

# Reaction of Colloidal and Bacterial MnO<sub>2</sub> with Iron (II)

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## Introduction

Recently, many efforts have been undertaken to investigate using molecular approaches the interactions between metal oxides and aqueous solutions [1]. These compounds are reactive in environmental systems because their surfaces present interesting acid-base, ligation, and/or redox properties. Among these oxides, manganese oxides present very attractive features for catalyzing a wide range of chemical reactions in the environment. They are characterized by open structures, and therefore provide an excellent potential for sorbing foreign ions. In addition to their scavenging properties, they can be efficient oxidizers for various reduced metal ions, such as As(III), Co(II), Cr(III), Fe(II), and organic compounds [2,3]. This oxidative reactivity is in part related to the presence of Mn(III) in the oxide structure [4].

Under environmental conditions, the formation of manganese oxide is generally catalyzed by the presence of microbes, and occurs at oxic/anoxic transitions [5]. The goal of this research project is to characterize the structure and reactivity of various manganese oxides produced by different bacterial strains, so that they can be used in remediation actions or as new catalysts. Often, optimal growth conditions for manganese oxidizing bacteria in the laboratory require the presence of substantial amounts of Fe(II), and other reactive trace elements. This iron interacts with the manganese oxides precipitated [6], and therefore should affect the oxide structure and its reactivity. In this work, we investigate the effects of the presence of this reducer on two strains and on chemically produced colloidal MnO<sub>2</sub>.

## Methods and Materials

*Leptothrix discophora* SP-6 (ATCC 51168) and a gram negative *Agrobacterium* manganese oxidizer isolated from a Green Bay manganese nodule were cultured in MSVP medium (ATCC Culture Medium 1917). The chemical composition of this medium was modified by varying the amount of iron present in the solution from about 0  $\mu$ M to 150  $\mu$ M of Fe(II) added as FeSO<sub>4</sub>. All the experiments were performed in presence of 50  $\mu$ M of Mn(II), provided as MnSO<sub>4</sub>, and under oxygen saturation conditions.

Colloidal size manganese dioxide particles were prepared following the inorganic synthesis method proposed by Perez-Benito et al. [7]. The colloids were reacted and precipitated by addition of FeSO<sub>4</sub> for comparison with the bacterially produced oxides.

All the samples were collected by filtration onto 0.45  $\mu$ m polycarbonate filters, and held in place between two layers of Kapton© tape. XAS measurements were carried out at station 5-BM-D operated by DND CAT at the Advanced Photon Source, Argonne National Laboratory. Data were collected in the Quick-XAS mode [8] to minimize and monitor potential chemical reactions under the beam.

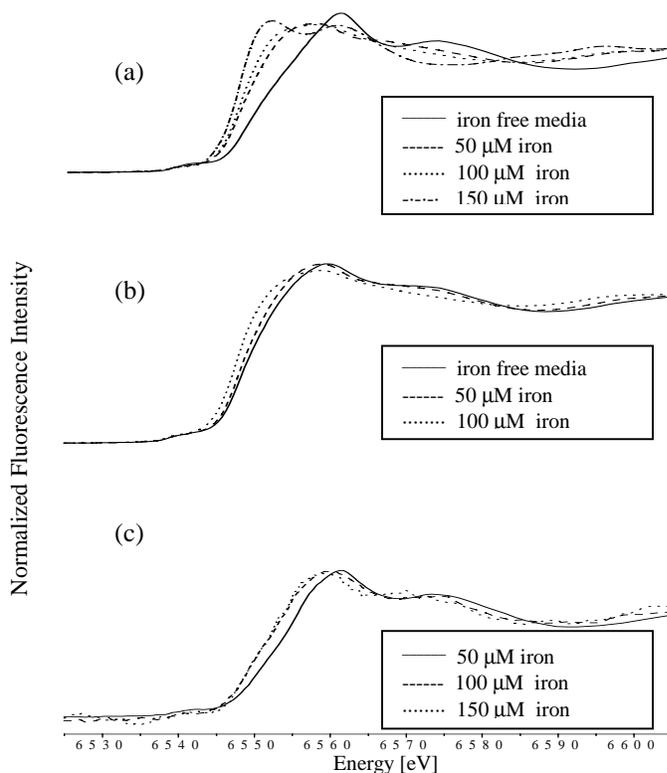


Figure 1: Manganese XANES data for oxide particles formed by (a) *L. discophora* SP-6, (b) the *Agrobacterium* species, and (c) chemically synthesized MnO<sub>2</sub> colloid. Typical MSVP media contains 10  $\mu$ M iron (II).

## Results

The XANES spectra and EXAFS RDF data of two bacterial oxides and one chemically synthesized manganese oxide particles are shown in Figures 1 and 2 as a function of increasing iron (II) concentration. As the amount of iron in the medium is increased, a clear shift of the XANES spectra towards Mn (II) (lower energy) is observed. This change in the identity of the particle is mirrored in the EXAFS data (Fig.2)

For the chemically synthesized samples, iron concentrations above 100  $\mu$ M Fe (II) resulted in a very weak Mn K edge absorption. This is due to the reductive dissolution of the colloidal MnO<sub>2</sub> in presence of excess Fe(II). This is also accompanied by a relatively smaller shift to lower energies in the XANES region.

## Discussion

As it is evidenced by the data presented, the amount of iron present in the medium can affect the structure of the manganese oxide formed by a particular bacterial species. In addition, different species appear to mediate the incorporation of iron into the manganese oxide particle differently, which can be seen by comparing Figures 1a and 1b. The XANES data indicate a more reducing effect for a given amount of iron present in the SP-6 culture compared to the *Agrobacterium* culture. The RDF data

also exhibit greater variability. There are still clear changes due to the incorporation of iron, but they are not as important for the *Agrobacterium* species studied here as for SP6. This lower sensitivity to the iron concentration may be in part due to the much slower manganese oxidation by the *Agrobacterium*, allowing for other mechanisms of iron oxidation to dominate. Manganese oxidation occurs with SP-6 within a few days of inoculation, while the other culture requires several weeks before any oxide can be formed.

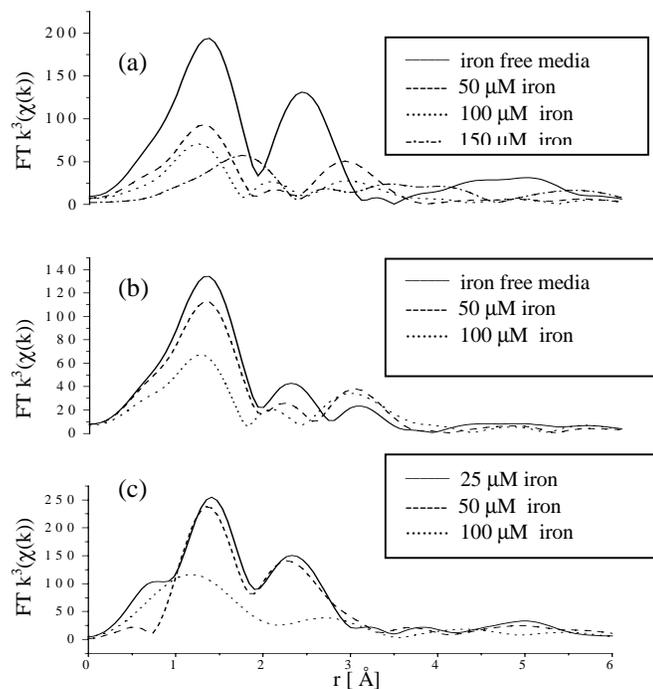


Figure 2: EXAFS RDF data for oxide particles formed by (a) *L. discophora* SP6, (b) the *Agrobacterium* species, and (c) chemically synthesized  $\text{MnO}_2$  colloid.

In contrast, only a slight shift in the XANES is observed for the chemically synthesized samples. The manganese in these particles is still largely Mn (IV). In the colloidal particles the reduced manganese doesn't become incorporated in the particle. As the concentration of iron increases, the amount of manganese present in the solid decreases, leading to weak fluorescence signals at the manganese K-edge. The EXAFS data in the absence of iron point to a structure of the oxide for the colloid and for the particles produced by SP-6 that closely matches the mineral psilomelane. The identification of the oxide structure produced by the *Agrobacterium* has not been elucidated yet. We think that the oxides formed in the presence of iron are chemical mixtures of several Fe and Mn oxidation states and structures that we plan to identify in the near future.

## Acknowledgments

This work was supported by the EMSI program of the National Science Foundation and the Department of Energy (CHE-9810378) at the Northwestern University Institute for Environmental Catalysis. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. We also thank John Quintana (DND-CAT) and Sam Webb (NWU) for their help with the XAS experimental setup, and

Barbara MacGregor for assistance in microbiology techniques, and many helpful discussions. The bacterial strains were kindly provided by Brett Baker (University of Wisconsin, Milwaukee, WI).

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