A Novel Photocatalytic Approach to Passive Mine Water Treatment

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Introduction

Vast amounts of mining process-affected water are produced during mine operations and closure which may have an impact on the local environment, community health, and overall sustainability due to contaminants, odours, and fugitive emissions. Typically, active mine effluent and tailings treatments require chemical additives or separation technologies that are capital and energy intensive. These methods are often operationally complex and require a high degree of maintenance oversight to operate successfully. Alternative passive treatment technologies, such as wetlands, offer a solution but are not well integrated with existing active treatment methods and are unable to provide a high-strength chemical oxidation required to effectively treat contaminants and emissions of concern.

To this end, H2nanO Inc. has developed SolarPass, a novel buoyant photocatalytic treatment system for passive advanced oxidation of dissolved contaminants, which naturally forms a floating reactive barrier that also intercepts and treats volatile emissions. The SolarPass system can be deployed and recovered in-situ for off-grid, high strength oxidative treatment of recalcitrant mining contaminants without the need for chemical or electrical inputs. Further, SolarPass can be continuously operated without gas handling, operator intervention, or adsorbent regeneration/disposal.

Previous bench-scale research has validated this floating solar-photocatalytic process for recalcitrant naphthenic acids treatment in mining process-affected water (Leshuk et al. 2018). Additionally, photocatalysis has been successfully demonstrated for the treatment of mining wastewater and tailings applications targeting ammonia (Altomare et al. 2012), cyanide (Chiang, Amal, and Tran 2003), and selenium (Holmes et al. 2022). Building upon previous work, H2nanO further validated the efficacy of the SolarPass system for two in-situ mine treatment applications: the bench-scale (1 L) treatment of organoselenium and the pilot-scale (500 L) treatment and mitigation of reduced sulfur emissions from a mining tailings pond containing anaerobic sludge.

Methodology

The preliminary evaluation of SolarPass for the oxidative treatment of selenomethionine as a representative organoselenium compound was performed at the lab-scale (1 L) under artificial UV light, using solutions of 25 mg/L and 25 µg/L seleno-L-methionine in deionized water to accurately quantify the reaction products. Treatment experiments were also performed using a simulated mine-water matrix (Holmes et al. 2022). The organic fraction of selenomethionine was quantified using low-range chemical oxygen demand (COD) measurements while the selenium species were quantified using ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS) by Brooks Applied Labs.

Additionally, SolarPass was validated for the treatment and containment of volatile reduced sulfur emissions using an outdoor pilot-scale system (500 L) for water containing biogenic H_2S from a tailings pond containing anaerobic sludge. Sulfurous compounds were tracked and quantified using in-field online measurements (electrochemical handheld sensors) and high-resolution laboratory analysis (colourimetric assays and inductively coupled plasma optical emission spectroscopy (ICP-OES)) to establish the effective conversion of volatile sulfurous compounds to sulfate.

Results and Discussion

Organoselenium Photocatalytic Treatment Results

The objectives of these experiments were to demonstrate an initial proof of concept for the photocatalytic treatment of selenomethionine at an elevated concentration while confirming the selenium mass balance. Organoselenium compounds are significantly more toxic and bioaccumulative than Se(VI) for various aquatic biota (Lemly, Finger, and Nelson 1993) and therefore, oxidative conversion of organoselenium to Se(VI) can significantly reduce the toxicity of selenium-containing effluents. Figure 1 presents the selenium speciation results during photocatalytic treatment and a control (UV exposure, no catalyst). The total selenium present (average of 9828 ± 134.5 µg/L) matched the theoretical selenium added with the selenomethionine stock solution (10000 µg/L Se) and remained constant during the experiment duration. Through photocatalysis, selenomethionine was treated from an initial concentration of 9140 µg/L to 2.19 µg/L, demonstrating a >99.97% reduction in the initial selenomethionine concentration with conversion to 98.1% selenate. Compared to the photocatalytic experiment, the UV control (no catalyst) showed only a 9.4% decrease in the initial selenomethionine concentration while receiving a similar UV dose. Additionally, the selenate concentration in the UV control only increased by 63.7 µg/L compared to

9460 µg/L using SolarPass, validating that UV exposure is insufficient on its own to effectively treat selenomethionine.

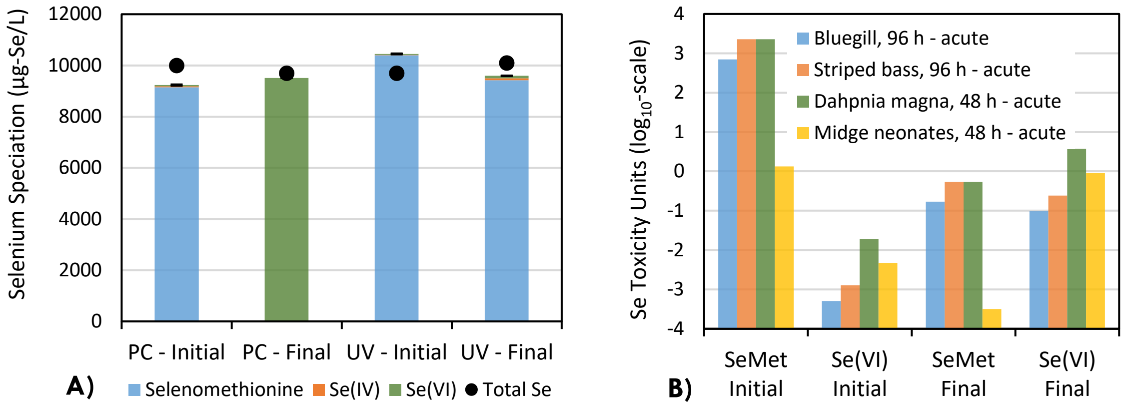

Figure 1 – A) Selenomethionine Photocatalytic (PC) Treatment Results Compared to a UV Control. B) Selenium Species Toxicity Reduction Results (Toxicity units derived by normalizing Se concentration by LC50 values obtained from Lemly, Finger, and Nelson 1993)

Based on reported selenomethionine toxicity (Lemly, Finger, and Nelson 1993), the initial solution in this study exceeds the LC50 concentration for bluegill juveniles (96 h acute), striped bass fingerlings (96 h acute), *Daphnia magna* (48 h acute), and midge neonates (48 h acute). Except for *Daphnia magna*, the selenomethionine levels were converted to non-toxic levels of Se(VI) via photocatalysis. These results demonstrate that photocatalysis is an effective method for the elimination of selenomethionine by converting it to selenate and significantly reducing the bioavailability and toxicity of selenium-contaminated effluent.

Reduced Sulfide Treatment Results from Biogenic Sources

At the pilot scale (500 L), the diurnal H_2S emissions were compared between two closed-cell reactors, one with the floating reactive barrier (FRB) and a bare control. To better elucidate the emissions blocking performance of the FRB at a larger scale, the initial aqueous sulfide concentration for both reactors was increased to 76-115 mg/L S^{2-}, approximately 4.5 times greater than the expected concentration in the mine tailings water. During this experiment there was a notable diurnal effect on the temperature profile and the H_2S emissions (Figure 2). Compared to the bare control, the FRB reduced H_2S emissions by >94% over the duration of the study, with negligible diurnal effects on the emission reduction. This proves that even during periods of low UV exposure the FRB is still an effective barrier for volatile sulfurous emissions. During this period, there was significant treatment of aqueous sulfide by either air oxidation in the control (55% decrease) or photocatalytic activity in the FRB reactor (71% decrease). Notably, while the FRB reactor reduced H_2S emissions by >95%, the decrease in the aqueous sulfide concentration proceeded at a rate 1.5 times faster than the air oxidation rate in the control.

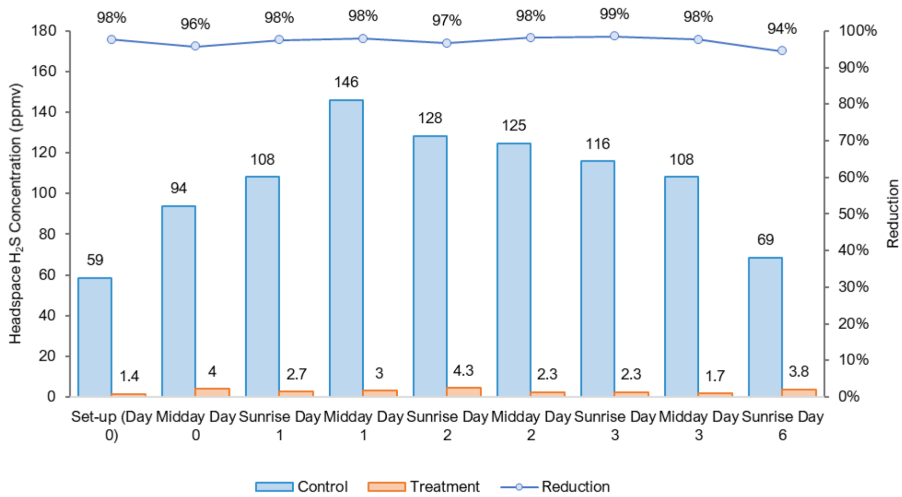

Figure 2 - Field Scale Headspace H_2S Reduction Results (Control vs. Treatment - Day/Night)

Conclusion

As a standalone process or part of a larger treatment system, SolarPass is a promising low-cost platform for the photocatalytic treatment of mine water contaminants, including persistent organics, organoselenium, and sulfur compounds. Under lab-scale simulated solar conditions, SolarPass effectively eliminated selenomethionine via photocatalysis by converting the organoselenium into the less toxic and bioavailable selenate. Further, when demonstrated at pilot-scale, SolarPass effectively mitigated volatile sulfur emissions while providing simultaneous passive aqueous treatment. These results demonstrate that SolarPass provides an effective solution for passive tailings management and can address diverse challenges in mining-impacted waters.

References

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