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Remediation of Acid Mine Drainage with Sulfate Reducing Bacteria

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Acid mine drainage (AMD) is a water quality issue associated with mining sites throughout the world, the impacts of which can persist for centuries (1). In the United States, thousands of miles of streams have been affected by AMD (Figure 1), which is characterized by extremely low pH water (2). For instance, water draining from Iron Mountain in California contains the world's most acidic water, with pH values as low as -3.6 (3). In addition to acidity, AMD is also associated with high concentrations of heavy metals (4).

Cause of AMD

AMD is formed by the interaction of oxygen and water with exposed surfaces of pyrite (FeS₂) and other sulfide-containing minerals. This interaction leads to the production of acidity and sulfate and the release of high concentrations of



Figure 1. Stream affected by acid mine drainage.

iron that form rust-colored iron hydroxides when AMD mixes with creeks and rivers (5, 6):

$$4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \rightarrow$$

$$4\text{Fe}^{3^+} + 8\text{SO}_4^{2^-} + 4\text{H}^+ \qquad (1)$$

The Fe³⁺, in turn, can directly oxidize the FeS₂:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (2)

The dissolution of sulfide-containing minerals causes the release of co-occurring heavy metals such as Zn, As, and Cu that also contribute to the deterioration of water quality.

Remediation

Most remediation techniques focus on the amelioration of the low pH associated with AMD (7). A common approach is to simply add alkaline chemicals to neutralize the pH and promote the precipitation of metal hydroxides and carbonates. Passive remediation systems, such as constructed wetlands, are also an option and require less maintenance by relying on naturally-occurring chemical and biological processes (8, 9).

Alternatively, sulfate reducing bacteria (SRB) have been used in bioreactors to improve water quality by decreasing the concentration of dissolved heavy metals. Under anoxic conditions, SRB facilitate dissimilatory sulfate reduction using $SO_4^{2^-}$ as a terminal electron acceptor, creating hydrogen sulfide (H₂S), and convert organic matter ("CH₂O") to hydrogen carbonate. The H₂S can form insoluble precipitates with heavy metal cations (M²⁺) (10, 11):

$$SO_4^{2-} + 2\text{"CH}_2O\text{"} \rightarrow H_2S + 2HCO_3^-$$
 (3)

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+$$
 (4)

Previous studies using anaerobic reactors with SRB demonstrated greater than 95% removal of dissolved Cd, Fe, Ni, Zn, and Cu (10, 11).

Objectives

During this experiment, students create their own bioreactors to simulate AMD remediation using different combinations of inputs to explore the efficacy of each treatment to remove dissolved metals, as well as to demonstrate that microbially produced sulfide is the major removal mechanism of dissolved metals from the water column.

Experimental Overview

This experiment has been used several times in our undergraduate environmental chemistry laboratory course and is intended to be run over the duration of a semester. Students create AMD bioreactors early in the semester, and subsequently record changes in pH and collect weekly aliquots of the aqueous solution that are analyzed at the end of the semester for dissolved metal concentrations.

Many aspects of this experiment can be tailored to emphasize various learning objectives. Students explore the chemical reactions involved with the production and treatment of AMD and gain an understanding of the interactions of biological and chemical reactions in environmental systems. In addition, the experiment provides the students an introduction to flame atomic absorption spectrophotometry. Alternatively, the instructor can emphasize experimental design by involving students in the process of selecting the types of control bioreactors, the number of replicates, as well as the merits of various sampling protocols (e.g., sample volume, collection frequency). Lastly, the students gain experience in data analysis and interpretation. The flexibility in both learning objectives, as well as methods of analysis, allows this lab experiment to be appropriate for students at many different levels from high school to graduate school.

Bioreactor Assembly and Sampling

The methods given here describe our default setup, but other variations are possible. Students created five sets of bioreactors run in triplicate: three controls and two experimental bioreactors. The controls are necessary to show that the metal removal results from the generation of sulfide and not from adsorption onto the soil, the leaves, or the bottle. All bioreactors contained simulated AMD water, plus combinations of SRB and organic carbon sources. The simulated AMD contained 10–20 mg L⁻¹ copper and iron and the pH was adjusted to pH 2–3 using sulfuric acid, which also provides sulfate for the SRB. Since SRB are found naturally in soil, any type of soil can be used, although a pre-enrichment step prior to the experiment accelerates the establishment of an active SRB population. For organic carbon sources, we focused on carbon of convenience, that is, leaves that can be collected near the science building. In particular, students compared the efficacy of adding whole versus crushed leaves to the bioreactors.

Analysis

Samples were analyzed on the last day of sampling with a PerkinElmer flame atomic absorption spectrophotometer (flame AAS). The absorbances for copper and iron standards, as well as for all dissolved metal samples, were measured at 324.8 nm for copper and 248.3 nm for iron. If the instructor does not have access to a flame AAS, other methods of metal analysis can be used, such as wet chemical methods or Hach kits.

Hazards

Sulfuric acid is corrosive and students should wear appropriately protective clothing. Neither metal is considered a hazard to human health. Waste material should be disposed according to local, state, and federal environmental regulations.

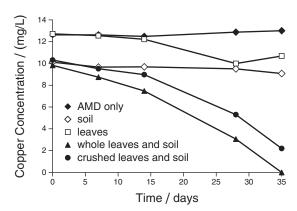


Figure 2. Dissolved copper concentration in the bioreactors throughout the experiment (n = 3).

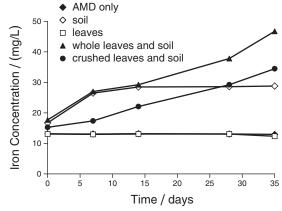


Figure 3. Dissolved iron concentration in the bioreactors throughout the experiment (n = 3).

Results and Discussion

The observed trends in dissolved copper concentrations matched the students' predictions that only the bioreactors containing both the soil (bacteria) and the leaves (carbon) displayed a decreasing trend in dissolved copper concentrations (Figure 2). These results led the students to conclude that the likely removal mechanism was the precipitation of Cu as CuS(s). These data also demonstrated a 20% decrease in dissolved copper concentrations in all bioreactors containing soil, compared to those without soil, following their assembly on day 0. The students postulated that since only the dissolved copper was measured, copper may bind to soil surfaces, thereby leading to copper removal from the dissolved phase. Previous research has shown that in fact copper does have a high affinity for the organic matter in soil (12, 13). However, the reduction in the copper concentration was smaller than the subsequent decline of the copper in the full treatment bioreactors during the duration of the experiment. These data provided students an opportunity to discuss whether the addition of carbon alone was sufficient as a remediation technique and to consider the relative time scales of the effects.

In contrast to copper, dissolved iron concentrations increased by 70–160% in three of the five bioreactors (Figure 3). This trend was not anticipated by the students, but based

on the fact that these three bioreactors were the only ones that contained added soil, the students were able to conclude that the iron was likely being solubilized from the soil by the low pH of the AMD. No removal of iron as FeS was observed, but based on the $K_{\rm sp}$ values, iron sulfide would not be expected to precipitate until all copper was removed from solution. By day 35, copper in our full-treatment bioreactors had either just reached or was approaching non-detectable levels, so given more time, dissolved iron concentrations would likely start to decrease. This fact highlights the importance of starting the experiment as early as possible in the semester.

In full treatment bioreactors, the pH increased steadily over the course of the experiment (Figure 4). The students were able to explain these data once they realized that bicarbonate ion is generated during sulfate reduction, thereby increasing the alkalinity in the bioreactor and neutralizing some of the acidity.

Summary and Conclusions

This laboratory experiment has been used successfully by our undergraduate environmental chemistry laboratory course. The students learned about the chemistry of acid mine drainage, as well as one effective technique for remediation. They also gained insight into designing bench-scale experiments to determine remediation efficacy. Lastly the students gained experience interpreting data that did not conform to their initial expectations.

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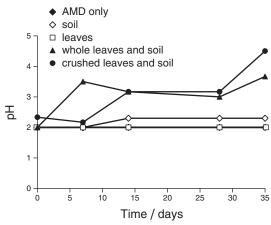


Figure 4. pH in the bioreactors throughout the experiments (n = 3).

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