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The WRC operates in terms of the Water Research Act (Act 34 of 1971) and its mandate is to support water research and development as well as the building of a sustainable water research capacity in South Africa.

TECHNICAL BRIEF

Mine-water

Passive biotreatment of mine-water

A completed Water Research Commission (WRC) funded project has investigated carbon flux and sulphide oxidation kinetics during passive biotreatment of mine water.

Background

The impact of acid rock drainage (ARD) on South Africa's already threatened water resources is a serious concern. while acid waters emanating from groundwater rebound through the Witwatersrand gold basins has received the majority of the media attention and elicited the strongest response from the authorities; ARD from diffuse sources, primarily associated with coal mining, is likely to impact a far larger area.

The traditional chemical and physical interventions are not particularly well suited to these discharges.

Passive treatment of mine-water

There has been a certain amount of research aimed at developing passive and semi-passive systems, specifically suited to the South African context. Some of these have been evaluated at demonstration scale, with varying degrees of success.

Typically, the components of these processes that target sulphate salinity make use of biological sulphate reduction, often utilising complex organic carbon sources to provide the electron donor.

The sulphide product is highly toxic and presents a significant risk to the environment and human health and needs to be carefully managed. The most attractive option is the partial oxidation of sulphide to elemental sulphur, which is stable and has commercial value.

A promising approach to achieving partial oxidation of sulphide involves using sulphide oxidising microbes in a floating biofilm. A linear flow channel reactor has been developed and tested, with fundamental aspects of the chemistry, microbiology engineering being reported (**WRC Report No. 18341/1/12**).

The organic carbon flux through the integrated process was identified as having a significant impact on overall performance, and required further investigation. In addition, a more comprehensive understanding of oxygen mass transport into the biofilm would facilitate further process optimisation.

Rationale for WRC project

The preceding approach identified that efficient sulphide oxidation, with the formation of elemental sulphur as the desired product, was dependent on the diffusion of sulphide from the bulk solution and oxygen from atmosphere into the reaction space within the biofilm.

There is a limited reaction space where the pH and redox potential conducive to the partial oxidation of sulphide. In addition, the reaction stoichiometry is critical. Too much oxygen or too little sulphide and the reaction proceeds to complete oxidation to sulphate.

The partial pressure of oxygen in the atmosphere cannot be controlled so the system depends on the control of oxygen penetration into the biofilm. This is dependent on the structure of the biofilm, which is influenced by its organic carbon content.

With the current process flowsheet the provision of organic carbon is dependent on the performance of the upstream sulphate reduction unit. Sustainable performance is dependent on the hydrolysis of the complex organic carbon at a

rate sufficient to sustain effective sulphate reduction, and provide overflow carbon to the sulphide oxidising unit. This latest WRC project aimed to provide a better understanding of the overall carbon flux across the system, and the effect this has on biofilm development and the control of oxygen penetration into the reaction zone.

Methodology

Two packed bead columns were used to investigate the sulphate reduction efficiency and carbon flux. The effect of packing material and supplementation with simple organic carbon was investigated.

A series of linear flow channel reactors (LFCRs) were used to investigate the effect of residence time and acetate supplementation on sulphide oxidation rate and elemental sulphur yield.

The oxygen mass transfer into the biofilm was investigated in a scaled-down reactor, using a dissolved oxygen microprobe. The composition and internal structure of the floating sulphur biofilm was analysed using scanning electron microscopy and elemental analysis. The structure of the biofilm informed the interpretation of the data.

Results and discussion

The packing material and packing configuration had a significant effect on void volume and subsequent hydraulic residence time. Of the individual packing material the greatest amount of organic carbon was liberated from the dry sludge, primarily as acetic acid, while butyric acid was liberated from the wood chips after approximately 3 weeks. Very little organic carbon was liberated from the grass.

The results suggested that organic carbon would not be sufficient to sustain efficient sulphate reduction for a prolonged period.

Both packed bed columns showed similar levels of performance over the first two months, with sulphate removal efficiencies of between 50% and 75% (feed sulphate concentration 2 g/ℓ). the performance of Column 2 (molasses supplementation) deteriorated after four months and failed completely within five months, while Column 1 (acetate supplementation) showed sustained sulphate reduction (up to 90%) for 12 months.

Volatile fatty acids (VFAs) were detected in the column effluents at decreasing concentrations for the first two months, after which no VFAs were detected, despite supplementation of the feed, indicating reduced hydrolysis of the packing material. The failure of Column 2 could be attributed to carbon deficiency.

In the absence of VFAs in the feed to the LFCRs a complete biofilm did not form and performance was poor. Supplementation of the reactor feed with acetate was required for efficient performance. A minimum acetate concentration of 100 mg/ℓ was required. The absence of soluble organic carbon had a profound effect on the microbial community, which lacked many of the heterotrophic organisms required for biofilm development.

The performance of the sulphate reducing community was not negatively affected by catechol or gallic acid (low molecular weight phenolic compounds) at concentrations up to 100 mg/l, although complete inhibition was observed with both compounds at 1 000 mg/ℓ.

The concentration of these compounds is highly unlikely to reach inhibitory levels within a packed bed reactor.

The mass transfer of oxygen into the reaction zone within the biofilm was shown to be significantly inhibited as the biofilm developed and more sulphur was deposited, although the rate depended on the operating conditions, particularly hydraulic residence time (HRT). The calculated mass transfer coefficient was shown to decrease by almost three orders of magnitude, from 1.64×10^{-4} m/s to 3.63×10^{-7} m/s over a five-day period of biofilm development (one day HRT).

From a performance perspective, the rate of sulphide oxidation peaked after two to three residence times and then decreased significantly, due to oxygen limitation. However, inhomogeneity in biofilm structure and uncertainty over a porosity factor precluded the development of an accurate mass transfer model.

General remarks

The experiments showed that efficient sulphide oxidation was possible within the floating sulphur biofilm in the LFCR, provided the feed was supplemented with organic carbon. A hydraulic residence time between one and two days was optimal.

In order to sustain optimal performance the biofilm would need to be harvested every two to three residence times. Under these conditions sulphide oxidation rates of up to 5.5 mmol/ℓ·day could be achieved, with at least 75% of the oxidised sulphide reporting to the biofilm as elemental

sulphur. Conservatively, this represents a sulphur recovery of 13.5 g/m^2/day, for the current reactor configuration.

Conclusions

The experimental programme illustrated that organic carbon liberation from packed bed reactors is unlikely to be sufficient to sustain efficient levels of sulphate reduction beyond the short term, once the readily labile organic carbon has been liberated. Supplementation with relatively significant (1 g/ℓ) concentrations of readily usable organic carbon, such as acetate, was needed to sustain sulphate reduction.

While the majority of the sulphate reduction (around 75%) was reliant on the acetate, continued hydrolysis of the lignocellulose was observed. Despite this, the VFA concentration in the effluent from the packed bed reactors was negligible after the first four months.

Therefore, further organic carbon supplementation (>100 mg/l acetate) of the feed to the LFCR was necessary for biofilm, development and efficient sulphide oxidation.

Under optimal conditions the biofilm formed within 12 hours, following which the oxygen mass transfer into the liquid was significantly reduced. The reduced mass transfer prevented complete sulphide oxidation, so the majority of the sulphide was oxidised to sulphur within the biofilm.

The HRT and sulphide loading affected the rate of formation and structure of the biofilm, influencing performance. Optimal performance was achieved at an HRT between one and two days. Harvesting of the biofilm would be required every two to three residence times to maintain optimum sulphide oxidation rates.

Further reading:
To order the reports, ***Investigation of carbon flux and sulphide oxidation kinetics during passive biotreatment of mine water*** (**Report No. 2139/1/13**) contact Publications at Tel: (012) 330-0340, Email: orders@wrc.org.za or Visit: www.wrc.org.za to download a free copy.