IMPROVING PASSIVE MINE TREATMENT THROUGH BETTER UNDERSTANDING OF BIOGEOCHEMISTRY AND MINERALOGY ASSOCIATED WITH MN(II) OXIDATION

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Project Description and Objectives

The purpose of this project was to improve our understanding of passive manganese(II)-removal systems for the treatment of coal mine drainage. The objectives of this research were to measure Mn(II)-removal kinetics in controlled laboratory experiments; characterize the microbial communities that promote Mn(II) oxidation, and; characterize the manganese oxides formed in these systems.

Applicability to Mining and Reclamation

We discovered that both bacteria and fungi are equally important in promoting biological Mn(II) oxidation. In comparing the two selected treatment systems, Mn(II) was consistently removed below detection limit from the site that included a wetland upstream of the Mn-removal bed. We believe that higher concentrations of dissolved organic carbon and nutrients from this wetland stimulated greater microbial activity that, in turn, promoted greater Mn(II) removal. In addition to a wetland, limestone beds designed for Mn(II)-oxidation should incorporate materials in the bed to promote fungal growth. We found that the predominant Mn oxides at all sites were poorly crystalline birnessite and buserite. Trace metals such as Ni, Zn and Co were removed effectively and preferentially into the Mn oxides.

Methodology

Two Mn-removal systems in western Pennsylvania were studied to measure Mn-removal efficiency in the field and in laboratory experiments. Sediments and water samples were collected from each site for laboratory experiments, and to isolate and culture microbes that catalyze Mn(II)-oxidation. Sediment "crust" samples were scraped from the black precipitates on the limestone cobbles in the beds. Filter-sterilized site water was added to the sediments, and Mn(II) kinetics were measured in a "fed-batch" mode, where supplemental Mn(II) was added to the reactors over time. A series of control reactors were used to measure the relative contributions of biological versus abiotic Mn(II) oxidation, and bacterial versus fungal Mn(II)-oxidation.

Sediment crusts were diluted into a variety of growth media to isolate Mn(II)-oxidizing bacteria and fungi. Isolates were tested for their ability to grow and oxidize Mn(II) in the presence of varying metal concentrations. Sediment crusts were characterized by X-ray diffraction (XRD), Mn K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) and scanning and transmission electron microscopy (SEM and TEM). Elemental content was determined by digestion and analysis by inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

Highlights

We selected one Mn-removal system that treats an exceptionally high concentration of 150 mg/L Mn(II), and conducted laboratory experiments to evaluate the relative importance of abiotic versus biotic processes responsible for Mn removal, and to evaluate the relative importance of bacteria versus fungi on biological Mn(II) oxidation. We found that while abiotic processes contribute to Mn removal, biological Mn(II)-oxidation was the most important process to ensure effective, long-term Mn removal. We found that fungal activity accounted for over 80% of Mn(II) oxidation in this Mn-removal bed. We selected four additional Mn-removal systems for a culture enrichment survey of bacteria and fungi and found that Mn(II)-oxidizing fungi were isolated more readily than Mn(II)-oxidizing bacteria. Fungal isolates outnumbered bacterial isolates 84:10, and fungi were extremely tolerant to elevated concentrations of Mn(II).

Based on field measurements, Mn-removal systems with an upstream wetland tended to perform better than those without one. Dissolved organic carbon (DOC) produced in the wetland presumably increased microbial Mn(II)-oxidation in the limestone bed. Glucose and carboxymethylcellulose (CMC) were selected to represent labile and recalcitrant DOC, respectively, in lab experiments. The addition of glucose was shown to slightly improve Mn(II) removal while the addition of CMC was shown to significantly inhibit Mn(II) removal. Based on phylogenetic assignments for the fungi we isolated from these Mn-removal systems, we found the most common fungi were Ascomycetes (not "wood rot" fungi). Therefore, the addition of a cellulosic substrate such as corn cobs (not a woody substrate) may be best for Mn-removal beds.

Results/Findings

In the two Mn(II)-removal systems we studied, fungi constituted 88 % of the Mn(II)-oxidizing cultures while bacteria constituted just 12 %. In laboratory experiments using sediments and site water, fungi accounted for over 80 % of Mn(II) oxidation activity in one Mn-removal bed. The predominant Mn oxides at all sites were poorly crystalline birnessite and buserite. Trace metals such as Ni, Zn and Co were removed effectively in these systems.

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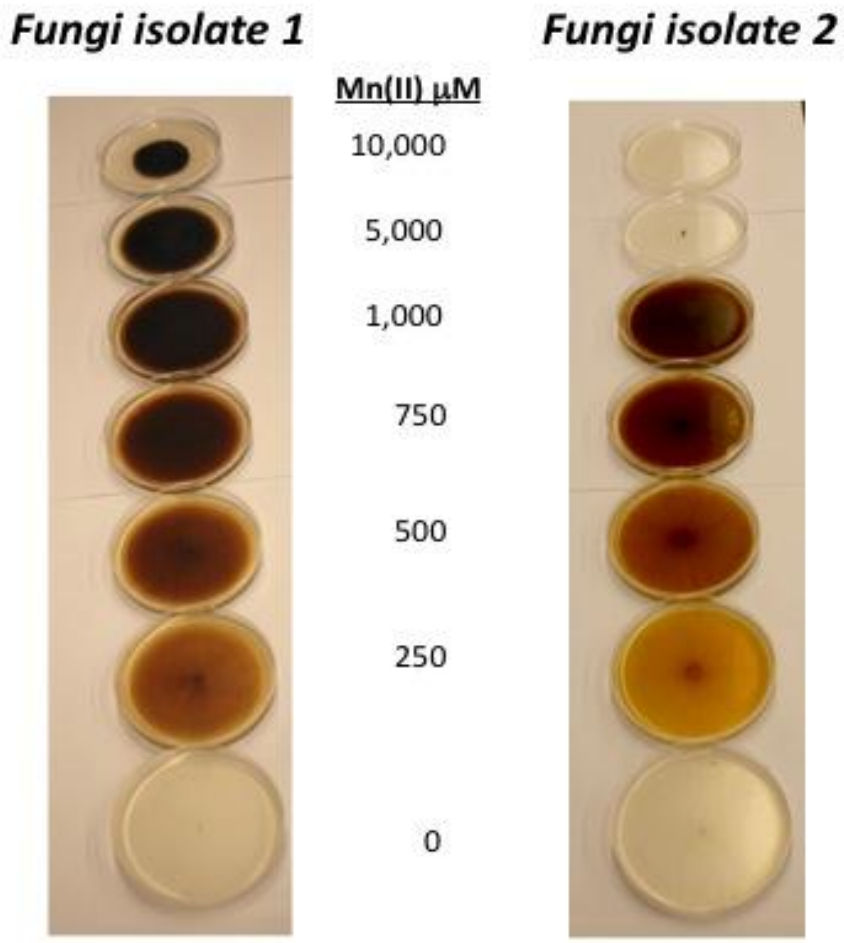
The final project report can be found at
http://www.osmre.gov/programs/tdt/appliedscience/projects.shtm

Manganese-removal bed



Two different Mn(II)-oxidizing fungi isolates grown in petri dishes on agar-based media with increasing (0 to 10,000 µM) concentrations of dissolved Mn(II). Isolates were inoculated by "stabbing" the center of the petri dish, allowing the fungal hyphae to grow radially outwards. The brown color is due to the Mn oxide minerals precipitated on the fungi during growth.

SEM images of Mn-rich sediments A and D) Typical “sponge-like” morphology; B, E and F) Bacterial cells in close proximity to Mn oxides. C) Fungal mycelium in close proximity to Mn oxides. Scale bar in all images represents 1 μm.