction conditions. The sharp reaction between Mn oxides and Fe(II) indicates that Cd(II) immobilization by Mn oxides is likely to be affected by coexisting Fe(II). However, the ternary Fe(II)–Cd(II)–Mn oxides reaction system is essentially unknown and, to our knowledge, unstudied. Most studies focused too much on the sorption behavior of Cd(II) on Mn oxides. A differential pair distribution function (d-PDF) analysis carried out by Genuchten et al. [16] demonstrated that Cd(II) was adsorbed at the vacancy sites of δ -MnO₂. According to the relationship between Mn average oxidation state and Cd(II) sorption behavior, Cd(II) was assumed to be adsorbed at the interlayer of H⁺-birnessite [17]. Cd isotopic fractionation was observed in the process of Cd(II) adsorption by H⁺-birnessite [18]. Extended X-ray absorption fine structure (EXAFS) spectroscopy showed that Cd(II) was adsorbed to the external surface or migrated into the tunnels in the cryptomelane structure (KMn₈O₁₆) [19]. However, all these studies neglected the impact of Fe(II) on Cd(II) immobilization by Mn oxides. This omission raises important questions directly relevant to the fate of Cd immobilized by Mn oxides in the environments undergoing redox oscillations. In the present study, we thus investigated the effects of Fe(II) on Cd(II) immobilization by Mn oxides. The experiments were conducted at pH 5.5 and 7.5, representing the acidic and slightly alkaline conditions respectively. Higher pH values were not considered in this paper because Cd toxicity is not a serious concern in strongly alkaline environments.

Vernadite, a nanoparticulate layered Mn oxide rich in Mn(IV), is a reactive and abundant Mn oxide in soils and sediments [1,20]. Laboratory studies showed that its synthetic analogue, δ -MnO₂, is readily reduced by natural organic matter (NOM) and as a result, Mn(III) accumulated at the edge and/or vacant sites of δ -MnO₂ [21]. Considering the abundance of NOM, Mn(III)-rich vernadite is probably more common than Mn(IV)-rich vernadite in natural environment. However, despite being easily reduced by NOM in the natural environment, Mn(IV) oxides are often used as the representative Mn oxides in studies dealing with heavy metal immobilization. In this study, Mn(III)-rich δ -

MnO₂, prepared by reducing δ -MnO₂ using sodium 4-(2-hydroxyethyl) piperazine-1-ethanesulfonate (HEPES) (denoted as HE-MnO₂), which was more environmentally relevant, was used as the representative Mn oxide, to determine the effects of Fe(II) on Cd(II) immobilization. The reaction products were thoroughly characterized using X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and EXAFS spectroscopy, which could help to disclose, at the molecular scale, the changes in the coordination environments for Cd(II) immobilization by HE-MnO₂ induced by Fe(II). The results provide new insights into the processes governing Cd(II) immobilization by Mn oxides in environments undergoing redox oscillations.

2. Materials and methods

All chemicals used here were of analytical grade or purer. Ultrapure deionized water (> 18 M Ω -cm) was used for preparation of solutions and for rinsing.

2.1. The preparation of HE-MnO₂

HE-MnO₂ was obtained by equilibrating δ -MnO₂ in HEPES buffer. The Mn(III) proportions before and after the treatment were 4.5% and 34% respectively determined using pyrophosphate extraction. The detailed preparation and determination are described in [Supplementary Material \(SM\)](#). It has been reported that δ -MnO₂ generally contained about 14% vacancy sites in the layer, and the HEPES treatment led to 12% of Mn(III) and 2% of Mn(II) occupying the vacancy sites in the form of triple corner-sharing (TCS) complexes above the vacancy sites [22]. The remaining Mn(III) created by the HEPES treatment was located at edge sites instead of the interior of the sheets as supported by the EXAFS and pair distribution function analyses [22]. Our previous study showed that Mn species located at the particle edge sites were all Mn(III), accounting for about 22% of the total Mn [23].

2.2. Cd(II) sorption and desorption on HE-MnO₂ in the absence and presence of Fe(II)

Sorption experiments were carried out in N₂ atmosphere to inhibit Fe(II) oxidation by O₂. 150 mM Fe(II) stock solution and 50 mM Cd(II) stock solution were prepared by dissolving FeSO₄·7H₂O or Cd(NO₃)₂·4H₂O to deionized water under N₂ atmosphere and stored in the serum bottles. HE-MnO₂ suspension was prepared by dissolving a certain amount of HE-MnO₂ stock suspension in 50 mM NaNO₃, which was buffered at pH 5.5 and 7.5 with 50 mM 2-morpholinoethanesulfonic acid (MES) and HEPES respectively and the final Mn concentration was 16.7 mM. Once purged with N₂, the suspensions (30 mL) were transferred to sealed 100-mL serum bottles. Aliquots of Cd(II) and Fe(II) stock solution were added to the HE-MnO₂ suspension, yielding final Cd(II) concentrations at 0, 0.1 and 0.5 mM and Fe(II) concentrations at 0, 0.5 and 5.0 mM. The sample IDs are summarized in [Table S1](#). The suspensions were shaken at 28 °C on a reciprocal shaker. After 76 h, a 1 mL aliquot sampled from the suspension was filtered through a 0.22- μ m membrane and added with an equal volume of 1 M HCl for the determination of dissolved Fe, Cd and Mn concentrations. Fe(II) and Fe(III) concentrations were analyzed by UV-vis spectroscopy (UV-2700, Shimadzu, Japan). Dissolved Cd and Mn concentrations were determined using a flame atomic absorption spectrophotometer (Z-2000, Hitachi, Japan).

Desorption experiments were conducted to determine the lability of Cd(II) in the solids. At the end of the sorption experiments, the suspensions were centrifuged, the supernatants were decanted, and the solid phase was resuspended in 30 mL of 50 mM NaNO₃ solution buffered at pH 5.5 and 7.5 with 50 mM MES and HEPES, respectively. The suspensions were shaken at 28 °C on a reciprocal shaker. After 42 h, 1 mL aliquots were sampled from the suspensions for the measurement

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