

Effects of Cd on reductive transformation of lepidocrocite by *Shewanella oneidensis* MR-1

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Abstract We investigated the reduction of lepidocrocite (γ -FeOOH) by *Shewanella oneidensis* MR-1 in the presence and absence of Cd. The results showed that Cd^{2+} retarded microbial reduction of γ -FeOOH and avoided formation of magnetite. The inhibitory effect on γ -FeOOH transformation may not result from Cd^{2+} toxicity to the bacterium; it rather was probably due to competitive adsorption between Cd^{2+} and Fe^{2+} on γ -FeOOH as its surface reduction catalyzed by adsorbed Fe^{2+} was eliminated by adsorption of Cd^{2+} .

Keywords Lepidocrocite · Cadmium · Microbial reduction

Lepidocrocite (γ -FeOOH) is an iron oxide-hydroxide commonly found in paddy soils. It is thermodynamically unstable and can be transformed to magnetite (Fe_3O_4) by Fe^{2+} via a reaction of $\text{Fe}^{2+} + 2\gamma\text{-FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+$ (Sørensen and Thorling 1991), where Fe^{2+} is not only a reactant but also a catalyst. Recent studies showed that coexisting metal cations can variously inhibit Fe^{2+} -catalyzed γ -FeOOH transformation, but the inhibitory effects of Cd^{2+} have not been reported. This study examined the effects of Cd^{2+} on transformation of γ -FeOOH during its

reduction by *Shewanella oneidensis* MR-1 (MR-1), a well characterized iron reducer. The aqueous and adsorbed species of Fe^{2+} and Cd^{2+} were quantified and the solid phases were characterized. Our hypothesis was that Cd^{2+} could inhibit transformation of lepidocrocite to magnetite during microbial reduction.

Three batch bioreactor systems were initiated, including (1) γ -FeOOH with $0.45 \text{ mg} \cdot \text{L}^{-1}$ aqueous Cd^{2+} and live MR-1, (2) Cd-loaded γ -FeOOH with live MR-1, and (3) a Cd-free system containing γ -FeOOH and live MR-1. Control systems with killed (autoclaved) MR-1 were also set up for comparison. The reactors were serum bottles of 100 mL, and each contained 0.0889 g synthetic γ -FeOOH or Cd-loaded γ -FeOOH, 47.5 mL PIPES buffer solution, 20 mM sodium lactate, and 2.5 mL suspension of live ($\text{OD}_{600} = 2.0$) or killed MR-1 cells (Li et al. 2012). The Cd-loaded γ -FeOOH contained 0.019 mol% Cd, which included 25% MgCl_2 -extractable [considered as exchangeable (Poulton and Canfield 2005; Li et al. 2016)] Cd^{2+} . Each reactor was bubbled with filtered N_2 gas for 40 min, sealed, and incubated in a shaker at 120 rpm and 30 °C in the dark. Three triplicate reactors were sacrificed at a predesigned time for analyses of the aqueous and MgCl_2 -extractable Fe^{2+} and Cd^{2+} concentrations using the *o*-phenanthroline photometry method and ICP-OES, respectively.

Figure 1 presents the XRD patterns of the solid phases after reaction for 31 days. Magnetite was present only in the Cd-free system, and γ -FeOOH remained unchanged when Cd was present in either solution phase or γ -FeOOH.

Figure 2 shows the concentrations of both Fe^{2+} and Cd^{2+} in aqueous and adsorbed forms as a function of reaction in Cd-containing systems with either live or killed MR-1. In the presence of live MR-1, the aqueous Fe^{2+} concentration increased from 0 to $35 \text{ mg} \cdot \text{L}^{-1}$ within

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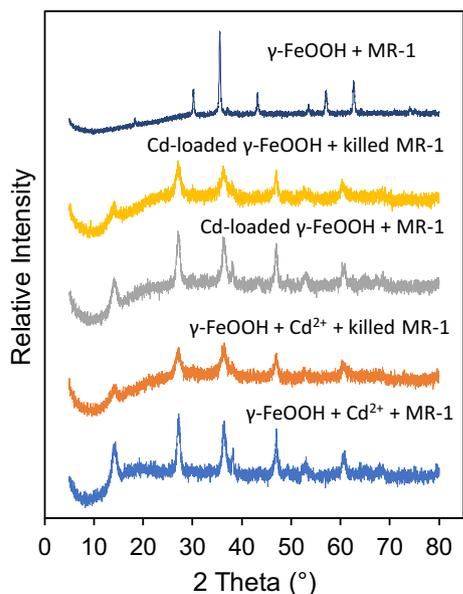


Fig. 1 XRD patterns of minerals on day 31. In the systems containing Cd, lepidocrocite was the only identifiable mineral, but in the system without Cd, magnetite was the identifiable mineral and lepidocrocite disappeared

3 days when Cd^{2+} was added as a background electrolyte and to approximately $60 \text{ mg} \cdot \text{L}^{-1}$ within 7 days when Cd^{2+} was added as an impurity bound to $\gamma\text{-FeOOH}$. In contrast, in the control Cd-containing systems with killed MR-1 the concentrations of aqueous Fe^{2+} were persistently low. This indicated that the aqueous Fe^{2+} in the live MR-1 systems was likely a product of biotic reduction of $\gamma\text{-FeOOH}$. The concentrations of MgCl_2 -extractable Fe^{2+} were consistently low in both Cd-containing systems with live or killed MR-1. However, in the Cd-free system with

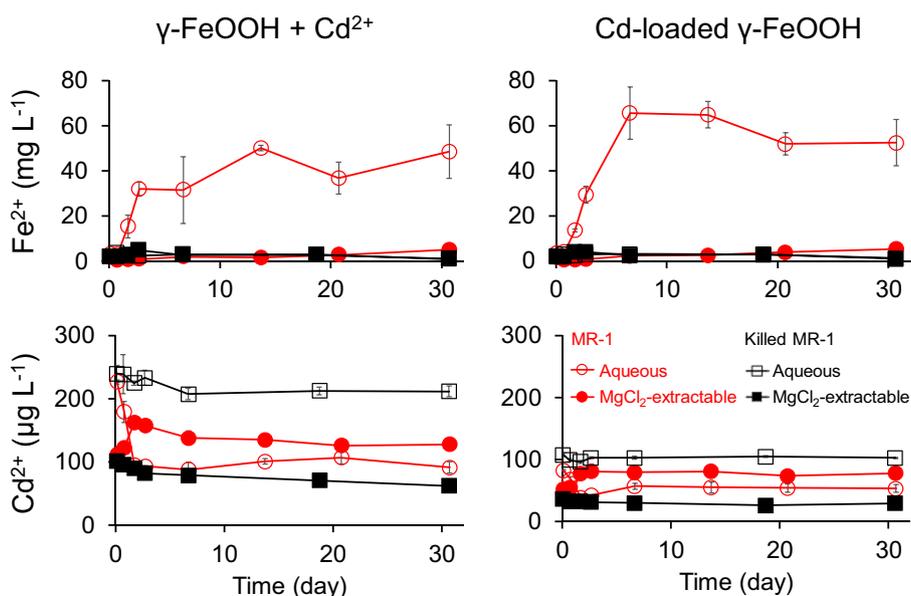
live MR-1, the aqueous and MgCl_2 -extractable Fe^{2+} were 140 and $10 \text{ mg} \cdot \text{L}^{-1}$, respectively, after reaction for 31 days. The high production of Fe^{2+} coupled with formation of magnetite indicated fast transformation of $\gamma\text{-FeOOH}$ by MR-1 in the absence of Cd.

In the systems with $\gamma\text{-FeOOH}$ and aqueous Cd^{2+} , the sum of aqueous and MgCl_2 -extractable Cd^{2+} decreased after 31 days by $120 \mu\text{g} \cdot \text{L}^{-1}$ when live MR-1 was added compared to only $67 \mu\text{g} \cdot \text{L}^{-1}$ when killed MR-1 was added (Fig. 2). In the systems with Cd-loaded $\gamma\text{-FeOOH}$, the sums of concentrations of aqueous and MgCl_2 -extractable Cd^{2+} on day 0 were around $130 \mu\text{g} \cdot \text{L}^{-1}$ and did not change after 31 days when either MR-1 or killed MR-1 was added.

The results showed the presence of Cd retarded $\gamma\text{-FeOOH}$ reduction by MR-1, but this might not be the reason for the absence of $\gamma\text{-FeOOH}$ transformation. Pedersen et al. (2006) found that $\gamma\text{-FeOOH}$ can be transformed to magnetite by $1.0 \text{ mM} \text{Fe}^{2+}$, which is close to the concentrations of aqueous Fe^{2+} produced in the systems with Cd and live MR-1. On the other hand, the high proportion of MgCl_2 -extractable Cd^{2+} in these systems indicated Cd^{2+} was adsorbed on the $\gamma\text{-FeOOH}$ surface. It is believed that the transformation of iron oxides during microbial reduction is catalyzed by Fe(II) produced, and the inhibition of coexisting metal cations including Cd^{2+} on Fe(II)-induced phase transformation has been reported for other iron (hydr)oxides (Li et al. 2016; Liu et al. 2016). The possible mechanisms include competition for adsorption sites on the surface of iron (hydr)oxides (Liu et al. 2016).

The results also show $\gamma\text{-FeOOH}$ reduction could result in immobilization of Cd in solution but no release of Cd incorporated in $\gamma\text{-FeOOH}$. The phase of $\gamma\text{-FeOOH}$ did not

Fig. 2 Time dependent concentrations of aqueous and MgCl_2 -extractable Fe^{2+} (upper) and Cd^{2+} (lower) in batch bioreactor systems containing $\gamma\text{-FeOOH}$ and Cd^{2+} (left) or Cd-loaded $\gamma\text{-FeOOH}$ (right) with live MR-1 (red circles) or killed MR-1 (black squares)



change in the presence of Cd (Fig. 1), but the shift of aqueous Cd^{2+} to MgCl_2 -extractable Cd^{2+} was observed (Fig. 2). Thus, it is likely that adsorption might be the mechanism for Cd immobilization in the tested systems. As iron reduction is a common biogeochemical process in flooded soils (such as paddy soils), improved understanding of the correlation between Cd geochemistry and iron reduction may be key to better management of Cd-polluted soils.

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

References

- Li X, Liu T, Li F, Zhang W, Zhou S, Li Y (2012) Reduction of structural Fe(III) in oxyhydroxides by *Shewanella decolorationis* S12 and characterization of the surface properties of iron minerals. *J Soil Sediment* 12(2):217–227
- Li C, Yi X, Dang Z, Yu H, Zeng T, Wei C, Feng C (2016) Fate of Fe and Cd upon microbial reduction of Cd-loaded polyferric flocs by *Shewanella oneidensis* MR-1. *Chemosphere* 144:2065–2072
- Liu C, Zhu Z, Li F, Liu T, Liao C, Lee J-J, Shih K, Tao L, Wu Y (2016) Fe(II)-induced phase transformation of ferrihydrite: the inhibition effects and stabilization of divalent metal cations. *Chem Geol* 444:110–119
- Pedersen HD, Postma D, Jakobsen R (2006) Release of arsenic associated with the reduction and transformation of iron oxides. *Geochim Cosmochim Acta* 70(16):4116–4129
- Poulton SW, Canfield DE (2005) Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chem Geol* 214(3–4): 209–221
- Sørensen J, Thorling L (1991) Stimulation by lepidocrocite (γ -FeOOH) of Fe(II)-dependent nitrite reduction. *Geochim Cosmochim Acta* 55(5):1289–1294