Biogenic Mn oxides for effective adsorption of Cd from aquatic environment

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Biogenic Mn oxides effectively adsorb Cd from aquatic environments.

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ABSTRACT

Biogenic Mn oxides exert important controls on trace metal cycling in aquatic and soil environments. A Mn-oxidizing bacterium *Bacillus* sp. WH4 was isolated from Fe–Mn nodules of an agrudalf in central China. The biogenic Mn oxides formed by mediation of this Mn oxidizing microorganism were identified as short-ranged and nano-sized Mn oxides. Cd adsorption isotherms, pH effect on adsorption and kinetics were investigated in comparison with an abiotic Mn oxide todorokite. Maximum adsorption of Cd to the biogenic Mn oxides and todorokite was 2.04 and 0.69 mmol g^{−1} sorbent, respectively. Thus, the biogenic Mn oxides were more effective Cd adsorbents than the abiotic Mn oxide in the aquatic environment. The findings could improve our knowledge of biogenic Mn oxides formation in the environment and their important roles in the biogeochemical cycles of heavy metals.

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1. Introduction

Manganese oxides (Mn oxides) are highly reactive mineral phases that play important roles in elemental biogeochemical cycles. They participate intensely in a wide variety of redox and adsorption reactions with heavy metals. Microorganisms can accelerate the rate of Mn oxidation processes by up to 10⁵ times compared to abiotic Mn oxidation (Hastings and Emerson, 1986). In the absence of microorganisms Mn oxidation in natural aquatic system often proceeds at very slow rates although it is thermodynamically favorable (Nealson et al., 1988). Therefore, the majority of naturally environmental Mn oxides are believed to be derived either directly from biogenic Mn oxidation processes or from the subsequent alteration of biogenic Mn oxides (Kim et al., 2003; Tebo et al., 2004).

Laboratory research directed toward the bacterial Mn oxidation has focused on three model microorganisms: *Leptothrix discophora* SS-1 (Corstjens et al., 1997) and SP-6 (Saratovsky et al., 2006), a freshwater bacterial species that deposits Mn oxides on its extracellular sheath; *Pseudomonas putida* MnB1 and GB-1 (Caspi et al., 1996; Caspi et al., 1998), common freshwater and soil bacteria that precipitate Mn oxides on the cell surface (Villalobos et al., 2003); and *Bacillus* sp. SG-1 (Van Waasbergen et al., 1996), a marine bacterium that produces Mn oxidizing spores. Biogenic Mn oxides

are often speculated to be poorly crystalline, short-ranged or amorphous nano-particulates. Kim et al. (2003) demonstrated that biogenic Mn oxides formed by *L. discophora* SP-6 are nano-sized, todorokite-like porous MnO₂. The Mn oxides produced by *P. putida* MnB1 are a poorly crystalline birnessite with hexagonal symmetry and each of the biogenic Mn oxides contains an average of only three stacked sheets and extends for roughly 8–9 nm in the horizontal plane, making them truly nano-particles (Villalobos et al., 2003). Such nano-sized biogenic Mn oxides are expected to be highly reactive with heavy metal ions (Villalobos et al., 2006).

Thus, the interactions between biogenic Mn oxides and heavy metals have been of great interest for their important roles in the biogeochemical cycles of heavy metals and their potential use in bioremediation of aquatic environments contaminated with toxic metals (Tournassat et al., 2002; Tani et al., 2004; Villalobos et al., 2005a; Wu et al., 2005; Webb et al., 2006). Techniques based on synchrotron radiation such as X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy have contributed to the better understanding of heavy metal ions associated with biogenic Mn oxides. Biogenic Mn oxides formed by *L. discophora* SS-1 show higher capacity to adsorb Pb ions than abiotic Mn oxides because of both higher surface areas and higher binding energy per unit area of the biogenic Mn oxides (Nelson et al., 1999, 2002). XANES and EXAFS results from Villalobos et al., (2005a,b) suggested that the large variation in Pb retention capacity can be divided into two types of Pb, one residing in the interlayer region of a crystallite and another residing on its external surfaces. Zn was adsorbed to biogenic Mn

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oxides in tetrahedral coordination to structural O atoms at low Zn loading, but in octahedral coordination at higher Zn loading (Toner et al., 2006). All these results suggest that the adsorption characteristics of biogenic Mn oxides appear to be different from the abiotic Mn oxides.

Cd is a hazardous heavy metal, but no studies are yet available on its adsorption to biogenic Mn oxides. The purpose of this study was to characterize Cd adsorption to biogenic Mn oxides, and to infer on possible adsorption mechanisms. The biogenic Mn oxides were formed by *Bacillus* sp. WH4, a Mn oxidizing bacterium isolated from Fe–Mn nodules collected from the soil in central China (Zhang et al., 2008). Cd adsorption isotherms, pH effect and kinetics were conducted to characterize Cd adsorption to the biogenic Mn oxides in comparison with an abiotic Mn oxide todorokite.

2. Materials and methods

2.1. Preparation and characterization of Mn oxides

Bacillus sp. WH4 was isolated from Fe–Mn nodules which were collected at 40 cm depth from the subsoil horizon of a subacid orthic aggradal developed from Quaternary siliceous and alluvial sediments of the Hubei Province, Central China (He et al., 2008; Zhang et al., 2008). This bacterium was grown in modified K medium (Rosson and Neilson, 1982; Boogerd and de Vrind, 1987; Jin et al., 2009) at 27 °C for 14 days. The medium contained (l^{-1}): 2 g of tryptone (Oxoid Ltd, UK), 0.5 g of yeast extract (Oxoid Ltd, UK), 10 mM HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid, Amresco Inc, USA), pH 7.5, 10 mM $MnCl_2$, 50% of artificial seawater (ASW: 0.3 M NaCl, 0.01 M KCl, 0.05 M $MgSO_4$ and 0.01 M $CaCl_2$) and 1 ml trace element solution. The trace element solution contained (l^{-1}): 10 mg of $CuSO_4 \cdot 5H_2O$, 44 mg of $ZnSO_4 \cdot 7H_2O$, 20 mg of $CoCl_2 \cdot 6H_2O$ and 13 mg of $Na_2MoO_4 \cdot 2H_2O$. Prior to the addition of HEPES and $MnCl_2$, the medium was autoclaved for 30 min at 115 °C. Then sterilized HEPES (0.22 μm filters, pH 7.5) and $MnCl_2$ were added before inoculation. After 14 days, the fresh biogenic Mn oxides suspension was harvested and stored at 4 °C before use. The kinetics of biogenic Mn oxides formation was determined at the same time. Biogenic Mn oxides concentration was detected by LBB assay (Krumbein and Altmann, 1973). Todorokite (Feng et al., 2004) was mixed with deionized water to make a stock suspension and kept at 4 °C prior to use. The formed biogenic Mn oxides were characterized by BET specific surface area, XRD, SEM-EDS and TEM.

2.2. Batch adsorption tests

A Cd stock solution was prepared with $Cd(NO_3)_2$ (Beijing Chemical Co, China) and kept acidic in 1% HNO_3 at 4 °C to be further diluted before use. Each test solution contained a certain amount of Cd stock solution, 0.1 g l^{-1} Mn oxide sorbent and 0.01 M $NaNO_3$ to make up 20 ml mixtures in 100 ml centrifugal tubes. The initial pH of the mixtures was selected carefully to ensure that no precipitation occurred in the solutions according to the K_{sp} of $Cd(OH)_2$ ($K_{sp}(Cd(OH)_2) = 5.27 \times 10^{-15}$). The initial solution pH values were adjusted with 0.1 M NaOH and 0.1 M HNO_3 . All batch experiments were carried out on a reciprocating shaker at 150 rpm and 25 ± 1 °C with three replicates. The Cd adsorption isotherms and pH effect experiments were conducted for 4 h while the kinetic experiments lasted for 24 h.

For Cd adsorption isotherms, each tube contained various Cd concentrations (0.01 to 0.80 mM) and initial solution pH was adjusted to 7.5. To determine the effect of solution pH on Cd adsorption (pH effect experiment), initial Cd concentration was 0.1 mM and initial pH values were between 2.7 and 8.3. To determine the rate of Cd adsorption by the Mn oxides (kinetics experiment), Cd adsorbed was determined after 0, 0.5, 1, 2, 4, 6, 8, 10, and 24 h.

All the reaction products were centrifuged (11000 rpm, 5 min) and filtered through a 0.22 μm filter. The obtained supernatants were acidified in 1% HNO_3 and stored at 4 °C for Cd and Mn determination by ICP-AES.

2.3. Measurements

The reductive dye Leucoberbelin blue I (LBB) (Sigma, USA) was used to estimate the Mn oxides concentration on a Spectra max190 reader (MD Co. Ltd.) Oxidized LBB is blue in color and the degree of coloration is a function to quantify the amount of Mn oxides (assuming all oxidized Mn exist as MnO_2) being reduced. Suspension of the Mn oxides were added to 0.2 ml of 0.04% LBB in 45 mM acetic acid, incubated in the dark for 15 min, and then centrifuged for 10 min at 11000 rpm. The supernatant was aliquoted into 96 well plates for OD₆₂₀ measurement. The LBB assay was also utilized to indicate the kinetics of biogenic Mn oxides formation by *Bacillus* sp. WH4. The cell optical density (OD₆₀₀) was measured with a spectrophotometric method at 600 nm.

The specific surface area of the biogenic Mn oxides was measured by BET–N₂ method with a Micromeritics ASAP 2000 analyzer. For the BET surface area analysis,

Fig. 1. Kinetics of biogenic Mn oxides formation by *Bacillus* sp. WH4 (a), growth curve (OD₆₀₀) of *Bacillus* sp. WH4 (b) and the photo of brown-black biogenic precipitates (c). The error bars are the standard deviation of three replicates.

the samples were centrifuged, followed by freeze-drying at –40 °C for 1 week. They were stored in a desiccator before measurement. XRD analysis was carried out on a revised D/max-rA 12KW X-ray diffraction instrument. The samples were placed on low-background quartz plates and scanned over the range $2\theta = 2.6\text{--}70^\circ$. The Mn oxides morphology and chemical contents were determined by SEM with an EDAX KEVEX level 4 (Hitachi S-3500N), and TEM (Hitachi H-7500, Japan). For SEM and TEM, the samples were prepared as biological samples. SEM biological samples were fixed with 2.5% (volume ratio) glutaraldehyde for 4.5 h at 4 °C, followed by dehydration with an ethanol series (30% (volume ratio), 50%, 70%, 80%, 90%, 95%, and 100%; 5 min for each). TEM biological samples were prepared by fixation with 2.5% (volume ratio) glutaraldehyde overnight at 4 °C, and then ultrasonic dispersion for 30 min. At last 10 μl suspension was dropped to copper grids, and the excessive solvent immediately evaporated. Total Cd and Mn concentrations in the final supernatants were determined by inductively coupled plasma spectroscopy (ICP-AES, Prodigy, Leeman Labs).

2.4. Data analysis

The Cd adsorption from solution by Mn oxides (q , mmol Cd g^{-1} sorbent) was quantified as:

$$q = ([Cd]_0 - [Cd]_t) / [sorbent] \quad (1)$$

where $[Cd]_0$ and $[Cd]_t$ are the Cd concentrations at time 0 and time t in solution (mM), $[sorbent]$ is the dry sorbent in mixture ($g\ l^{-1}$).

Fig. 2. XRD patterns of todorokite and biogenic Mn oxides.

Fig. 3. SEM (20 KV)-EDS and TEM (80 KV) analysis of Mn oxides. SEM image of todorokite ($\times 3000$) (a); EDS analysis of todorokite (b); SEM image of the biogenic Mn oxides ($\times 5000$) (c); EDS analysis of the biogenic Mn oxides (d); TEM image of the fresh biogenic Mn oxides formed by *Bacillus* sp. WH4 ((e), $\times 10\,000$; f, $\times 500\,000$).

The adsorption capacity of Mn oxides was described using the Freundlich model (Sposito, 2004):

$$q = AC^{1/n} \quad (2)$$

where q is the amount of Cd adsorbed (mol Cd g^{-1} sorbent); C is the equilibrium Cd concentration in the mixture (mM); and A and $1/n$ are empirical constants.

To understand the kinetics of Cd adsorption, the kinetic adsorption data were modeled empirically with the pseudo-first order Lagergren model (Lagergren, 1898). The Lagergren model is a widely used sorption rate model for the sorption of a solute from a liquid solution. It may be represented as:

$$\log(q_e - q_t) = \log q_e - (K_{ad}/2.303)t \quad (3)$$

where q_e and q_t are the amounts of Cd adsorbed at equilibrium time and at time t , respectively (mol Cd g^{-1} sorbent). K_{ad} is the equilibrium rate constant of the adsorption (min^{-1}). All mathematical and graphical operations were made using the software Sigmaplot 10.0 (Systat Software Inc., USA). Error bars in plots indicate the standard deviation of three replicates.

3. Results

3.1. Kinetics of biogenic Mn oxides formation

The growth of *Bacillus* sp. WH4 reached a stable phase after 1 day, and then bacterial spores started to be observed under the

Fig. 4. The isotherms of Cd adsorption to todorokite (a) and the biogenic Mn oxides (b). Mn oxides concentration was 0.1 g L⁻¹ and the solution pH was 7.5. The error bars are the standard deviation of three replicates.

microscope. As shown in Fig. 1, the Mn oxidation rate began to increase quickly within the first 7 days, and brown-black precipitates were formed. By contrast, there was no change in the control medium (CK), which containing only 10 mM MnCl₂ (no *Bacillus* sp. WH4) (Fig. 1c). The biogenic Mn oxides formation reached a plateau at day 10 and the fresh biogenic Mn oxides were harvested at day 14 with 2.3 mM MnO₂.

3.2. Characterization of biogenic Mn oxides

3.2.1. XRD patterns

There were no obvious crystalline peaks on the XRD patterns of the biogenic Mn oxides (Fig. 2), which indicated that they were poorly crystallized. No detectable changes were found in the XRD patterns for our samples with preservation as suspension for several months. The XRD pattern of todorokite was consistent with todorokite standards from mineral index files provided by the Joint Committee for Powder Diffraction Studies (JCPDS-ICDD).

Fig. 5. Effects of pH on Cd adsorption by Mn oxides in the pH range of 2.7–8.2. Initial Cd concentration was 0.1 mM and Mn oxides concentration was 0.1 g L⁻¹. The error bars are the standard deviation of three replicates.

3.2.2. Physicochemical characteristics

The morphology and surface elements distribution of the Mn oxides were studied by SEM-EDS and TEM (Fig. 3). The SEM image of the todorokite showed that it was well crystallized (Fig. 3a). By contrast, the images of the biogenic Mn oxides were aggregated particles with irregular geometric shape, indicating their poor crystallinity and very small particle size. These fine particles had densely aggregated filamentous structures. Some deposits directly adhered to the surface of the spores, while others distributed around the spores (Fig. 3e). The EDS analysis indicated that the Mn oxidation activity was not only located on the spore surface, but also excreted into the surrounding culture medium (Fig. 3d). The TEM image of biogenic Mn oxides (Fig. 3f) shows clearly that the biogenic Mn oxides were nano-sized. The BET specific surface area of freeze-dried biosorbent and pure spores were 30.6 m² g⁻¹ and 2.4 m² g⁻¹, respectively.

3.3. Adsorption isotherm

The biogenic Mn oxides adsorbed 2.04 mmol Cd g⁻¹ biosorbent at the highest initial Cd concentration, which corresponds to a Cd/Mn molar ratio of 0.69. The todorokite adsorbed 0.71 mmol Cd g⁻¹ sorbent, which was less than the biogenic Mn oxides (Fig. 4). The Freundlich model was suitable for the present systems. The Langmuir model, in contrast, was not suitable to describe the adsorption isotherms (data not shown).

3.4. pH effect on Cd adsorption

The results in Fig. 5 illustrate the effects of pH on Cd adsorption to Mn oxides. The Cd adsorption was evidently dependent on pH for both of the Mn oxides. The adsorption capacity increased steadily with increasing pH up to pH 4.5 and then slowed down with a plateau at pH 4.5–8.3. The maximum adsorption capacity approached 0.36 and 0.54 mmol g⁻¹ sorbent for todorokite and biogenic Mn oxides, respectively.

3.5. Kinetics adsorption

Kinetic experiments were performed to determine Cd adsorption rates by the two Mn oxides. As shown in Fig. 6, the rates of

Fig. 6. Kinetics of Cd adsorption to Mn oxides (a) and the rate constant determination by Lagergren model (b). Initial Cd was 0.1 mM, Mn oxides concentration was 0.1 g L⁻¹, and the solution pH was 7.5. The error bars are the standard deviation of three replicates.

adsorption were very fast initially and then reached a plateau at equilibrium. For both Mn oxides, maxima were obtained within 12 h. The changes in the adsorption capacity with time was found to fit Lagergren model with the straight-line plots of $\log(q_e - q_t)$ versus t (Fig. 6b). The values of K_{ad} , the rate constants, were calculated to be $1.17 \times 10^{-2} \text{ min}^{-1}$ for the biogenic Mn oxides and $0.76 \times 10^{-2} \text{ min}^{-1}$ for the todorokite. The K_{ad} values indicated that the adsorption rate of Cd adsorbed to the biogenic Mn oxides was faster than to the todorokite.

To understand the possible mechanism of Cd adsorption to the biogenic Mn oxides, the changes of Mn concentration in solution and pH values in the kinetics experiment were determined. Mn concentration and pH value of control, in which no Cd was added (only Mn oxides and NaNO₃ solution), were also assessed. During Cd adsorption to the biogenic Mn oxides, more Mn in solution was

detected than CK (Fig. 7a). However, this phenomenon was not observed when Cd adsorbed to the todorokite. For pH value, the trends of biogenic Mn oxides and todorokite were similar, i.e., quick decreasing and then keeping smooth (Fig. 7b).

4. Discussion

In this study, the biosorbent was actually a mixture of biogenic Mn oxide particulates and spores, and the BET specific surface area was the value of this mixture. Therefore, it is not surprised that the BET specific surface area of the biosorbent was lower than that of the todorokite ($77 \text{ m}^2 \text{ g}^{-1}$) (Feng et al., 2004) and values reported in other studies (Nelson et al., 1999; Villalobos et al., 2006). The spores, wrapped by the fine biogenic Mn oxides particulate (Fig. 3e), may be considered to have little effect on the adsorption

Fig. 7. Changes of Mn concentrations in solution (a) and pH values (b) in kinetics experiment. Initial Cd was 0.1 mM, Mn oxides concentration was 0.1 g L⁻¹ and the initial solution pH was 7.5. The error bars are the standard deviation of three replicates.

process. Toner et al., (2006) and Sasaki et al., (2008) also reported that the biogenic functional groups present in the biofilm do not intervene in metal adsorption to the biogenic Mn oxides.

It is not surprising that the Langmuir equation failed in describing the adsorption behavior, and this result is consistent with the result of Zn adsorbed to biogenic Mn oxides produced by *P. putida* strain MnB1 (Toner et al., 2006). Langmuir model assumes that the adsorption is the coverage of the surface by a mono-molecular layer. This assumption may be not suitable for the adsorption to the Mn oxides, especially to the biogenic Mn oxides. Cd adsorption capacity to the biogenic Mn oxides was about three times greater than to the todorokite. This result was similar with Pb adsorption to biogenic Mn oxides formed by *L. discophora* (2–5 times greater than adsorption to fresh δ -MnO₂) (Nelson et al., 1999). Table 1 shows maximum adsorption of metals on several biogenic Mn oxides as reported in literature. The data show that the maximum adsorption of diverse biogenic Mn oxides, expressed as metal/Mn molar ratio, varies from 0.12 to 0.76 between metals.

Although the biogenic Mn oxides have shown a higher adsorption capacity and a higher adsorption rate for heavy metals, the characteristics and mechanisms of metal adsorption to biogenic Mn oxides are still unclear because the biogenic Mn oxides are amorphous, nano-sized and often mixed with organisms. Metal adsorption to Mn oxides could occur through three pathways (Tebo et al., 2004; Miyata et al., 2007): (a) surface adsorption on layers or edges of Mn oxides involving the formation of either inner sphere or outer sphere complexes; (b) sorption into the interlayer regions or tunnels; and (c) incorporation into vacancies or substitution for Mn within the mineral lattice structure. In our kinetic experiment, changes in pH were observed when Cd adsorbed to both Mn oxides, while a significant Mn concentration change was only detected in the case of biogenic Mn oxides. Since the biogenic Mn oxides were poorly crystalline and rich in nano-sized fine pores, a part of exchangeable charge-balancing cations, such as Mn²⁺ and H⁺ are loosely involved in the structure to compensate the charge balance. These structural Mn²⁺ and H⁺ could be easily exchanged by Cd ions during the adsorption process. By contrast, the todorokite is a well crystallized Mn oxide with average Mn oxidation state 3.82 (Feng et al., 2004). Less Mn(II) or Mn(III) could exist in the lattice structure of the todorokite and be exchanged during Cd adsorption to the todorokite. Therefore, the greater adsorption to nano-sized biogenic Mn oxides is likely due to the amorphous or short-ranged nature and more reactive cation exchange sites of the biogenic Mn oxides compared to those of the more crystalline abiotic Mn oxide. The biogenic Mn oxides may also have greater binding energy per unit surface area than the chemical Mn oxides (Nelson et al., 1999).

The Mn oxides, biogenic or abiotic, were affected by the solution pH. Lower pH is favorable for the protonation of the sorbent surface. Increased protonation is thought to increase the positively charged sites, reduce the attraction force between the Mn oxides surface and Cd ions, and decrease the amount of adsorption in the

lower pH region. With increasing pH, the negatively charged sites dominate and adsorption increases. The high adsorption capability of the biogenic Mn oxides within wide pH ranges (4.5–8.3) indicates its potential to control the fate of heavy metals in the natural environment.

In this study, the fresh biogenic Mn oxides were formed by *Bacillus* sp. WH4, a Mn oxidizing bacterium which was isolated from the subsoil. The results provide evidence that the Mn oxidizing bacteria and biogenic Mn oxides may play important roles in various environments, more than previously acknowledged. The biogenic Mn oxides could be formed quickly by Mn oxidizing bacteria and have a large adsorption capacity of heavy metals in a short time. This could be useful for application in environmental engineering. Further research is needed to characterize the heavy metal adsorption and other properties of the biogenic Mn oxides.

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References

- Boogerd, F.C., de Vrind, J.P., 1987. Manganese oxidation by *Leptothrix discophora*. *Journal of Bacteriology* 169, 489–494.
- Caspi, R., Haygood, M.G., Tebo, B.M., 1996. Unusual ribulose-1,5-bisphosphate carboxylase/oxygenase genes from a marine manganese-oxidizing bacterium. *Microbiology* 142, 2549–2559.
- Caspi, R., Tebo, B.M., Haygood, M.G., 1998. c-Type cytochromes and manganese oxidation in *Pseudomonas putida* MnB1. *Applied and Environmental Microbiology* 64, 3549–3555.
- Corstjens, P.L.A.M., de Vrind, J.P.M., Goosen, T., de VrinddeJong, E.W., 1997. Identification and molecular analysis of the *Leptothrix discophora* SS-1 mofA gene, a gene putatively encoding a manganese-oxidizing protein with copper domains. *Geomicrobiology Journal* 14, 249–249.
- Feng, X.H., Tan, W.F., Liu, F., Wang, J.B., Ruan, H.D., 2004. Synthesis of todorokite at atmospheric pressure. *Chemistry of Materials* 16, 4330–4336.
- Hastings, D., Emerson, S., 1986. Oxidation of manganese by spores of a marine bacillus: kinetic and thermodynamic considerations. *Geochimica et Cosmochimica Acta* 50, 1819–1824.
- He, J.Z., Zhang, L.M., Jin, S.S., Zhu, Y.G., Liu, F., 2008. Bacterial communities inside and surrounding soil iron–manganese nodules. *Geomicrobiology Journal* 25, 14–24.
- Jin, S.S., He, J.Z., Zheng, Y.M., Meng, Y.T., Zhang, L.M., 2009. Adsorption of heavy metals by biogenic manganese oxides. *Acta Scientiae Circumstantiae* 29, 132–139.
- Kim, H.S., Pasten, P.A., Gaillard, J.F., Stair, P.C., 2003. Nanocrystalline todorokite-like manganese oxide produced by bacterial catalysis. *Journal of the American Chemical Society* 125, 14284–14285.
- Krumbein, W.E., Altmann, H.J., 1973. A new method for the detection and enumeration of manganese oxidizing and reducing microorganisms. *Helgolander Marine Research* 25, 347–356.
- Lagergren, 1898. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens. Handlingar, Band* 24, 1–39.
- Miyata, N., Tani, Y., Sakata, M., Iwahori, K., 2007. Microbial manganese oxide formation and interaction with toxic metal ions. *Journal of Bioscience and Bioengineering* 104, 1–8.
- Nealson, K.H., Tebo, B.M., Rosson, R.A., Allen, I.L., 1988. Occurrence and mechanisms of microbial oxidation of manganese. *Advances in Applied Microbiology* 33, 279–318.
- Nelson, Y.M., Lion, L.W., Ghiorse, W.C., Shuler, M.L., 1999. Production of biogenic Mn oxides by *Leptothrix discophora* SS-1 in a chemically defined growth medium and evaluation of their Pb adsorption characteristics. *Applied and Environmental Microbiology* 65, 175–180.
- Nelson, Y.M., Lion, L.W., Shuler, M.L., Ghiorse, W.C., 2002. Effect of oxide formation mechanisms on lead adsorption by biogenic manganese (hydr)oxides, iron (hydr)oxides, and their mixtures. *Environmental Science & Technology* 36, 421–425.
- Rosson, R.A., Nealson, K.H., 1982. Manganese binding and oxidation by spores of a marine bacillus. *Journal of Bacteriology* 151, 1027–1034.
- Saratovsky, I., Wightman, P.G., Pasten, P.A., Gaillard, J.F., Poeppelmeier, K.R., 2006. Manganese oxides: parallels between abiotic and biotic structures. *Journal of the American Chemical Society* 128, 11188–11198.
- Sasaki, K., Matsuda, M., Urata, T., Hirajima, T., Konno, H., 2008. Sorption of Co²⁺ ions on the biogenic Mn oxide produced by a Mn-oxidizing fungus, *Paraconiothyrium* sp. WL-2. *Materials Transactions* 49, 605–611.

Table 1

Maximum adsorption of metals on biogenic Mn oxides expressed as a molar ratio of metal to Mn.

Metals	Maximum adsorption (metal/Mn, molar ratio)	Biogenic Mn oxides sources	References
Pb	0.55, pH 6.0 at 25 °C	<i>L. discophora</i>	(Nelson et al., 1999)
Pb	0.27, pH 5.8 at 23 °C	<i>P. putida</i> strain MnB1	(Villalobos et al., 2005a)
Zn	0.76, pH 6.9 at 20 °C	<i>P. putida</i> strain MnB1	(Toner et al., 2006)
Zn	0.23, pH 7.0 at 25 °C	<i>Acremonium</i> sp. KR21–2	(Tani et al., 2004)
Ni	0.12, pH 7.0 at 25 °C	<i>Acremonium</i> sp. KR21–2	(Tani et al., 2004)
Co	0.30, pH 7.0 at 25 °C	<i>Acremonium</i> sp. KR21–2	(Tani et al., 2004)
Co	0.16, pH 6.5 at 25 °C	<i>Paraconiothyrium</i> sp. WL-2	(Sasaki et al., 2008)
Cd	0.69, pH 7.5 at 25 °C	<i>Bacillus</i> sp. WH4	Present study

- Sposito, G., 2004. The Surface Chemistry of Natural Particles. Oxford University Press, New York.
- Tani, Y., Ohashi, M., Miyata, N., Seyama, H., Iwahori, K., Soma, M., 2004. Sorption of Co(II), Ni(II), and Zn(II) on biogenic manganese oxides produced by a Mn-oxidizing fungus, strain KR21-2. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering* 39, 2641–2660.
- Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. *Annual Review of Earth and Planetary Sciences* 32, 287–328.
- Toner, B., Manceau, A., Webb, S.M., Sposito, G., 2006. Zinc sorption to biogenic hexagonal-birnessite particles within a hydrated bacterial biofilm. *Geochimica et Cosmochimica Acta* 70, 27–43.
- Tournassat, C., Charlet, L., Bosbach, D., Manceau, A., 2002. Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate. *Environmental Science & Technology* 36, 493–500.
- Van Waasbergen, L.G., Hildebrand, M., Tebo, B.M., 1996. Identification and characterization of a gene cluster involved in manganese oxidation by spores of the marine *Bacillus* sp. strain SG-1. *Journal of Bacteriology* 178, 3517–3530.
- Villalobos, M., Bargar, J., Sposito, G., 2005a. Mechanisms of Pb(II) Sorption on a biogenic manganese oxide. *Environmental Science & Technology* 39, 569–576.
- Villalobos, M., Bargar, J., Sposito, G., 2005b. Trace metal retention on biogenic manganese oxide nanoparticles. *Elements* 1, 223–226.
- Villalobos, M., Lanson, B., Manceau, A., Toner, B., Sposito, G., 2006. Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist* 91, 489–502.
- Villalobos, M., Toner, B., Bargar, J., Sposito, G., 2003. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochimica et Cosmochimica Acta* 67, 2649–2662.
- Webb, S.M., Fuller, C.C., Tebo, B.M., Bargar, J.R., 2006. Determination of uranyl incorporation into biogenic manganese oxides using X-ray absorption spectroscopy and scattering. *Environmental Science & Technology* 40, 771–777.
- Wu, Y., Deng, B., Xu, H., Kornishi, H., 2005. Chromium(III) oxidation coupled with microbially mediated Mn(II) oxidation. *Geomicrobiology Journal* 22, 161–170.
- Zhang, L.M., Liu, F., Tan, W.F., Feng, X.H., Zhu, Y.G., He, J.Z., 2008. Microbial DNA extraction and analyses of soil iron–manganese nodules. *Soil Biology and Biochemistry* 40, 1364–1369.