

Enhanced passive treatment systems: addition of nutrients to bioreactors

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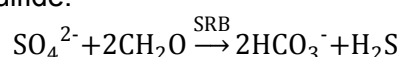
Abstract

Bioreactors utilise microbial metabolic pathways and have been applied to mine water treatment for metal and sulfate removal. Traditional bioreactors for passive water treatment systems typically require a large footprint, and sometimes encounter performance issues that deliver treatment below design specifications. This paper presents results of experiments that add water soluble nutrients to traditional bioreactors targeting sulfate and nitrate removal from water. Nutrient addition led to a more than 15-fold improvement to the amount of sulfate removed from mine influenced water relative to the control systems. Initial results from the nitrate removal experiments show significantly lower effluent nitrate concentrations in some of the nutrient dosed reactors. Nutrient addition can extend the capacity of sulfate reducing bacteria technologies to treat mine influenced water discharges.

Keywords: bioreactor, water treatment, passive treatment, sulfate, nitrate, bacteria

Introduction

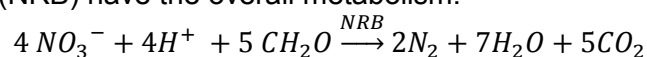
Sulfate reducing bacteria (SRB) can obtain energy by oxidizing organic compounds while reducing sulfate to hydrogen sulfide:



SRB activity consumes SO_4^{2-} , and the metabolic products HCO_3^- and H_2S can neutralise acidity, and precipitate metals as sulfides respectively, presenting an attractive option for mine influenced water (MIW) treatment.

Passive MIW treatment systems that utilise SRB have been implemented in many systems. They take advantage of a variety of carbon sources, and alkalinity sources where applicable (DiLoreto et al., 2016; Gusek, 2002; McCauley et al., 2009). Active treatment systems have also taken advantage of SRB metabolism, and a variety of water soluble organic carbon compounds have been used in such systems (Hao et al., 2014; Zagury et al., 2006; Zamzow et al., 2006). The effectiveness of bioreactors to treat MIW depends on operating conditions, environmental conditions, the MIW chemistry, and the desired water quality outcomes.

Nitrogen can enter mine water from several processes during mineral extraction and can impact receiving environments by disturbing nutrient balances (Zaitsev et al., 2008). Nitrate reducing bacteria (NRB) have the overall metabolism:



NRB have been used in woodchip bioreactors to successfully reduce nitrate concentrations in agricultural and other enriched waters (Christianson et al., 2017, Hoover et al., 2016). Similar systems could also be applied to nitrate rich MIW resulting from the use of nitrogen-based explosives.

The success of passive treatment systems relies on the success of an entire ecosystem within the bioreactor. In passive sulfate reducing bioreactors, fermenting bacteria breakdown the organic material present and release labile carbon compounds that SRB can metabolise. When the growth conditions for fermenting bacteria are compromised, this can reduce SRB

activity and whether treatment goals are achieved. For example, the rate of breakdown of organic material can slow at low temperatures, and this can reduce the bioreactor efficiency. The use of these systems is also limited to relatively low flow drainages because often a long hydraulic retention time (HRT) is required for successful treatment.

In this study an experiment was designed to test whether addition of nutrients to passive SRB and NRB bioreactors lead to improved removal of sulfate from acidic mine drainage and nitrate from a pH neutral agricultural drainage. Influent water was dosed with two nutrient additives, providing additional nourishment to the bacteria.

Methods

Water collection and characterisation

Acidic MIW was collected from an opencast sub-bituminous coal mine located near Coalgate on New Zealand's South Island. Three cubic metres of water containing 1300 mg/L of sulfate was collected on the 22nd December 2015, and stored in polyethylene containers prior to use. A 20 L sample of mud was also collected from a wetland that received drainage water from the mine. The mud had black zones with an H₂S smell, and these were stored at 16 °C in a polypropylene bucket prior to the start of the experiment.

Nitrate enriched agricultural water was collected from a drain near Hinds on New Zealand's South Island which had an estimate flow of 40 L/s. One cubic metre of water containing 47 mg/L nitrate was collected into a polyethylene container, and was stored in the dark to prevent photosynthetic growth.

Experimental setup: SRB bioreactors

Twelve cylindrical up-flow reactors were built using polyvinyl chloride pipes (Fig. 1). The reactors were filled with 300 g of quartz chips, and then packed with a mixture of limestone, bark, bark mulch, and compost in a 3:3:2:2 volume ratio. A small proportion of the reduced mud (1 % of the mixture volume) was mixed through to inoculate the system with SRB.

Reactors were kept in a 16 °C temperature-controlled room, and batch fed once per day with MIW. Control reactors received only MIW, and the two nutrient mixtures PX1.0 and PX1.5 were added to the MIW in the experimental reactors. PX 1.0 and PX 1.5 differed in their carbon compound compositions. An application for intellectual property rights to the nutrient mixture compositions may be filed, and their composition is not described in this paper.

At the start of the experiment, the reactors were filled with a mixture of 50 % MIW and 50 % municipal drinking water, and left for 48 hours. They were then dosed with MIW to generate an HRT of 10 days. After 3 weeks, the HRT was reduced to 5 days and nutrient addition of PX1.0 and PX1.5 to the MIW feeds for 4 reactors commenced. Nutrients were applied such that the chemical oxygen demand (COD):SO₄ ratio was 3; a ratio between 2.4 and 5 is suggested to achieve the maximum sulfate reduction rates (Hao et al., 2014). The effluent water chemistry was monitored, and periodically the nutrient addition rates and HRTs were altered according to Table 1.

Experimental setup: NRB bioreactors

Four cylindrical up-flow bioreactors were filled with 2.2 kg of woodchip, and 100 g of quartz was placed on top to keep the chips submerged. Reactors were kept in a 16 °C temperature-controlled room, and prior to commissioning were filled with water for a two-week period to

allow reducing conditions to develop. Reactors were then continuously fed with agricultural water, targeting a 24-hour HRT. A control reactor received only agricultural water, while the three other reactors were dosed with the PX 1.0 nutrient additive in varying concentrations such that the COD:NO₃ ratio was 0.3 (low dose), 0.6 (mid-dose) and 1.2 (high dose). These ratios were determined using the stoichiometry of the nitrate reduction reaction.

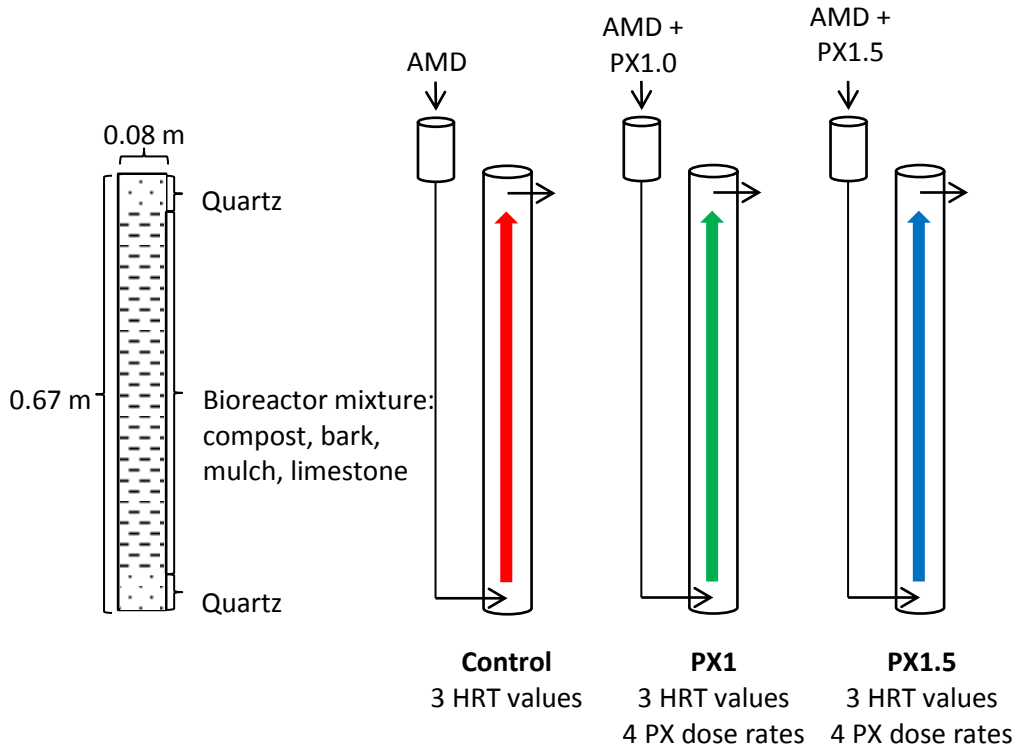


Figure 1. SRB experimental setup: a total of twelve reactors were built that were dosed with MIW, with the addition of nutrient additives PX1.0 and PX1.5.

Chemical analysis

Each week pH, ORP, conductivity and temperature were measured for the MIW and the reactor effluent, and samples were collected for alkalinity, Ca, and SO₄ analysis. Metres used for measurements were calibrated on the day of use. At the beginning of the experiment trace metals in the MIW were also analysed. Alkalinity was analysed by titration with 0.1 M HCl, Dissolved metals were analysed by ICP-MS using the APHA method 3125 B. Sulfate was analysed using the APHA ion chromatography method 4110 B, and the QuikChem flow injection analysis method 10-116-10-1-A. Total sulfide concentrations were periodically analysed in reactor effluent according to the HACH spectrophotometric methylene blue method 8131.

Effluent water from the NRB experiment was analysed for nitrate weekly with a benchtop spectrophotometer using the HACH powder pillow method 8171, and these results were corroborated by less frequent analysis using APHA method 4500-NO₃⁻.

Table 1. The hydraulic retention time (HRT) in days, and the COD:SO₄²⁻ ratio that were used to feed the reactors with MIW. A COD:SO₄²⁻ ratio of 0 indicates that no nutrient additive was used. Red = control, green = PX 1.0 and blue = PX 1.5. Darker shades represent a higher COD:SO₄ ratio.

| Day | Reactor | Control | | PX1.0 | | PX1.0 | PX1.5 | | PX1.5 |
|-----|---------------------|---------|----|-------|-----|-------|-------|-----|-------|
| | | A | B | A | B | C | A | B | C |
| 1 | HRT | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | COD:SO ₄ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20 | HRT | 5 | 5 | 5 | 5 | 10 | 5 | 5 | 10 |
| | COD:SO ₄ | 0 | 0 | 3 | 3 | 0 | 3 | 3 | 0 |
| 97 | HRT | 2.5 | 5 | 2.5 | 5 | 5 | 2.5 | 5 | 5 |
| | COD:SO ₄ | 0 | 0 | 3 | 6 | 1.5 | 3 | 6 | 1.5 |
| 140 | HRT | 2.5 | 5 | 2.5 | 2.5 | 5 | 2.5 | 2.5 | 2.5 |
| | COD:SO ₄ | 0 | 0 | 3 | 6 | 1.5 | 3 | 6 | 1.5 |
| 153 | HRT | 2.5 | 5 | 1.25 | 2.5 | 2.5 | 1.25 | 5 | 2.5 |
| | COD:SO ₄ | 0 | 0 | 3 | 6 | 1.5 | 3 | 6 | 1.5 |

Results

Mine water chemistry

The MIW used for the SRB experiment had pH 3.4 and conductivity of 1.66 mS/cm. Concentrations of metals typically enriched in New Zealand coal mine drainage were below 6 mg/L (Table 2). The Ca concentration was 250 mg/L, and SO₄ concentrations ranged from 1290 – 1370 mg/L throughout the experiment.

Table 2. Metal concentrations in the MIW used in the experiment

| Metal | Al | Mn | Fe | Ni | Zn |
|----------------------|-----|-----|-----|-----|-----|
| Concentration (mg/L) | 5.4 | 5.2 | 0.7 | 0.2 | 0.7 |

Treated effluent from the reactors had circum-neutral pH, and alkalinity of more than 100 mg/L CaCO₃ (Table 3). The effluent from the nutrient-dosed reactors had 3 or more times the alkalinity that was measured in the control reactors. The reactors dosed with PX1.5 had effluent with lower pH, yet higher alkalinity than that from the PX1.0 dosed reactors. The PX1.5 reactors also had effluent with higher conductivity than the influent MIW, in contrast to the control and PX1.0 reactors that consistently reduced the MIW conductivity by a small amount.

Table 3. Indicative water chemistry of MIW and reactor effluents

| Water type | Control effluent | PX1.0 effluent | PX1.5 effluent | Influent MIW |
|--------------------------------------|------------------|----------------|----------------|--------------|
| pH | 7.2 | 7.3 | 6.6 | 3.4 |
| Alkalinity (mg/L CaCO ₃) | 170 | 500 | 840 | - |
| Conductivity (mS/cm) | 1.60 | 1.64 | 2.18 | 1.66 |

Sulfate removal

Sulfate was removed from solution in the control reactors, and in the reactors dosed with nutrients (Fig. 2). At the beginning of the experiment (day 21), the reactors had similar effluent sulfate concentrations close to 1200 mg/L. Between 21 and 50 days of operation, the concentration of sulfate in the nutrient dosed reactors decreased by approximately half, to around 600 mg/L, whilst the control reactors remained close to 1200 mg/L. Throughout the experiment, the nutrient dosed reactors released water that was compliant with the New Zealand stock water quality guideline (1000 mg/L).

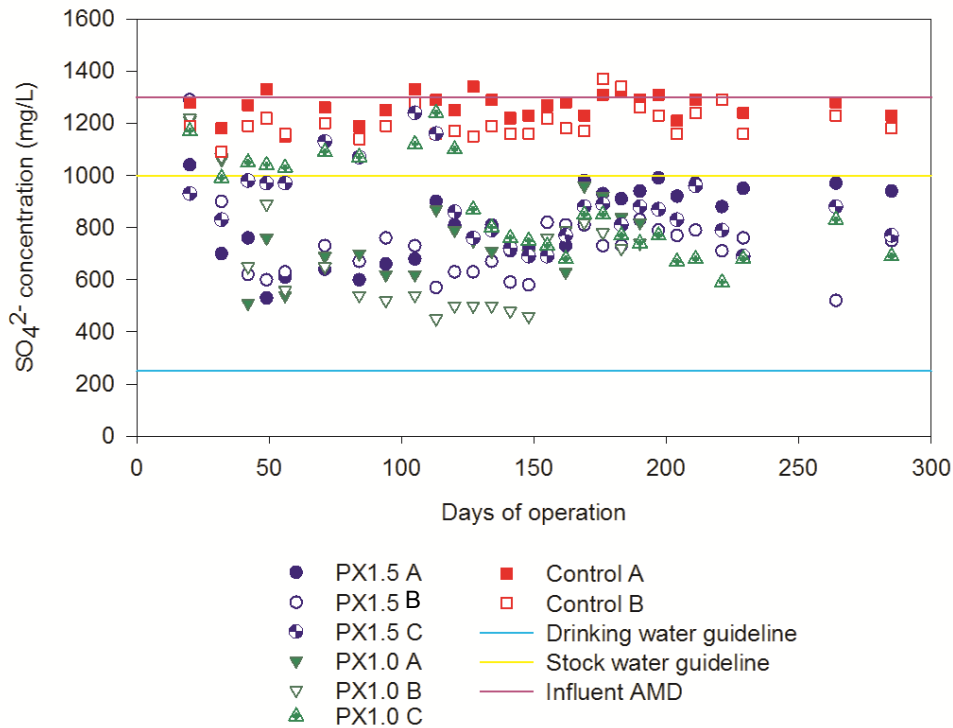


Figure 2. Sulfate concentrations in the reactor effluent. The influent MIW sulfate concentration, and pertinent water quality guidelines are also displayed.

The dosing regime was changed on the 97th day of the experiment. The HRT was halved to 2.5 days in the Control A, PX1.5 A, and PX1.0 A reactors, which caused the effluent sulfate concentrations to increase. During the following 50 days, the effluent sulfate concentrations from the PX1.5 A and PX1.0 A reactors slowly decreased to close to 700 mg/L. The effluent from the control A reactor remained above 1200 mg/L. The HRT was further decreased to 1.25 days in the PX1.5 A and PX1.0 A reactors after 150 days of operation. A similar increase in effluent sulfate concentration was observed. Effluent sulfate concentrations in the PX1.5 reactor varied between 880 – 980 mg/L thereafter. In the PX1.0 A reactor, the effluent sulfate concentration decreased over the following weeks, however flow ceased from the reactor after 190 days and it was decommissioned.

In reactors PX1.5 B and PX1.0 B, the nutrient dose rate was doubled after 97 days of operation. The effluent from the systems showed a slight decrease in sulfate concentration, dropping below 600 and 500 mg/L for the PX1.5 B and PX1.0 B reactors respectively. After 140 days of operation, the HRT was halved, and effluent sulfate concentrations increased to around 800 mg/L. A slight decrease in effluent sulfate was observed in the following weeks to closer to 700 mg/L. The PX1.0 B reactor failed due to flow obstructions after 190 days of operation and it was decommissioned.

Nutrient dosing of the PX1.5 C and PX1.0 C reactors began after 97 days of operation. The nutrients were dosed to achieve a COD:SO₄²⁻ ratio of 1.5. Effluent sulfate concentrations decreased in both reactors to approximately 700 mg/L by 150 days of operation. At this stage the HRT was decreased to 2.5 days, and the effluent sulfate concentrations increased to close to 900 mg/L following the change. Over the subsequent weeks the sulfate concentrations decreased to close to 600 mg/L in the PX1.0 C reactor, however in the PX1.5 C reactor, sulfate concentrations remained between 690 and 880 mg/L.

Nitrate removal

Preliminary results show a decrease in nitrate concentration of more than 80 % in all four trial reactors (Fig. 3). The reactor with the highest PX 1.0 dose rate has the best performance, with nitrate typically below detection (0.1 mg/L) in the reactor effluent. The reactor with the medium PX 1.0 dose rate has had variable flow, and an HRT that decreased to 14 hours in mid-July. Nitrate concentrations in this reactor increased when the HRT reduced. With the exception of the reactor with reduced HRT, all of the nutrient dosed reactors have achieved lower nitrate concentrations than the control after a one month settling period, though the margin between the low dose and control reactors was generally small.

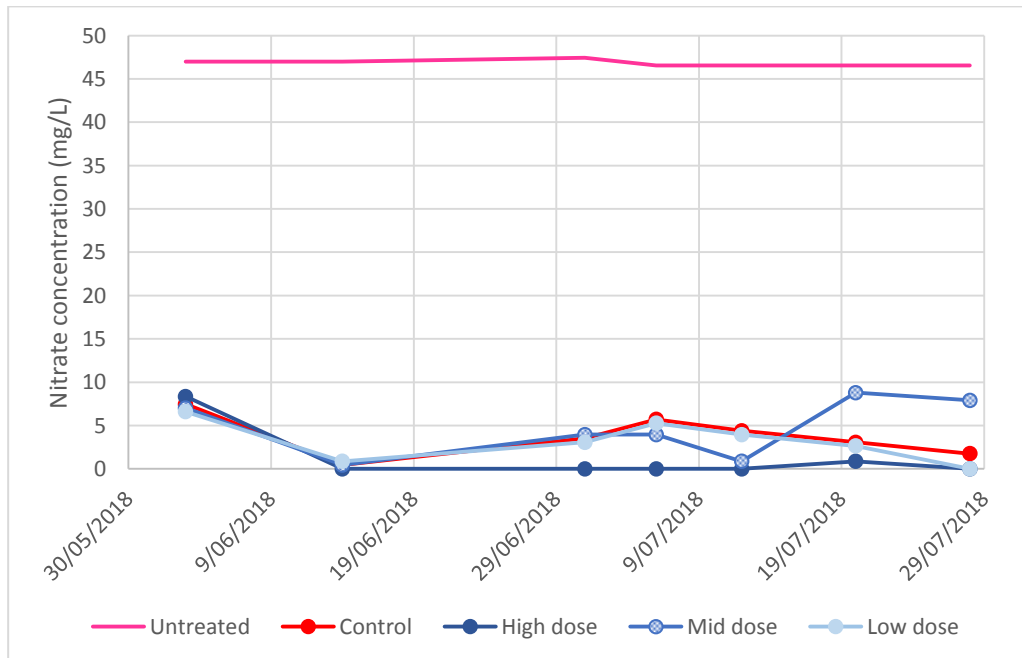


Figure 3. Nitrate concentrations in the reactor effluent. The influent nitrate concentration is also displayed.

Discussion

Addition of nutrients to MIW treated by sulfate reducing bioreactors delivers lower effluent sulfate concentrations than those not treated with nutrient (Fig. 2). At the start of the experiment, the reactors that were fed nutrients had effluent sulfate concentrations that decreased over a six-week period to stabilise at around 600 mg/L. The decrease in sulfate concentration is attributed to SRB, and the change over time is likely due to an increasing population of the bacteria in response to the available nutrients. Decreasing the HRT increased the SO₄ load to the system, and the populations present in the reactors were unable to consume the increased SO₄ load. Over a six-week period, it appears that the SRB population responds to the new conditions, and effluent sulfate concentrations decrease and seem to stabilise. Although SO₄ and COD were present in the same ratio in each reactor, the minimum concentration of SO₄ seemed to be achieved at greater HRT. Despite this, the

higher load at low HRT meant the sulfate removal rate (and therefore net sulfate removal) was greater at low HRT (Fig. 4).

When the rate of nutrient application to the PX1.5 B and PX1.0B reactors was doubled, a slight decrease in the effluent sulfate concentration was observed. The decrease was not proportional to the rate of nutrient application. This was also observed when a COD:SO₄ ratio of 1.5 was used. At low nutrient applications in reactors PX1.5 C and PX1.0 C, sulfate concentrations below 700 mg/L could still be achieved. Although an excess of COD:SO₄ was supplied to the reactors, complete sulfate reduction was not achieved. Soluble sulfide compounds can inhibit SRB activity. The measured total sulfide concentrations ranged up to 250 mg/L. This is lower than documented concentrations where sulfide toxicity to SRB has been documented (477 – 617 mg/L, Neculita et al., 2007). Removal of sulfide from the system is being investigated as a way to identify if sulfide concentrations may limit the rate of sulfate removal by SRB.

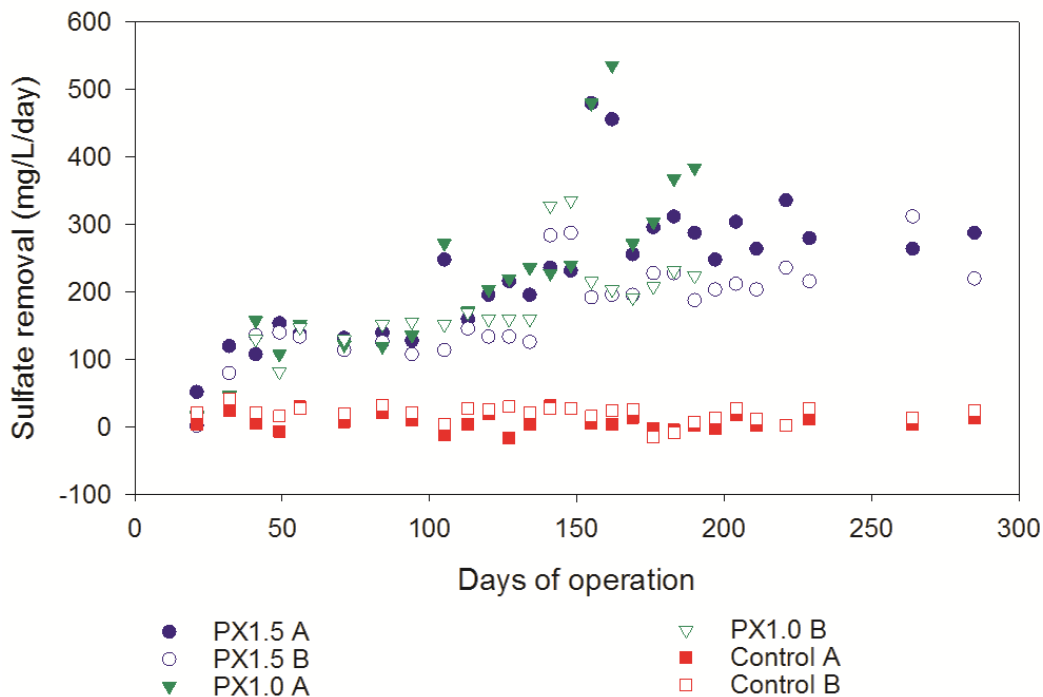


Figure 4. Sulfate removal rate in the control, PX1.5 and PX1.0 dosed reactors.

The rate of sulfate reduction in the control reactors was close to 20 mg/L/day (Fig. 4). This was similar in Control A and Control B at 5 and 2.5-day HRT respectively. Nutrient addition led to significantly increased sulfate reduction rates. At a 5-day HRT the PX1.5 and PX1.0 reactors removed close to 120 mg/L/day of sulfate from the MIW. Decreasing the reactor HRT was the factor that led to the best improvements in sulfate reduction rates. At a 1.25-day HRT the PX1.5 reactor removed close to 300 mg/L/day of sulfate; a 15-fold increase relative to the control reactor.

These results indicate that nutrient dosing can extend the capability of passive SRB bioreactors to treat MIW in a wide variety of circumstances. The increased sulfate removal enables smaller, cheaper reactors to treat larger volumes of MIW, and consequently allows treatment of higher flow rates than traditional passive systems allowed. The semi-passive set up means that the reactor performance can be changed over time by varying flows or nutrient concentrations. This aspect will be useful in systems where seasonal changes in flow or MIW chemistry require different treatment outcomes.

Compared to the sulfate removal experiment, the difference between dosed and control reactors is less stark in the nitrate removal experiment. However dosed reactors are delivering lower effluent nitrate concentrations than the control. These systems will be tested at lower hydraulic retention times to ascertain how much benefit can be derived by nutrient addition in NRB reactors.

Conclusions

Dosing MIW with nutrient additives can improve sulfate removal in sulfate reducing bioreactors. Reactors that had additional nutrients added delivered consistent low sulfate concentrations at higher flow rates than the control reactors, showing up to a 15-fold improvement on the rate of sulfate removal in a reactor. This reduces the required retention time in reactors, and therefore decreases the investment required to install passive SRB reactors at mine sites. The improvements in nitrate removal using nutrient additives warrant further research. The flow rates and additive concentrations are continuing to be optimised in the lab to deliver successful contaminant removal with minimal nutrient addition and hydraulic retention time requirements.

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An update on biogeochemical surveys of epithermal gold occurrences in the Hauraki Goldfield and Taupo Volcanic Zone

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Abstract

In 2017, biogeochemical surveys were conducted at the Pine Sinter and Ohui Au-Ag prospects located approximately 15 km north of Whangamata and west of Oputere in the Hauraki Goldfield, Coromandel Volcanic Zone. Foliage from 138 samples of common tree ferns was collected at 117 sample sites (several species from selected sites). In addition, 18 samples of two common plant species were collected from 6 sites around the geothermal pools at Waiotapu, 27 km south southeast of Rotorua. All 156 samples were reduced to ash and analysed for 52 elements.

At Pine Sinter and Ohui, silver fern (*Cyathea dealbata*; 'ponga') proved to be the most widespread species and was the primary focus for these surveys. At Pine Sinter, a rhyolite dome is overlain by a sequence of rhyolitic tuffs and breccias, and andesite units. Remnants of a sinter sheet are present on the surface. To the east, the sequence is overlain by post-mineral Omahine Andesite. Silver ferns have slightly anomalous Ag content in a north-trending zone located near and parallel to the Omahine Andesite contact. Several elements (Ba, Ca, Sr, Se and REE) are elevated in a parallel trend but c. 100 m to the west. All Au levels were low and no definitive trends were obvious.

At Ohui, Au-Ag-bearing quartz veins are present in andesite and rhyolite. The Phoenix and Staircase vein areas in rhyolite flows and pyroclastic rocks, are defined by elevated Ag and Sb in the ferns, but not by Au. The Staircase veins also show some weak enrichment of As. Nickel, Co, and to a lesser degree S and Ca, define a north-easterly trend between the Phoenix and Staircase area. Zinc, Tl, Pb and Cu enrichment west of Staircase are indicative of base metal mineralisation. From earlier soil surveys, there were patterns of Au, As, Sb and Hg that indicated enrichments near the Great Mexican fault, but these signatures are either not present in the ferns or the weak signatures are laterally displaced. Concealed deposits tend to be reflected in plants growing directly above mineralisation, whereas in such rugged terrain, soils may show mechanical dispersion.

At Waiotapu, Kanuka (*Kunzea ericoides*; 'white tea tree') has higher concentrations than Manuka (*Leptospermum scoparium*; 'tea tree') of the epithermal related elements Ag, Au, Sb and As, especially close to Champagne Pool.

Keywords: Biogeochemical surveys, mineral exploration, geochemical analyses, epithermal, gold, Ohui, Pine Sinter, Hauraki Goldfield, silver fern (*Cyathea dealbata*), Waiotapu, geothermal, Manuka (*Leptospermum scoparium*), Kanuka (*Kunzea ericoides*).

