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Improving Coal Mine Drainage Remediation Methods to More Rapidly and Effectively Remediate Manganese with a Dual 'Myco-Zeo' System

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Remediating aqueous manganese (Mn) from coal mine drainage (CMD) can prove challenging, as it necessarily relies on the oxidative precipitation of aqueous Mn(II) to form solid Mn(III/IV) (oxyhydr)oxide minerals, which can be a kinetically slow process. CMD passive bioremediation sites utilize carbonate-bearing liner rocks to increase pH, making Mn(II) oxidation preferable, and microbial communities of Mn oxidizers to increase the rate of Mn oxidation. Despite these substantial improvements in remediation efforts, Mn remediation effectiveness varies considerably across sites.

Our work examines the potential for a dual passive bioremediation system combining Mn oxidation by fungi with rapid sorption by zeolites. In abiotic systems, zeolites remove Mn(II) from solution primarily via adsorption but also partial Mn oxidation over time. Mn(II) removal from solution over time in the presence and absence of two Ascomycete Mn oxidizing fungi, *Stagonospora* sp. SRC1lsM3a and *Paraconiothyrium sporulosum* AP3s5-JAC2a, was examined in systems with limestone and zeolite. Post experiment, solids were analyzed with scanning electron microscopy paired with energy dispersive X-ray spectroscopy (SEM-EDS) as well as Mn K-edge X-ray absorption near edge structure (XANES) spectroscopy to determine average Mn oxidation state. In zeolite systems (both fungi-free and with fungi), 95-99% aqueous Mn is removed from synthetic CMD within 24 hours. Meanwhile, limestone systems do not achieve a similar threshold until day 12. While there is no difference between macroscopic Mn(II) removal from solution in the presence of zeolites with fungi vs. fungi free experiments initially, by experiment end the presence of fungi improves remediation by 10-17% and produces Mn oxides with higher average Mn oxidation states, suggesting that zeolites and fungi together better sequester Mn in the solid phase over the long term. Samples were also reacted with copper (Cu) chloride to assess the long-term stability of the Mn bound to zeolites, as zeolites preferentially adsorb Cu(II) over Mn(II). The addition of Cu(II) slightly increases aqueous Mn concentrations and reduces the average Mn oxidation state of the resulting solids. These results suggest that a system incorporating Mn oxidizing fungi and zeolites into passive bioremediation systems may prove as a rapid yet also effective long-term strategy for CMD remediation.