Removal of Mn from an Alkaline Mine Drainage Using a Bioreactor with Different Organic Carbon Amendments

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Background

In the 1990's, a portion of the Cumberland Plateau in Eastern Kentucky was mined for coal using the surface mine and valley fill technique (Fig. 1). The calcareous bedrock geology of the area provides considerable buffering capacity for the acidity commonly generated from mine drainage. After the seepage from the underdrain exits the toe of the fill, it is rapidly oxidized, removing virtually all iron (< 5 mg L^{-1}) and most other trace metals (Fig. 2). However, manganese concentrations remain high (25-35 mg L^{-1}) along with extremely high concentrations of sulfate (1200-1400 mg L^{-1}). A natural wetland developed below the toe of the fill treats some of the sulfate but has no impact on the manganese. In an attempt to remediate the contamination, a bioreactor will be installed between the toe of the fill and the wetland. The bioreactor will be designed to treat manganese using sulfate reduction. The goal is to reduce the sulfate to sulfide and then precipitate with the Mn as MnS, thereby removing both contaminants.

Research Objectives

1. Determine the capability of various organic sources to enhance sulfate reduction and Mn removal in laboratory experiments.
2. Determine the optimal retention time for treatment of the mine drainage.
3. Estimate the required regeneration time of the substrate.

Methods

Step 1

In laboratory batch experiments, a mixture of an inorganic substrate and an organic amendment in a 10:1 (mass: mass) ratio was used to create a physical support and provide the nutrients necessary for sulfur reducing bacteria. Limestone, marble, sand, river gravel, and creek sediment were used for the inorganic substrate and corn mash from a bourbon distillery, wood mulch, soybean oil, sorghum molasses, and biosolids were used for the organic amendments.

The limestone is crushed stone obtained from a quarry; the marble, sand and river gravel are products purchased from a home improvement store, and the creek sediment was obtained from the top several inches of a Kentucky reference stream. The corn mash is the end product of bourbon distilling, the biosolids was obtained from a local wastewater treatment plant, the wood mulch was collected from a University of Kentucky research farm and consists of the mulched farm refuse, and the soybean oil and sorghum molasses were purchased from a grocery store.

Nitrogen gas was used to create and maintain a reducing environment in the flasks and gas traps containing sodium thiosulfate were used to restrict oxygen flow into the flasks. A picture of the experimental setup is show in Fig. 3. A sample was removed each day from each batch and analyzed for Mn, SO_4^{2-}, and dissolved organic carbon concentrations. In addition, redox potential and pH were measured at each sampling point.

Step 2

Two of the most effective combinations of inorganic substrates and organic amendments will be tested using a flow-through system modeled after the full scale bioreactor to be built in the field. Each of the systems will consist of a 15 gallon (56.8 L) plastic tank filled with one of the most successful substrates defined by the previous batch experiments. Redox conditions will be measured within the tank and pH and Eh will be measured in the effluent. Samples will be collected daily and analyzed as for the batch experiments.

Fig. 1 View of the valley fill site

Fig. 2 Mine drainage directly below toe of the fill

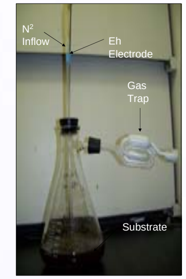

Fig. 3 Photograph of an experimental batch

Substrates	Amendments
Creek Sediment	Biosolids
Limestone	Corn Mash
Marble	Sorghum Molasses
River Gravel	Soybean Oil
Sand	Wood Mulch

Fig. 4 Substrates and organic amendments used in the research

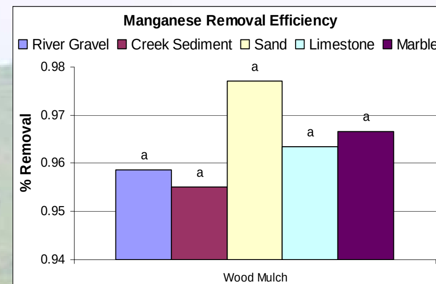

Fig. 5 Mn removal by the substrates based on the wood mulch amendment

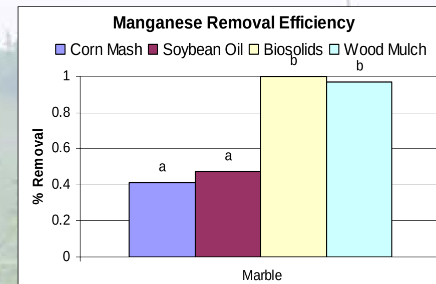

Fig. 6 Mn removal by the amendments based on the marble substrate

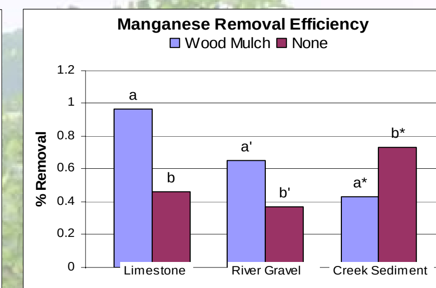

Fig. 7 Change in Mn removal caused by the addition of wood mulch to three substrates

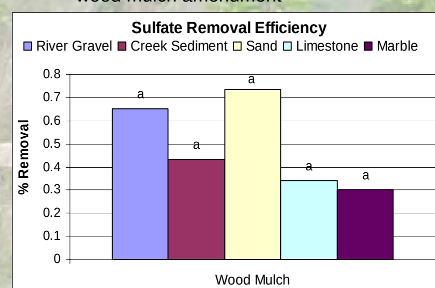

Fig. 8 Sulfate removal by the substrates based on the wood mulch amendment

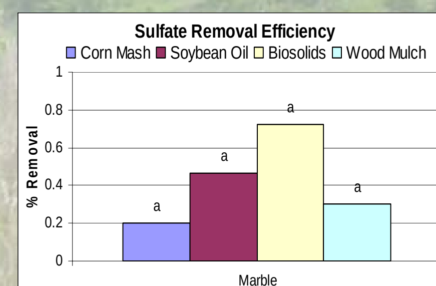

Fig. 9 Sulfate removal by the organic amendments based on the marble substrate

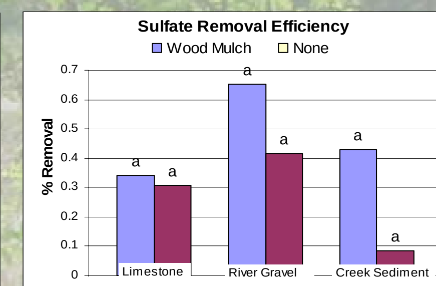

Fig. 10 Change in sulfate removal caused by the addition of wood mulch to three substrates

Results

- Wood mulch successfully removed virtually all of the Mn from solution in each substrate.
- Using a marble substrate, biosolids and wood mulch more successfully removed manganese than either corn mash or soybean oil (Fig. 6). The biosolid amendment also removed more sulfate than any other treatment (Fig. 9), but the difference was not statistically significant.
- There was no statistical difference between substrates for wood mulch but differences were detected between substrates for other amendments (Figs. 5-6).
- Despite widely variant sulfate removal efficiencies, as shown in Figs. 8-10, there was no significant difference between treatments.

Discussion & Conclusions

Manganese was removed very rapidly from solution in batches utilizing either biosolids or wood mulch. This may be due primarily to sorption; however, until the flow-through portion of the experiment is completed, it will be difficult to confirm that interpretation.

Analysis of the relationship between dissolved organic carbon and Mn and SO_4^{2-} concentrations in solution (not shown), indicated weak relationships (R^2=0.2-0.3).

The addition of wood mulch to the creek sediment substrate caused a significant decrease in Mn removal efficiency, but in sulfate removal, the results were inconsistent. The large increase in sulfate removal efficiency with the addition of wood mulch to creek sediment is potentially due to the addition of a more diverse bacterial community.