Cr(III) oxidation coupled with Mn(II) bacterial oxidation in the environment

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Abstract

Purpose Cr(III) oxidation to Cr(VI) significantly increases Cr mobility and toxicity and thus its environmental risks. Manganese (Mn) oxides may serve as the potential oxidants of Cr(III) in environment. Natural Mn oxides in the environment are believed to be derived from bacterial oxidation. The objective of this study was to examine the Cr(III) oxidation capacity of biogenic Mn oxide and the role of Mn-oxidizing bacteria in Cr(III) oxidation.

Materials and methods Batch experiments were conducted to investigate the capacities of Cr(III) oxidation by chemically synthetic Mn oxides and biogenic Mn oxide. Biogenic Mn oxide was formed by *Bacillus* sp. WH4, a Mn-oxidizing bacterium isolated from Fe–Mn nodules of a Chinese soil. Various Cr(III) and Mn(II) were added to the growth medium of *Bacillus* sp. WH4 to evaluate Cr(III) oxidation coupled with Mn(II) bacterial oxidation.

Results The Cr(III) oxidation capacity of biogenic Mn oxide was 0.24 mmol g^{-1} and higher than three chemically synthetic Mn oxides. No Mn(III) intermediate was detected during Mn(II) bacterial oxidation. *Bacillus* sp. WH4 could promote Cr(III) oxidation through oxidizing Mn(II), although it could not oxidize Cr(III) directly.

Conclusions The participation of Mn-oxidizing bacteria makes Cr(III) oxidation more complicated in environment.

These findings illustrate the need to consider bacterial activity and the Mn(II) level when predicting the fate of Cr and the potential applications of Mn oxides in the remediation of pollutants in environment.

Keywords Biogenic Mn oxide · Chromium · Mn(III) intermediate · Mn-oxidizing bacteria · Oxidation

1 Introduction

Hexavalent chromium (Cr) is a toxic heavy metal and often considered to be originating from industrial activity (Bartlett and James 1988). However, natural high Cr(VI) concentration in aqueous solution (up to $73 \mu\text{g l}^{-1}$) was observed in many sites far away from the industrial areas (Oze et al. 2007), suggesting natural Cr(III) oxidation and transport in the environment. The conversion of Cr(III) oxidation to Cr(VI) increases its mobility and toxicity in the environment. Mn oxides, which are common in various environments, are the only known natural oxidants of Cr(III) (Fendorf and Zasoski 1992; Silvester et al. 1995; Nico and Zasoski 2000) and therefore could control the fate and transport of Cr in the environment.

Natural Mn oxides in the environment are believed to be derived either directly from biogenic Mn(II) oxidation or from the subsequent alteration of biogenic Mn oxides ((Kim et al. 2003); (Tebo et al. 2004)). Mn oxidation in natural aquatic systems often proceeds at very slow rate if there is no participation of microorganisms (Nealson et al. 1988). Mn-oxidizing microorganisms can accelerate the Mn oxidation rate by up to 10^5 times compared to the abiotic Mn oxidation (Hastings and Emerson 1986). Mn-oxidizing bacteria are a diverse group and have been found in various environments such as soils ((He et al. 2008); (Zhang et al. 2008)), fresh water ((Nelson et al. 1999); (Villalobos et al. 2003)), and

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oceans (Rosson and Nealson 1982). Molecular genetic approaches have revealed that all Mn-oxidizing organisms share sequence similarity with multicopper oxidase enzymes (Tebo et al. 2004). Biogenic Mn oxides are often poorly crystalline nano-sized particulates with many structural defects (Bargar et al. 2005). Such biogenic Mn oxides are expected to be reactive with heavy metals effectively through adsorption ((Nelson et al. 1999); (Villalobos et al. 2005); (Toner et al. 2006); (Meng et al. 2009); (Jin et al. 2009)) and oxidation (Lee and Tebo 1994; (Murray and Tebo 2007); (Murray et al. 2007); (Chinni et al. 2008); (Ohnuki et al. 2008)).

Cr(III) oxidation by various Mn oxides has been studied with abiotic Mn oxides ((Chung et al. 1994); (Silvester et al. 1995); (Nico and Zasoski 2000)). Despite considerable studies, the mechanism by which Mn oxides transform Cr (III) to Cr(VI) is not fully understood. Mn(III) is considered to be typically the initial product of the abiotic oxygenation of aqueous Mn(II) (Morgan 2005) or formed from Mn(II) bacterial oxidation (Webb et al. 2005). As a specific structural and compositional feature, Mn(III) plays an important and previously unrecognized role in the fate and transport of many multivalent compounds ((Murray and Tebo 2007); (Murray et al. 2007); (Nico and Zasoski 2000)). Although there are some empirical and theoretical evidence that Mn(III) be related to Cr(III) oxidation (Chung et al. 1994), some other researches obtained contrasting results ((Silvester et al. 1995); (Weaver and Hochella 2003); (Murray and Tebo 2007)).

The purpose of this study was to evaluate Cr(III) oxidation capacity of the biogenic Mn oxide compared with chemically synthetic Mn oxides and the Cr(III) oxidation process in the presence of Mn-oxidizing bacteria and Mn(II). *Bacillus* sp. WH4, a Mn-oxidizing bacterium isolated from Fe–Mn nodules of a Chinese soil, was suitable for this study because the mature spores can oxidize Mn(II) but the vegetative cells cannot, thus excluding bacterial cell growth as an experimental variable (Zhang et al. 2008). To detect whether Mn (III) intermediate was formed and played a role in Cr(III) oxidation, pyrophosphate and EDTA were chosen as trapping ligands of Mn(III) in Mn(II) bacterial oxidation (Klewicki and Morgan 1998).

2 Materials and methods

2.1 Chemicals

Deionized water and analytical grade or better chemicals were used to prepare all aqueous solutions. Cr(III) and Mn (II) stock solutions were prepared with CrCl_3 and MnCl_2 . Mn(III) trapping ligands were sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$; Sinopharm Chemical Reagent Co. Ltd, China) and ethylenediaminetetraacetate ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, EDTA; Amersco Inc, USA).

2.2 Mn oxide preparation

2.2.1 Chemically synthetic Mn oxides

Three chemically synthetic Mn oxides were used. Todorokite was synthesized by refluxing process at atmospheric pressure (Feng et al. 2004b). Birnessite was synthesized by mixing MnCl_2 and NaOH (Feng et al. 2004a). Cryptomelane was synthesized by heating MnSO_4 and KMnO_4 solution (Feng et al. 2007).

2.2.2 Biogenic Mn oxide

Bacillus sp. WH4 was isolated from the Fe–Mn nodules of a Chinese soil (Zhang et al. 2008). By XRD and TEM analyses, the biogenic Mn oxides formed by *Bacillus* sp. WH4 was of poor crystallinity and nano-sized particulates (Meng et al. 2009). In this study, *Bacillus* sp. WH4 was grown in modified K medium (Meng et al. 2009) at $27 \pm 1^\circ\text{C}$ with 1.0 mM MnCl_2 . Prior to the addition of sterilized *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES, Amresco Inc, USA) and MnCl_2 (0.22- μm filters, pH 7.5), the medium was autoclaved for 30 min at 115°C . After 14 days, the fresh biogenic Mn oxide was harvested and cleaned with deionized water three times. The preformed biogenic Mn oxide was prepared to evaluate its Cr(III) oxidation capacity. The fresh and performed biogenic Mn oxide concentration was measured by LeducoBerbelin Blue (LBB) assay (Krumbein and Altmann 1973).

2.3 Experimental setup

2.3.1 Direct oxidation of Cr(III) by Mn oxides

Cr(III) oxidation by the chemically synthetic Mn oxides and the performed biogenic Mn oxide were evaluated on a reciprocating shaker at 150 rpm and $25 \pm 1^\circ\text{C}$. The oxidation tests were performed in 100-ml centrifugal tubes containing 10 ml mixed suspension at pH 5.0. The standard suspension for all experiments contained 10.0 mM NaCl, 2.0 g l^{-1} Mn oxides, and 0.5 mM Cr(III) (as CrCl_3). The blank control contained 0.5 mM Cr(III) in 10.0 mM NaCl. All reactions were carried out with three replicates.

At the end of each experiment, Cr(VI) concentration was obtained from the supernatant by centrifugation (11,000 rpm, 10 min).

2.3.2 Cr(III) oxidation by the fresh biogenic Mn oxide

To detect whether *Bacillus* sp. WH4 could oxidize Cr(III) directly, 0–100 μM Cr(III) (as CrCl_3) was directly inoculated into the growth medium (section 2.2.2) with *Bacillus* sp. WH4 (no Mn(II) added). The concentration of

Cr(VI) in the medium and the growth curve (OD600) of *Bacillus* sp. WH4 were measured.

To determine whether Mn(III) intermediate was formed during Mn(II) bacterial oxidation, 0.1–1.0 mM Mn(II) (as MnCl₂) and 0.4 mM pyrophosphate or EDTA were added into the growth medium with *Bacillus* sp. WH4. Mn(III) content was measured after filtration through 0.22-μm filter (Klewicki and Morgan 1998; Webb et al. 2005). In the blank control (only Mn(II) and *Bacillus* sp. WH4), LBB assay (see Section 2.4) was also used to test the production of Mn(III) in the supernatant (centrifugation at 11,000 rpm, 10 min). If Mn(III) was formed and existed in the aqueous solution, it could be reduced by LBB.

To test Cr(III) oxidation coupled with Mn(II) bacterial oxidation, 0–100 μM Cr(III) and/or Mn(II) was added to the growth medium in the presence of *Bacillus* sp. WH4. Firstly, the 100-ml flasks with 30 ml medium were incubated with *Bacillus* sp. WH4 for 3 days (after 3 days, the spores reached about 90% in the medium). The sterilized Mn(II) and/or Cr(III) (0.22-μm filter) were added into the medium. After another 5 days, aliquots of the incubations were removed with a syringe to analyze fresh biogenic Mn oxide concentrations. For Cr(VI) analysis, cells and Mn oxides were removed by filtration (0.22-μm filters), which could also quench the Cr(III) oxidation reaction. Cr(VI) concentration in the pure growth medium (without Mn(II)) and *Bacillus* sp. WH4 was also determined.

2.4 Measurements

The reductive dye LBB (Sigma-Aldrich, USA) was used to determine the Mn oxide concentration (OD620; (Krumbein and Altmann 1973)). 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 MnO₂). No color reaction between LBB and Cr(III) (or Cr(VI)) was observed. LBB assay was also used to detect possible Mn(III) during Mn(II) bacterial oxidation. Cr(VI) was analyzed by colorimetric diphenylcarbazide assay at 540 nm (Urone 1955), and its detect limit is 4 μg l⁻¹ with 50 ml colorimetric tube. All colorimetric measurements were made on a Spectra Max190 reader (MD Co. Ltd.).

2.5 Data analysis

The efficiency of biogenic Mn oxide was defined as follows:

$$\text{Efficiency of biogenic Mn oxide} = [\text{Cr(VI)}]/[\text{biogenic Mn oxide}] \quad (1)$$

where [Cr(VI)] is the Cr(VI) concentration oxidized in the medium, mM; [biogenic Mn oxide] is the biogenic Mn oxide concentration in the medium, mM.

All mathematical and graphical operations were made using the software Sigmaplot 10.0 (Systat Software Inc., USA), and the error bars in the plots indicated the standard deviation of three replicates.

3 Results

3.1 Cr(III) oxidation by biotic and abiotic Mn oxides

As shown in Fig. 1, Cr(III) oxidation by the preformed biogenic Mn oxide was higher than those of three chemically synthetic Mn oxides. The Cr(III) oxidation capacity of four Mn oxides were 0.02, 0.08, 0.15, and 0.24 mmol g⁻¹ for cryptomelane, todorokite, birnessite, and biogenic Mn oxide, respectively.

3.2 Cr(III) oxidation by the fresh biogenic Mn oxide

3.2.1 No Mn(III) formation during Mn(II) oxidation by *Bacillus* sp. WH4

As shown in Fig. 2, the absorbance peaks of Mn(III)–pyrophosphate and Mn(III)–EDTA complexes in birnessite suspension appeared at 480 and 450 nm, respectively, suggesting that Mn(III) was trapped by pyrophosphate and EDTA (Klewicki and Morgan 1998; Webb et al. 2005).

By adding 0.4 mM sterilized pyrophosphate or EDTA, no absorbance peak at 480 nm (Mn(III)–pyrophosphate) or 450 nm (Mn(III)–EDTA) was detected during Mn(II) bacterial oxidation by *Bacillus* sp. WH4. No color reaction between supernatant and LBB

Fig. 1 Cr(III) oxidation by chemically synthetic and performed biogenic Mn oxides at pH 5.0. [Mn oxides]=2.0 g l⁻¹, [Cr(III)]=0.5 mM, [NaCl]=10.0 mM. All experiments were conducted for 4 h. The error bars in plots indicated the standard deviation of three replicates

Fig. 2 The absorbance peaks of Mn(III)-pyrophosphate and Mn-EDTA in birnessite suspension at pH 5.0. [Pyrophosphate] or [EDTA]=0.4 mM, [birnessite]=2.0 g l⁻¹, [NaCl]=10 mM

was detected. These results indicated that no Mn(III) intermediate was formed when Mn(II) was oxidized by *Bacillus* sp. WH4.

3.2.2 No Cr(III) oxidation directly by *Bacillus* sp. WH4

With 0–100 μ M Cr(III) in the growth medium of *Bacillus* sp. WH4, no Cr(VI) was detected, implying that *Bacillus* sp. WH4 could not oxidize Cr(III) directly. The growth curves of *Bacillus* sp. WH4 were measured, and the microbial growth were not suppressed significantly by the added Cr(III) after 24 h, as shown in Fig. 3. Thus, the inhibitions of Cr(III) on microbial growth and the direct microbial oxidation of Cr(III) were excluded.

Fig. 3 Growth curves of *Bacillus* sp. WH4 in culture medium with various Cr(III) at pH 7.5. No Mn(II) was added. The error bars in plots indicated the standard deviation of three replicates

3.2.3 Cr(III) oxidation under various Mn(II) and Cr(III) concentrations

Biogenic Mn oxide concentration increased with Mn(II) concentration and did not reach a plateau up to 1.0 mM Mn(II) regardless what levels of Cr(III) (Fig. 4a). Higher Cr(III) concentration led higher biogenic Mn oxide production, implying that Mn(II) oxidation was stimulated by Cr(III).

The highest Cr(VI) concentrations in the medium were 1.0 μ M (equal to 52.0 μ g l⁻¹) and 1.9 μ M (equal to 98.9 μ g l⁻¹) for 50 μ M Cr(III) and 100 μ M Cr(III), respectively. The efficiencies of biogenic Mn oxide decreased with Mn(II) concentration and then reached a plateau for two Cr(III) concentrations. Furthermore, the efficiency of biogenic Mn oxide with 100 μ M Cr(III) was lower than that with 50 μ M Cr(III), indicating that Cr(III) oxidation was not proportional to biogenic Mn oxide concentrations.

4 Discussion

Cr(III) oxidation was largely affected by its adsorption on the surface of Mn oxides. Biogenic Mn oxides are poorly crystalline nano-size particulates with huge specific surface area and higher binding energy (Tebo et al. 2004). Therefore, Cr(III) could be easily adsorbed on the surface of biogenic Mn oxide and then be oxidized. The results in this study supported this explanation. It is shown that the Cr(III) oxidation capacity of biogenic Mn oxide formed by *Bacillus* sp. WH4 was higher than three

Fig. 4 Mn(II) and Cr(III) oxidation with various of Mn(II) and Cr(III) concentrations in the presence of *Bacillus* sp. WH4. pH=7.5. [Mn(II)]=0–1.0 mM, [Cr(III)]=0–100 μ M. **a** Biogenic Mn oxide concentration; **b** the efficiency of biogenic Mn oxide. The efficiency of biogenic Mn oxide was the molar ratio of Cr(VI) to biogenic Mn oxide. The error bars in plots indicated the standard deviation of three replicates

Table 1 Summary of Cr(III) oxidation in relation to Mn(III) intermediate in literatures

Mn oxides types	Relationship with Mn(III)	Reference
Mn(III)	Yes—aqueous Mn(III) showed to oxidize Cr(III) in acidic conditions	(Rophael 1982)
Three abiotic Mn oxides: birnessite, pyrolusite, hausmannite	Yes—Mn oxides containing highest Mn(III) concentration increase the rate of Cr oxidation	(Chung et al. 1994)
Abiotic δ -MnO ₂	Yes—Cr oxidation rate slowed when pyrophosphate was used to trap available Mn(III)	(Nico and Zasoski 2000)
Six natural Mn oxides: pyrolusite, hausmannite, manganite, romanechite, cryptomelate, lithiophorite; One synthetic birnessite	Yes—Cr(III) oxidation is most related to the presence of Mn(III)	(Weaver and Hochella 2003)
Abiotic Na-buserite	No	(Silvester et al. 1995)
Mn(III) (pH 3, aqueous)	No	(Weaver et al. 2002)
Five Mn(III) complex: Mn(III)–PVD, Mn(III)–DFO, Mn(III)–pyrophosphate, Mn(III)–citrate, Mn(III)–Bis Tris	No	(Murray and Tebo 2007)
A biogenic Mn oxide formed by <i>Bacillus</i> sp. WH4	No	This study

chemically synthetic Mn oxides. Recent studies also reported that biogenic Mn oxide produced by *Bacillus* sp. SG-1 had a higher reactivity than synthetic Mn oxides and oxidized Cr(III) seven times faster than δ -MnO₂ (Murray and Tebo 2007).

Since Cr(III) oxidation capacity of preformed biogenic Mn oxide was higher than synthetic Mn oxides, how about the Cr(III) oxidation in real environment? Do Mn-oxidizing bacteria play a role in Cr(III) oxidation? Therefore, various concentrations of Cr(III) and Mn(II) were added to *Bacillus* sp. WH4 to detect the possible reactions. In the presence of Mn-oxidizing bacteria, Cr(III) could be oxidized by Mn oxides via several approaches (Murray and Tebo 2007): (1) the direct Cr(III) oxidation by Mn-oxidizing bacteria, (2) Mn(III) intermediate formation during bacterial oxidation to oxidize Cr(III), or (3) rapid biogenic Mn oxide formation to oxidize Cr(III). Therefore, there are three key questions to answer.

The first one was about the Cr(III) oxidation by Mn-oxidizing bacteria. Since *Bacillus* sp. WH4 was tolerant to Mn(II) and could oxidize Mn(II) efficiently (up to 10 mM; (Meng et al. 2009)), could it oxidize Cr(III) directly? In this study, Cr(III) could not be oxidized by *Bacillus* sp. WH4 and neither significant toxic effect of Cr(III) on this bacterium was found. It was the same with the results of *Bacillus* sp. SG-1 and *Pseudomonas putida* strain GB-1, which could not oxidize Cr(III) directly ((Murray et al. 2007); (Murray et al. 2005)).

The second question was that whether Mn(III) intermediate was formed during the Mn(II) bacterial oxidation. Mn(III) intermediate in Mn oxides was assumed to play a role in the Cr(III) oxidation according to the electron-transfer theory (Nico and Zasoski 2000). The theory suggested that an inner-sphere complex formation between Cr(III) and Mn(IV) could easily be rate limiting since both Mn(IV) and Cr(III) are d^3 ions with very slow ligand exchange rates.

Conversely, Mn(III) is a high spin d^4 ions with much faster ligand exchange kinetics (Klewicki and Morgan 1998). Therefore, the inner-sphere complex formation of Cr(III) with Mn(III) is likely to be quicker than with Mn(IV). Furthermore, one Mn(III) and one Mn(IV) could oxidize one Cr(III) as following reaction equation (Nico and Zasoski 2000):

Although Mn(III) seemed to be important in Cr(III) oxidation, no Mn(III) intermediate was detected during Mn(II) bacterial oxidation in this study. This is consistent with the result of *Bacillus* sp. SG-1 where no relationship of Mn

Fig. 5 Schematic pathway of Cr oxidation coupled with Mn(II) bacterial oxidation. Biogenic Mn oxide formed by Mn-oxidizing bacterium could oxidize Cr(III) to Cr(VI). The reductive Mn(II) was re-supplied to the Mn-oxidizing bacterium. Then a cycle was created: Mn-oxidizing bacteria promote Cr(III) oxidation through oxidizing Mn(II), and Mn was recycled. Higher Mn(II) would inhibit Cr(III) oxidation through physical blocking or site competition

(III) and Cr(III) oxidation was found (Murray and Tebo 2007) and the result of *P. putida* MnB1, which showed that Cr(III) oxidation was only dependent upon the biogenic Mn (IV) oxides formation (Wu et al. 2005). Although Mn(III) in aqueous solution was shown to oxidize Cr(III) (Rophael 1982), the acidic condition was not comparable to those found in natural pH in this study (Table 1).

The third question was whether reactive biogenic Mn oxide was formed and the answer was yes. It is proposed that the process of Cr(III) oxidation be described as: (1) biogenic Mn oxide formation by *Bacillus* sp. WH4 and (2) Cr(III) adsorption and reaction on the surface of the biogenic Mn oxide. Although Cr(III) could not be oxidized directly by the bacterium, it could bind to the oxidizing sites of the bacterium and compete for the sites with Mn(II) at the same time. If this were true, high levels of Mn(II) could alleviate the inhibition of both Mn(II) and Cr(III) oxidation caused by Cr(III) competition. Although Mn oxide concentration increased with increasing Mn(II), high level Cr(III) in the system promoted Mn(II) oxidation by *Bacillus* sp. WH4 (see Fig. 4a). This is different from the result of *Bacillus* sp. SG-1, which showed that neither Cr(III) nor Cr(VI) influenced Mn(II) oxidation (Murray and Tebo 2007). Furthermore, higher Mn(II) concentration led to decreasing efficiencies of biogenic Mn oxide for two Cr(III) concentrations (Fig. 4b), which is similar to the recent result of *Bacillus* sp. SG-1 where higher Mn(II) concentration inhibited Cr(III) oxidation (Murray and Tebo 2007). For two concentrations of Cr(III), the efficiency of biogenic Mn oxide with lower Mn oxide concentration was higher than the higher one, and it is similar with the result of *P. putida* MnB1 where Cr(III) oxidation rate was not directly proportional to the amount of Mn oxides (Wu et al. 2005). There are two possible reasons to explain these results.

One is alluded to the surplus Mn (II) inhibition. With a little Mn(II), the formed fresh Mn oxides started to adsorb and oxidize Cr(III), after then, Mn(II) was regenerated to be oxidized by *Bacillus* sp. WH4. It means that a cycle of Mn (II) and Cr(III) oxidation could be created, and Mn is recycled. The Mn-oxidizing bacterium could promote Cr (III) oxidation through forming reactive biogenic Mn oxide, as presented in Fig. 5. Additionally, Mn(II) could also be adsorbed on biogenic Mn oxide and be oxidized. Higher concentration of Mn(II) would compete with Cr(III) for the site on the biogenic Mn oxide and thus inhibit Cr(III) oxidation. Another reason is the rate limit. The Cr(III) oxidation by Mn oxides can be expressed by the following reaction (Fendorf and Zasoski 1992):

In this reaction, Cr(III) must lose three electrons in order to become Cr(VI). The standard voltages (E^0) for the

oxidation of Cr(III) to Cr(IV), Cr(IV) to Cr(V), and Cr(V) to Cr(VI) are -2.10 , -1.34 , and -0.55 V, respectively. Thus the removal of the first electron from Cr(III) should be the slowest electron-transfer step (Nico and Zasoski 2000). In this system, no Mn(III) was involved in Cr(III) oxidation. Therefore, the formation of an complex between Cr(III) and Mn(IV) could easily be the rate limit since both Mn(IV) and Cr(III) have high ligand field stabilization energies and slow ligand field stabilization (Klewicky and Morgan 1998).

5 Conclusions

The present study focused on the Cr(III) oxidation capacities of biogenic and chemically synthetic Mn oxides and the possible Cr(III) oxidation mechanism in the presence of Mn-oxidizing bacterium *Bacillus* sp. WH4. Results showed that the Cr(III) oxidation capacity of biogenic Mn oxide was higher than synthetic Mn oxides. *Bacillus* sp. WH4 promoted Cr(III) oxidation through biogenic Mn oxide formation. In a system with *Bacillus* sp. WH4, an oxidation cycle was created. Although Mn(II) was needed, higher Mn(II) concentration would inhibit Cr(III) oxidation through physical blocking or site competition.

The binding of Cr to Mn oxides could greatly affect their phase distributions and fate in many natural systems. The participation of Mn-oxidizing bacteria makes this system more complicated. A better understanding of Cr(III) oxidation in the presence of Mn-oxidizing bacteria in the natural aqueous system is essential to consider the fates and transports of not only Cr but also many other heavy metals. It is also important when considering the potential application of Mn oxides in the remediation of environmental pollutants because Mn oxides may lead unexpected risks. Further research is needed to analyze the Cr speciation in natural system and fully understand Cr(III) oxidation coupled with Mn(II) bacterial oxidization.

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