A Toolbox for Characterizing Organic Media in Passive Biotreatment Cells

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Extended Abstract

The mining industry may choose to use passive biotreatment cells with organic media to remove dissolved sulfate and metals from mine-influenced waters (MIW) before discharge. Over time, the organic media changes as nutrients are consumed by microorganisms, microbial biomass accumulates, and inorganic material (including sequestered metals) is deposited. Characterizing the media and how it changes can provide insight into improvements, bioreactor longevity, nutrient limitations, mechanisms of metal sequestration, and safer disposal of used media.

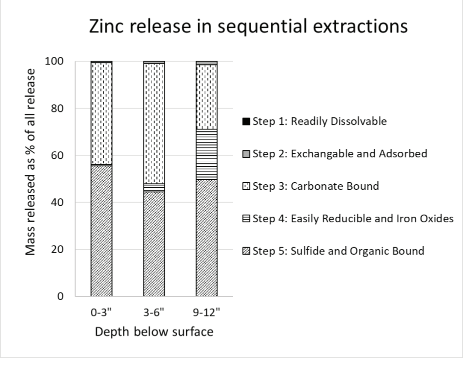
This paper describes the analysis of organic media containing wood chips and shavings, steer manure, and alfalfa hay collected from sulfate-reducing bioreactors that operated for nearly a decade in southwest Colorado. A broad toolbox of techniques was developed to characterize the used media and compare it to the initial media, stored in a controlled temperature environment. A method was developed to preserve and isolate inorganic surface fines from organic media, and standard techniques showed the spatial distribution of metals (e.g. aluminum, arsenic, cadmium, copper, iron, lead, manganese, nickel, and zinc) and nutrients (e.g. total organic carbon, ammonia, total Kjeldahl nitrogen, sulfur, and phosphorus). Sequential extractions using organic solvents were performed by a commercial biomass laboratory to characterize the lignocellulosic components and availability of carbon forms, using methods to Drennan et al. (2016). A modified Tessier sequential extraction method (Klock et al., 1986) was used to quantify weakly-adsorbed metals and metals associated with iron and manganese oxides, carbonates, sulfides, and organic material. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS) were used to visualize shapes and elemental distributions on the media surfaces. Finally, leachate tests, including the synthetic precipitate leaching procedure (SPLP) and toxicity characteristic leaching procedure (TCLP) provided insight into potential metal mobility during precipitation or leaching in the environment during storage.

The combined results highlighted trends with depth below the media surface in down-flow reactors: the relative mass of sulfur, total organic carbon, and total Kjeldahl nitrogen increased with depth, while iron, aluminum, manganese, copper, lead, and arsenic decreased with depth and were primarily sequestered in the top foot of a 4-foot reactor. Analyses of fines that were dried and removed from larger particles indicated that after 8–9 years of reactor operation, nutrients such as ammonia and phosphorus had been depleted overall by 55% and 73% respectively. Ammonia was specifically depleted near the surface, while phosphorus was depleted similarly throughout the reactor.

A primary function of these bioreactors was to remove zinc from water, and most zinc was removed in the top foot. Sequential extraction data (e.g. Fig. 1, left) indicated that zinc was associated with carbonates near the surface and with sulfides deeper. EDXS elemental maps (e.g. Fig. 1, right) showed that this zinc was spatially associated with wood surfaces and manganese, not iron. In these bioreactors, which allowed some

water-level fluctuation and were therefore not operated entirely as classical reducing bioreactors, the results point to a mechanism of zinc removal that is associated with the more oxic zone near the surface, and possibly MnO_2.

Zinc removal was successful, but zinc was not entirely removed as zinc sulfide: this knowledge the effects of design and operation and highlights the influences of water-level fluctuation when dissolved zinc is the primary constituent for removal.



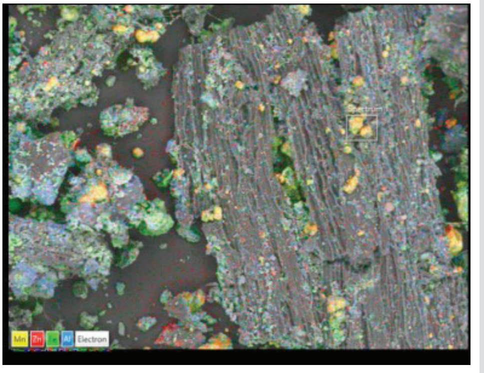


***Figure 1** (left) Sequential extraction data for zinc, based on a modified Tessier method (Klock et al.). (right) EDXS elemental map showing the distribution of particles and selected elements on a wood media particle*

Lignocellulosic analyses comparing the used media to the original media highlighted decreases in total sugars and some specific forms, and combustion showed an increase in ash (i.e., the non-combustible fraction). Ash and sugar analyses could therefore be useful as general measures of media aging, particularly when coupled with reactor performance over time. To inform storage and disposal methods, samples of the media were removed and exposed to air/oxidation for up to 90 days. For some metals (e.g. cadmium), leachability increased over storage time, while for other metals (e.g. chromium, lead, selenium, and arsenic), leachability decreased.

It should be noted that these results and lessons describe a unique situation of water and media type, environmental conditions, and reactor design; however, this toolbox of techniques can be similarly applied to any passive bioreactor that treats MIW. Passive bioreactors are often viewed as 'black boxes' with complicated processes and limited lifespans; but techniques such as these can provide insight into optimization, troubleshooting, design, and decommissioning. In this presentation, methods and results will be described, with a focus on the value of individual and combined methods to understand changes in the media, and the spatial and chemical character of the media and sequestered metals.

Keywords: Sulfate-reducing bioreactors, organic media, sequential extractions, electron microscopy, metal mobility

References

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