Sulfate Reducing Bioreactor Longevity Estimates based on Substrate Characterization and Initial Carbon Release

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Abstract

Sulfate reducing bioreactors have the potential to provide treatment of mining influenced water (MIW) with low operation and maintenance requirements. However, there is a lack of validated design guidance on the specifications of the organic substrate to ensure longevity of bioreactors for metals removal. Current design criteria are based on an assumed rate of carbon release coupled to sulfate reduction from a generic substrate. Linking the specifications of the organic substrate mixtures to the rate and extent of carbon release is a first step in improving design guidance.

Three 18-liter columns were filled with one of three organic materials: woodchips, sawdust or alfalfa hay, and operated for 500 days with a MIW containing Zn ≈ 170 mg/L, Sulfate ≈ 5000 mg/L with a pH ≈ 6. The composition of organic materials was characterized using sequential chemical extractions to operationally define carbohydrate, cellulose and lignin like fractions. The carbon released by the substrate was calculated using the effluent carbon concentration and flow plus estimated carbon utilized for sulfate removal. The potential longevity was estimated based the calculated bioavailablility of the individual substrate components, the carbon released after 1.2 year of operation and two scenarios for future effluent carbon and sulfate reduction rate.

Half of the bioavailable carbon in all columns was utilized in the first 1.2 years of operation and primarily was related to effluent carbon. The estimated longevity of the columns was influenced by the effluent carbon assumption. The high value of effluent carbon used (500 mg/L as COD) was the average measured value at 1.2 years from all the columns. Zero effluent carbon was used to set a theoretical maximum longevity assuming a sulfate reduction rate of 0.3 mol/m^3/d. Our data supports a conservative estimate of SRBR substrate longevity in the 2 to 5 year range.

Key words: Treatment, Anaerobic, Bioavailability

Introduction

Mining influenced water (MIW) may contain heavy metals, metalloids, and sulfate due to the production of sulfuric acid from sulfide existing in ore bodies under aerobic condition. Physicochemical treatment processes are typically used to treat MIW by alkaline addition. Anaerobic biological treatment of MIW using sulfate-reducing bacteria (SRB) to biogenically produce sulfide is an attractive treatment alternative. Metal sulfide sludges are less voluminous that hydroxide sludges produced by alkaline treatment. Biological sulfate reduction requires the addition of a suitable electron donor, which may be provided by a range of organic materials.

Biological sulfate reduction may be implemented in a passive configuration that requires low levels of operation and maintenance. Passive treatment processes are ideal for closed mine sites characterized by remoteness and lack of accessibility for low MIW flow and projected long-term treatment duration. To date, diverse natural organic substrates such as hay, woodchips, sawdust, alfalfa, manure, walnut shells, and corn stover, have been used as the source of electrons for the biological sulfate reduction (Bless et al. 2008, Doshi 2006). The relatively low bioavailability and degradation rate of natural organic substrates will control the design and thus the treatment efficiency and rate in passive biological treatment system.

The number of passive biological MIW treatment systems in operation is still limited and the design is usually based on short-term experiments with a black box approach. The scope of this paper focuses on the evaluation of expected longevity of sulfate reducing bioreactors based on substrate bioavailability, effluent carbon and sulfate removal rates.

Methods

The sulfate reducing bioreactor columns were fed MIW collected from an inactive mine site. MIW collected from the site was stored in a 2,500 gal capacity non-transparent polyethylene tank to maintain the influent quality and to prevent algae growth during reactor operation. The key characteristics of the influent MIW were: pH ≈ 6; sulfate ≈ 5,000 mg/L; zinc ≈ 167 mg/L. PVC column reactors with an operating volume of 18-liters with height and inner diameter (ID) of 1.32 m and 0.15 m, respectively, were used to evaluate the carbon release and sulfate reduction.

The columns were packed with a single substrate or mixtures of ponderosa pine woodchip, pine sawdust, alfalfa hay, as electron sources and limestone as an alkalinity source. The packed height of the mixture of organic substrate and limestone was ≈ 1 m. The mass of substrate and limestone used in each column is shown in Table 1.

Table 1. *Substrate compositions in SRBR Columns*

Reactor ID	Organic material 70% by weight, g	Limestone 30% by weight, g
Hay	2,450	1,070
Saw dust	4,370	1,870
Wood chip	2,790	1,150

Ponderosa pine woodchip and sawdust were obtained from a lumber mill in New Mexico, USA. Locally grown alfalfa hay was purchased from a feed store in Arizona, USA. Limestone aggregate was from a limestone quarry in Arizona.

Each column was filled with MIW and liquid was recirculated from bottom to top of reactor at ~15 L/day for 1 month followed by inoculation with ≈ 500 mL of a sulfate reducing mixed culture. Column liquid was subsequently recirculated for 1 month. Column operation was then changed to continuous down-flow mode with an initial flow rate of 0.4 L/day, flow rate varied between 0.1 and 1.6 L/day over the 500 days of operation. Additional details about the experimental system may be found in Landkamer et al. (2013).

Effluent organic carbon was measured using a Shimadzu TOC analyzer. COD and sulfate concentrations were measured by the HACH methods. Anaerobic bioassays (modified from Owen et al. 1979) were conducted to estimate the bioavailable fraction of the substrates. The biodegradable component was defined as the difference between the initial and final mass of the organic substrate evaluated. The bioavailability of the substrate was also calculated based on lignin fraction using a modification of the Chandler et al. (1980) and Van Soest (1967) methods. Operationally defined organic fractions of organic substrate were estimated by sequential extraction in hot water (TAPPI Method 207 om-88) followed by acid (National Renewal Energy Laboratory, Chemical and Analytical Testing Laboratory Analytical Procedure - Determination of Acid-Insoluble Lignin in Biomass, 1995).

The amount of carbon released from the organic substrate in the column was estimated by the cumulative amount of effluent organic carbon and the calculated organic carbon needed to support the measured sulfate reduction. Units of chemical oxygen demand (COD) were used to evaluate organic matter consumption. Organic carbon (OC) concentration was converted to COD units by a factor of 2.67 g COD/g OC. A ratio of 70.4 g COD/mmol sulfate removed was used to convert sulfate to COD units. The ratio is based on the amount of COD needed for sulfate reduction and cell growth.

Results and Discussion

The results presented herein focus on estimating organic carbon release and prediction of the bioreactor column longevity. Information on metal removal and microbiology is presented in Landkamer et al. (2013). The initial organic carbon content of the substrate was based on the measued COD of the solid phase organic substrate and a conversion factor of 2.67 g COD/g C. The amount of solid phase organic mass degraded in the anaerobic bioassay was comparable to the value calculated from the operationally defined composition and the Chandler and Van Soest equations. The estimated total carbon, initial bioavailable carbon and remaining bioavailable carbon at 1.2 years is presented in Table 1. The longevity of the substrate is presented relative to the fraction of bioavailable carbon remaining with time for hay, sawdust and woodchip in Figures 1, 2 and 3, respectively. The fraction of bioavailable carbon released versus time in the first 1.2 years is based on the cummulative amount of effluent carbon and the estimated carbon consumption associated with the measured sulfate reduction. The high value of effluent carbon used (500 mg/L as COD) in predicting longevity, was the average measured value at 1.2 years from all the columns. Zero effluent carbon was used to set a theoretical maximum longevity assuming a sulfate reduction rate of 0.3 mol/m^3/d.

Table 2. *Estimated total and bioavailable organics in columns*

Reactor ID	Initial organic carbon, grams	Estimated initial bioavailable organic carbon, grams	Estimated bioavailable organic carbon remaining at 1.2 years, grams
Hay	1080	550	260
Saw dust	2110	105	50
Wood chip	1370	70	35

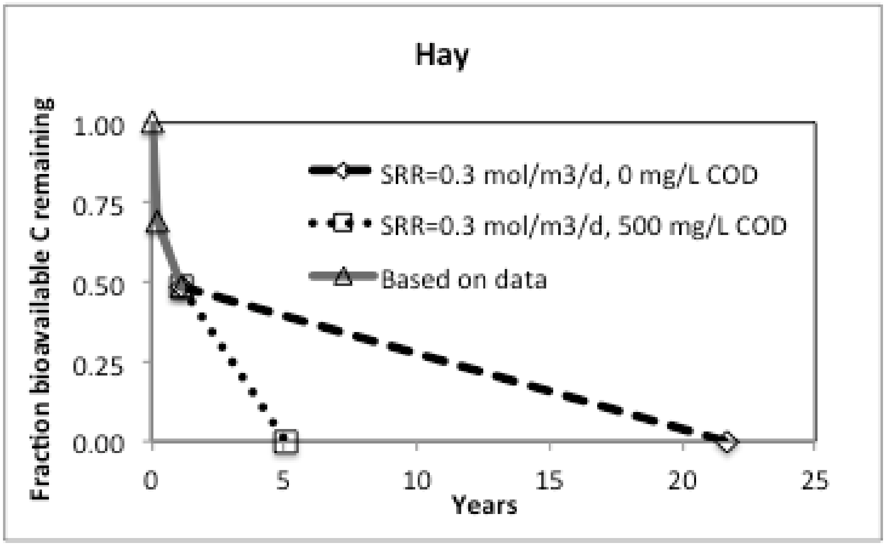

Figure 1 *Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for hay under two scenarios of effluent carbon concentration and sulfate reduction rate.*

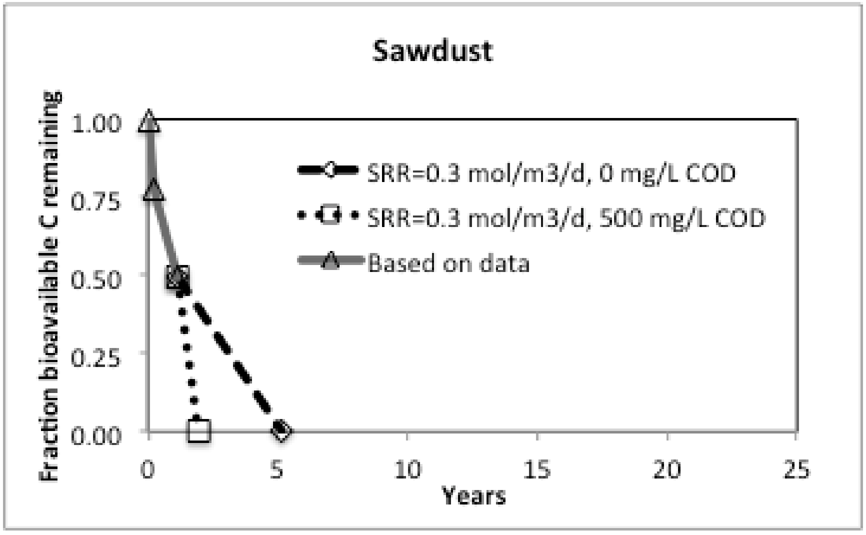

***Figure 2** Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for sawdust under two scenarios of effluent carbon concentration and sulfate reduction rate*

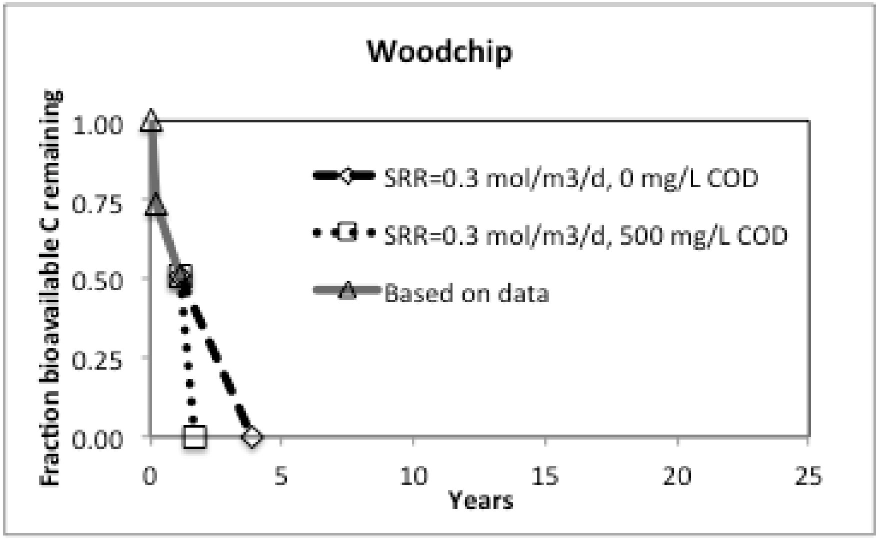

***Figure 3** Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for woodchip under two scenarios of effluent carbon concentration and sulfate reduction rate.*

It is important to establish a method to estimate the expected longevity of sulfate reducing bioreactors to appropriately evaluate the comparative costs relative to other technologies. The expected life-time of sulfate reducing bioreactors has been projected to be up to 50 years (Gusek and Schneider 2010). However, there is no data to support long-term operation of sulfate reducing bioreactors at the projected sulfate reduction rate of 0.3 mol/m^3/d. In a recent review of sulfate reducing bioreactors, the rate of sulfate reduction was reported to range from 0.02 to 3.5 mol/m^3/d (Fitch 2015). The longevity of sulfate reducing bioreactors for metal removal will depend on amount of biodegradable organic substrate, the rate of carbon release and utilization by the microbial community. Two methods were used to estimate bioavailable organic carbon from initial total organic content of the organic substrates. Methods to predict the rate of organic carbon release and utilization are still needed. The effect of the assumed rates of carbon release and utilization resulted in a wide range of predicted longevity.

Conclusions

Our data suggests that predicted sulfate reducing bioreactor life-time of decades is overly optimistic. Half of the bioavailable carbon in both the alfalfa and woodchip columns was utilized in the first 1.2 years of operation and primarily was related to effluent carbon. The estimated longevity of the columns was influenced by the effluent carbon and the sulfate reduction rate assumptions. Our work supports a conservative estimate of sulfate reducing bioreactor substrate longevity in the 2 to 5 year range.

Acknowledgements

The authors are grateful to Freeport-McMoran Inc. for support of column construction and operation, laboratory analysis, financial resources and editorial input.

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