Design and Operation of a Scalable Electrochemical–Biological Sulfur Bioreactor for Mine Water Treatment

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Abstract

Sulfur management poses environmental and economic challenges for mining due to complex sulfur chemistry and its ecological impacts, especially in low sulfate freshwater systems. Improving sulfur recovery remains a key need. We developed a low-current, electrode-integrated sulfate bioreactor that promotes microbial sulfate reduction and sulfide removal, offering an in-situ remediation option. Bench and pilot studies demonstrate sulfate removal performance from mine pit lake water with concurrent recovery of solid elemental sulfur. This work presents the engineering design for an upscaled system, outlining operational and maintenance considerations needed for next-stage treatment development. These efforts advance sustainable, interdisciplinary solutions for sulfur management.

Keywords: Sulfate, in situ bioremediation, bioreactor, pilot-scale, and sulfur recovery

Introduction

Sulfate-laden water is a biogeochemical stressor in freshwater environments and is a burden to many industries and municipalities, both in Minnesota and globally. Although natural sources of sulfate exist, elevated concentrations in freshwater ecosystems are often linked to anthropogenic sources such as industrial and municipal waste streams, or mining drainage (Zak *et al.*, 2021 and Berndt *et al.*, 2016). Introducing sulfate into ecosystems that naturally have low background levels can alter natural biochemical processes and, under certain conditions, cause adverse ecological consequences such as mercury methylation and methane production (Zak *et al.*, 2021 and Weiss *et al.*, 2024). Globally, sulfate limits for freshwater aquatic ecosystems and drinking water typically range from 10 mg/L to 250 mg/L (Weiss *et al.*, 2024 and Xiao *et al.*, 2024). With increasing demand for critical minerals and the expansion of green technologies, managing sulfate loading has become even more challenging. These ecological, industrial, and regulatory pressures have driven interest in developing low-cost and efficient approaches to reduce sulfate levels.

Current treatment technologies for sulfate removal remain hindered largely by high costs, intensive maintenance, and sludge management requirements of membrane-based treatment technologies (Andrews *et al.*, 2018). Moreover, sulfate concentration levels and water chemistry in mine waste streams vary widely from processing water to drainage, requiring a treatment train approach. Among currently available options, biological treatment processes have been applied beneficially for waters with a wide sulfate concentration range (250-2000 mg/L) in both active and passive treatment systems.

In situ remediation is an engineered approach being deployed directly at contaminated sites for treating and managing pollutants, often as passive treatment systems such as constructed wetlands, permeable reactive barriers, and biofiltration units. Passive or semi-passive treatment systems rely on natural processes (physical, chemical, biological, hydrological) to transport and reduce contaminants in a targeted treatment zone, thus requiring relatively little infrastructure and routine maintenance. However, their treatment performance has been reported to vary depending on site characteristics, season, or substrate availability.

One promising treatment technology that addresses limitations of current technologies for sulfate treatment is the use of bioelectrochemical systems. These systems enable controlled and direct delivery of substrates, which provides design and operational flexibility. Our recent work has developed a treatment approach which low-voltage electrical potential is used to promote and sustain biological sulfate reduction and to support chemical and biological sulfide immobilization by providing electrolytic hydrogen and oxygen in a controlled manner for in-situ remediation. The system has been evaluated with sulfate-rich mine pit lake water and industrial wastewater at a bench scale (Johnson *et al.* 2019) and through mathematical modelling (Berens *et al.* 2024). Those results indicate that sulfate removal efficiency in bioelectrochemical systems is determined by both hydraulic residence and the rate of electrochemical hydrogen generation (Berens *et al.* 2024).

Building on these findings, **this project aims to evaluate an upscaled bioelectrochemical treatment system for sulfur management for mine water, providing key operational and maintenance considerations needed for reliable, full-scale treatment.** This will help establish an engineering foundation and increase confidence in the technology for the management of sulfate-rich mine water.

Conceptual Bioelectrochemical Treatment

To evaluate an upscaled bioelectrochemical treatment system, a pilot-scale electrochemical biofiltration was designed and constructed. Successful sulfate bioremediation relies on both biological sulfate reduction [Equation 2] and sulfide immobilization [Equations 3 & 5]. The bioelectrochemical treatment system integrates two major pathways mediated by water electrolysis [Equations 1 & 4]. Figure 1 shows the conceptual reaction pathways through the pilot-scale system. Specifically, sulfate reduction is stimulated by providing electrolytic hydrogen to sulfate-reducing bacteria (SRB) at the cathode [Equation 1] while oxygen or other oxidants generated at the anode are involved in both chemical and biologically-mediated sulfide immobilization to either elemental sulfur or iron sulfide. In this pilot-scale treatment system, elemental sulfur is the desired solid-phase sulfur species for recovery.

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [1]
$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$ [2]
$HS^- + Fe^{2+} \rightarrow FeS(s) + H^+$ [3]
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ [4]
$2HS^- + O_2 + 2H^+ \rightarrow 2S^0 + 2H_2O$ [5]

Methods

Electrode-integrated biofiltration system

The pilot-scale treatment system is comprised of a series of individual circular bioreactor columns made of clear PVC with an upflow design. The column is modular, allowing for up to 3 1-ft paired electrode columnar sections (Figure 1), totalling a maximum height of about 5 ft. Each column is equipped with an underdrain at the base, a gas vent at the top, and porewater collection ports between each electrode pair to allow for accessible sampling points. A twisted-titanium wire carbon fiber brush (Surface area: ~2 m2, Mill Rose, Inc.) was used for the cathode, and a carbon fiber cloth (Surface area: ~0.18 m2; Composite Envisions, Inc.) was chosen for the anode. The electrode system was powered by a BK Precision Model 9130 Triple-Output Programmable DC Power Supply. The bioreactor columns are filled with a variety of conductive geomedia compositions for operational comparison. Media is composed of varying volume ratios of C-33 washed sand (particle size range, 0.075-4.75 mm), pea gravel (6.35-12.2 mm), and biochar (0.1-2.0mm; Wakefield Biochar, GA, USA) for biofilm formation and filtration.

Mine Pit Lake Water

The performance of the electrode-integrated biofiltration system has been evaluated with

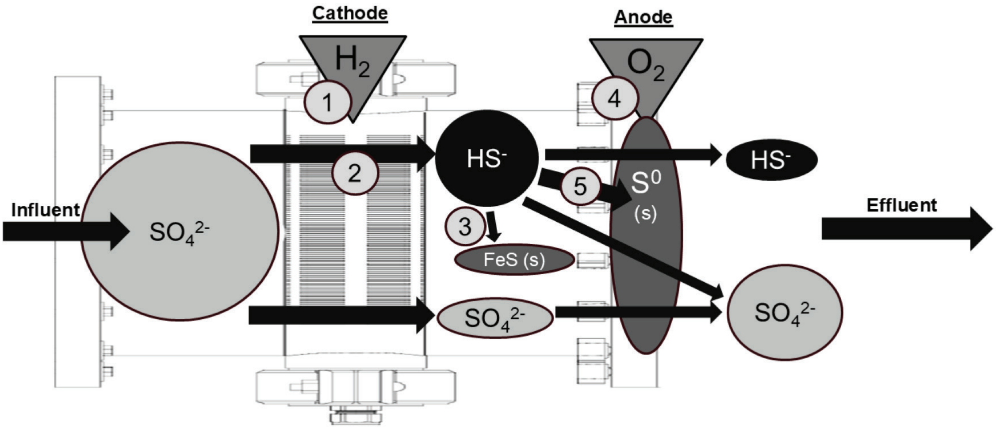

Figure 1 Conceptual diagram of sulfur transformation and water electrolysis reactions in the electrode-integrated biofiltration system, including: [1] electrolytic hydrogen (H_2) generation at the carbon brush cathode; [2] sulfate (SO_4^{2-}) reduction to sulfide (HS^-) by sulfate reducing bacteria; [3] precipitation of iron sulfide (FeS); [4] electrolytic oxygen (O_2) generation at the carbon cloth anode; and [5] partial oxidation of sulfide (HS^-) to elemental sulfur (S^0)

water associated with a mine pit lake as a result of historic iron ore mining in Aurora, Minnesota (USA). The lake water contained elevated levels of dissolved solids, primarily sulfate (300-400 mg/L), calcium, and magnesium. Low concentrations of nitrogen, phosphorus, and organic carbon within the pit lake water indicate the predominance of oligotrophic conditions (Table 1). Water is circumneutral pH with moderate alkalinity levels, suggesting a well-buffered system. For the pilot-scale operation, both unaltered pit lake water and pit lake water amended with calcium sulfate and magnesium sulfate to create elevated sulfate concentrations (up to 1200 mg/L) were used.

Pilot System Operation

Initially, the treatment system was operated in a batch mode to establish the microbial community responsible for sulfur transformation, accomplished by inoculating SRB culture enriched with the mine pit lake water and a nutrient solution composed of a 100:10:1 C:N:P. Sufficient biological activity was verified by measuring sulfate and sulfide levels in sampling port between two electrodes. After verification, the systems were operated to evaluate key operational parameters, including different geomedia compositions (7:3 sand to biochar and 7:3 gravel to biochar v/v), hydraulic retention times (HRT; 1-5 days), and applied currents (5-50 mA).

***Table 1** Water chemistry of the mine pit lake water.*

Parameters	Unit	Value
Total organic carbon	mg/L	1.6
Total hardness	mg/L as $CaCO_3$	531
Total alkalinity	mg/L as $CaCO_3$	177
Total sulfur	mg/L	123
SO_4^{2-}	mg/L	370
Ca^{2+}	mg/L	37.9
Mg^{2+}	mg/L	91.1

The amount of biochar amendment was based on amounts previously determined in microcosm biokinetic experiments of sulfate reduction.

To evaluate the performance of sulfur transformation, aqueous samples were collected at three locations within the treatment system (influent, sampling ports, and effluent) for measurement of sulfur speciation (SO_4^{2-}, $S_2O_3^{2-}$, HS-, and S^0). Sulfate concentration was determined by Ion Chromatography (Dionex ICS 2000; EPA Method 300.0). For sulfide measurements, samples were immediately preserved in a zinc acetate and sodium hydroxide solution and subsequently quantified using Methylene Blue (EPA Method 376.2). Elemental sulfur was extracted with chloroform and quantified using High Performance Liquid Chromatography (Dionex UltiMateTM 3000; Aliboni et al, 2015).

Results

Preliminary sulfate treatment performance at pilot scale

Upon the establishment of sulfur-transforming biofilm in batch mode, the gravel–biochar biofiltration systems were operated in a regime with a 3-day HRT and a constant current of 10 mA (applied voltage: 1.5-4.0 V). Influent water containing ~400 mg/L as S (1200 mg/L sulfate) was pumped into the system. Sulfate concentrations in samples collected between the electrode pair and at the effluent decreased during operation, with net removal ranging from 100 to 300 mg/L as S (Figure 2). These reductions were presumably supported by the continuous production of electrolytic hydrogen. Although sulfide was observed to accumulate in the effluent during operation, concentrations remained below 30 mg/L as S, a level approximately tenfold lower than the net sulfate removal, indicating substantial sulfide immobilization by the geomedia and/or conversion to other sulfur species.

To verify sulfide immobilization by geomedia, sorption isotherm experiments were conducted for both sulfate and sulfide using the fresh biochar used in this study. Sulfide solutions with different concentrations were added to biochar masses ranging from 0.01 to 1.0 grams. The mixtures were placed on a shaker for 24 hours to reach equilibrium. We observed high sorption affinity of sulfide onto the biochar. Using the Freundlich isotherm, the sorption capacity constant (Kf) was estimated as 238±1.15 L/Kg, which is much greater than observed for sulfate (35-85 L/kg). This enhanced affinity for sulfide compared to sulfate is likely attributable to the iron content of the biochar, consistent with metal sulfide precipitation (Equation 3). These results suggest that biochar used in this study not only supports biofilm development and enhances biokinetics but also effectively sequesters dissolved sulfide produced during biological sulfate reduction.

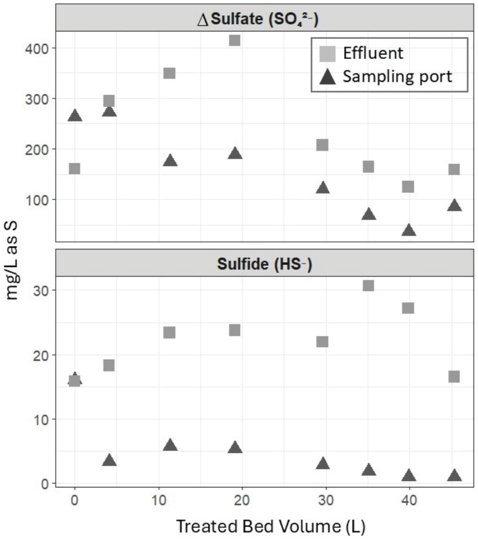

Figure 2 *The change of sulfate concentration from influent and sulfide concentration in sampling port between each electrode pair and effluent of the electrode-integrated biofiltration filled with gravel-biochar (7:3 v/v) operated with 10 mA of constant current application and 3-day HRT. Concentration unit is mg/L as S (on a sulfur mass basis).*

During the operation of the pilot-scale system, white-yellow film-like solids were visually observed on the surfaces of the carbon-cloth anode, suggesting the formation of elemental sulfur was occurring, in addition to sulfide immobilization on the geomedia. Through Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (Hitachi TM3030), we verified the solids were largely crystalline elemental sulfur. Comprehensive characterization of these solid-phase materials will be conducted at the conclusion of the pilot-scale operation.

Effect of geomedia types on the performance

Concurrently, we operated treatment systems filled with either sand alone or a sand–biochar mixture (7:3 v/v) at 3–5-day HRT and constant current applications up to 50 mA. Compared with the gravel–biochar system, sulfate reduction was initially observed in both the sand alone and sand-biochar configurations but declined over time. At the same time, the voltage required to maintain a 50-mA current increased to as high as 30 V, indicating unfavorable conditions for both water electrolysis and biological activity. This performance decline was attributed to substantial gas accumulation within the biofiltration beds, which required periodic manual release by tapping the reactors. Gas buildup increased electrical resistance by insulating electrolytic reactions. This behavior was more pronounced at higher current applications, where excess H_2 and O_2 were generated beyond the amounts needed to sustain biomass activity on the geomedia.

Additionally, geomedia with smaller particle sizes and heterogeneous composition exhibited higher internal electrochemical resistance due to limited hydraulic conductivity and mass transfer. As reported by Quejigo *et al.* (2019), such conditions require higher voltages to achieve target water-electrolysis reactions. These observations suggest that larger pore spaces and more fluidic bed structures may be important design considerations for optimizing system performance. In consideration of the current findings, a treatment system with geomedia with greater fluidic bed structure characteristics is under investigation.

Relationship of net sulfate removal and current density

As the pilot-scale treatment systems have been operated under various combinations of HRTs and applied currents, these results will be used to develop a relationship between required current and target sulfate removal to guide future system design and operational parameters. To enable broader applicability across treatment scales, a theoretical relationship between applied current density and sulfate load reduction was developed based on the stoichiometric electron balance of the biochemical reactions (Reactions 1–5; red line in Figure 3). Net sulfate load reduction is a function of the magnitude of sulfate concentration change from influent to effluent and HRT. As pilot-scale system evaluation progresses, this theoretical relationship will be compared with the emerging empirical relationship (green line in Figure 3).

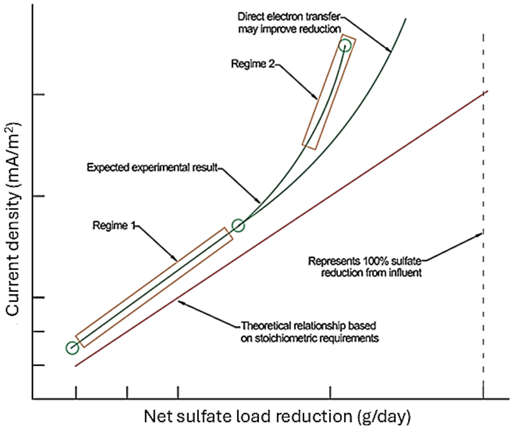

Figure 3 *Theoretical and empirical relationship of current density and sulfate load reduction.*

Based on current testing, the empirical trend is expected to exhibit two regimes: When biomass and sulfate are abundant relative to available electron donors, increasing current density increases electrolytic H_2 production, which proportionally enhances sulfate reduction by SRB (Regime 1 of green line in Figure 3). When influent sulfate concentrations fall below the threshold needed to sustain biological activity or when sulfate is limiting, further increases in current are expected to yield diminishing or no additional sulfate reduction. In this range, sulfate reduction may approach thermodynamic or biological limits, and excess H_2 may instead be consumed by competing side reactions (e.g., iron reduction, methanogenesis). This relationship will help define the effective treatment window and inform optimal electron donor delivery at given biomass levels, which can be influenced through biochar amendment.

Conclusions

Bioelectrochemical systems provide a promising treatment approach for sulfate remediation and sulfur recovery, with the potential to reduce some of the costs associated with existing technologies. Pilot scale operation has helped identify essential design considerations for a future field deployable system. Ongoing work is focused on refining hydraulic retention time and current application to better target sulfate removal. At the pilot scale, managing electrical resistance and biomass sensitivity has emerged as an important factor for informing next stage design. Overall, this study demonstrates the capabilities of pilot scale bioelectrochemical systems for sulfur remediation and offers an engineering basis to guide further treatment development.

Acknowledgements

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