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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 treatment

Improving sulphate reduction for treatment of AMD

A completed Water Research Commission (WRC) study worked to address the challenges facing biological sulphate reduction as a strategy for acid mine drainage (AMD) treatment.

Background

The contamination of surface and groundwater by AMD or acid rock drainage (ARD) and the consequences for the environment, agriculture and human health are serious concerns in the regions of South Africa impacted by mining activities.

The biological treatment of AMD is centred on the activity of sulphate-reducing bacteria (SRB), which are able to reduce sulphate or sulphide, coupled to the oxidation of an electron donor, typically an organic carbon molecule.

A number of commercial processes, based on biological sulphate reduction, have been developed, but their widespread application has been constrained by three factors. These are the cost of the electronic donor, the relatively slow growth of sulphate reducers and the associated kinetic constraints, as well as the management of the sulphide product.

The research undertaken in this WRC project addressed the first two constraints by assessing the potential of whole and partially digested microalgae as the electron donor and investigating novel reactor configurations aimed at biomass retention and recycling. Together, these studies demonstrate potential for development of a feasible integrated process for operation in a passive, semi-passive or active configuration, allowing treatment of AMD sources with concomitant sulphur recovery.

Methodology

A set of baseline data was generated for suspended culture, using continuously stirred tank reactors (CSTRs) and a defined growth medium with lactate as the electron donor and carbon source. Three feed sulphate

concentrations (1.0, 2.5 and 5.0 g/*l*) were tested at a constant chemical oxygen demand (COD) to sulphate ratio (0.7).

The reactors were operated at hydraulic retention times (HRTs) from five days to 12 hours and steady state data were used to determine volumetric sulphate reduction rates (VSRR).

Three experimental reactor configurations were evaluated: a standard reactor without active agitation; a standard reactor coupled to a cross-flow microfiltration unit for biomass recycling, and a novel linear flow channel reactor (LFCR) with carbon fibres for biomass retention. Experiments were confined to a feed sulphate concentration of 1 g/*l* and HRTs from four days to 12 hours.

The potential of whole cell and anaerobically digested microalgae as electron donors was evaluated in standard CSTRs. *Spirulina*, a cyanobacterim and *Scenedesmus*, a green algae were assessed as candidate substrates for anaerobic digestion, both as whole cells and mechanically pre-treated slurries.

The resulting digestate was characterised in terms of COD and volatile fatty acids (VFA) profile. Anaerobically digested *Spirulina* was used as the electron donor in sulphate reduction studies. The experiments were conducted in standard CSTRs at feed sulphate concentrations of 2.5 and 5 g/l. A COD to sulphate ratio of 0.7 was maintained.

The potential for growing algae on treated AMD (raw and nutrient supplemented) was evaluated in small-scale growth studies. A number of known species as well as uncharacterised environmental isolates were tested. Selected isolates were grown in airlift photobioreactors to compare growth on treated AMD against defined growth media.

Results and discussion

The baseline study data were consistent with previous studies conducted under similar conditions. At a feed sulphate concentration of 1 g/l, efficient (>85%) sulphate reduction was observed at HRTs from five days to a day, with a linear increase in the VSRR and complete utilisation of the lactate substrate.

The sulphate reduction efficiency fell significantly at a 12-hour HRT, to around 50%, although lactate conversion remained complete. The VSRR increased to 41 mg/l.h but deviated from the linear trend. The results suggest washout of part of the sulphate reducing community and a shift toward a lactate fermenting community.

The data generated at the feed sulphate concentrations of 2.5 and 5 g/l showed lower sulphate reduction efficiencies (50-60%) at the longer HRTs (4-5 days), becoming even less efficient at the shorter HRTs.

Lactate conversion was complete in the reactor receiving 2.5 g/l sulphate across the HRTs and ranged from 90% to 60% in the 5 g/l reactor, indicating that the majority of the lactate was consumed by fermenters, rather than sulphate reducers. The shift in community structure was consistent with previous studies.

Sulphate reduction in the non-agitated control reactor was similar to that in the CSTR, indicating that constant agitation was not necessary. A separate mixing study confirmed that while mixing was slow in the non-agitated reactor, complete mixing was achieved in less than the HRT for all dilution rates tested. Biomass accumulation, as suspended flocs, was observed.

The inclusion of the crossflow microfiltration unit to ensure biomass recycling significantly improved the sulphate reduction efficiency of the system at low HRTs. The permeate from the membrane was free of cells, indicating 100% efficiency in terms of biomass recycling as expected using filtration through an exclusion membrane.

The pH of the permeate was typically 0.5 pH units higher than the bulk fluid; its light yellow colour suggested the presence of polysulphides. These catalysed the abiotic oxidation of a portion of the sulphide to elemental sulphur in the permeate drainage tube.

The deposition of elemental sulphur resulted in periodic blocking of the permeate line, resulting in overflow from the reactor and the loss of some biomass. The problem became more significant at lower HRTs, with the proportion of permeate relative to overflow falling from 76% at a HRT of 1.5 days to 44% at a HRT of 12 hours.

The problem was most likely caused by the permeability of the silicone tubing and the autocatalytic effect of polysulphide. It could be addressed by selecting materials that excluded oxygen more efficiently.

Notwithstanding the loss of some of the accumulated biomass, the VSRR at a 12-hour HRT was approximately 65 mg/l.h, 50% higher than in the CSTR under similar conditions. This clearly demonstrates the benefit of biomass recycling and the associated increase in the biomass concentration.

The carbon microfibers used at the site of biofilm formation for cell retention in the LFCR proved to be an excellent support material. They were rapidly colonised, demonstrated by a substantial amount of attached biomass being removed with them at the end of the experiment.

The benefit of the biomass retention was apparent at HRTs below 24 hours. The VSRR at a 12-hour HRT was approximately 47.5 mg/l.h, almost 20% higher than in the baseline study. the microbial community was particularly robust, surviving extremely alkaline (pH 13) and acidic (pH 2.5) conditions for several hours following an event where over a third of the reactor volume was replaced with 0.5 M sodium hydroxide.

It is unlikely that a purely planktonic community would have been able to recover under similar conditions. The lack of turbulent mixing in the LFCR limited the partial oxidation of the sulphide, resulting in a higher aqueous concentration.

This increased the selective pressure on non-sulphate reducing species and prevented the proliferation of lactate fermenters at low HRTs. It was not possible to exclude oxygen completely from the headspace and the reactor developed a floating sulphur biofilm at the air-water

interface, resulting in a significant decrease in the effluent sulphide concentration relative to that in the bulk liquid owing to the characteristic flow patterns.

Biological sulphate reduction was achieved using the whole *Spirulina* biomass as the electron donor and carbon source, although the performance was inconsistent. More predictable performance was achieved when the hydrolysis and acidogenesis reactions were decoupled from the sulphate reduction.

Spirulina proved to be a good substrate for anaerobic digestion with relatively rapid liberation of volatile fatty acids, predominantly acetate and butyrate. Mechanical pre-treatment did not significantly improve the concentration of VFAs leaving anaerobic digestor.

Digestion of whole cell *Scenedesmus* by anaerobic digestion was less efficient than *Spirulina*, probably due to the recalcitrane of the cellulosic cell wall. Mechanical pre-treatment was required to facilitate more rapid information of VFAs.

The use of effluent from the anaerobic digestion of *Spirulina* as an electron donor and carbon for sulphate reduction was successfully demonstrated at feed sulphate concentrations of 2.5 and 5 g/*l*. The digestate was blended with the sulphate feed to ensure the COD: sulphate ration was maintained at 0.7. A high degree of sulphate reduction was obtained at hydraulic HRTs of 5, 4 and 3 days.

In order to operate a sulphate reducing system cost effectively on raw or partially digested microalgae, the biomass should be cultivated on site, preferably using wastewater or treated AMD as the basis of the medium.

Effluent from the LFCR showed a consistently low sulphide concentration, which was reduced to zero following a brief period of aeration. While *Spirulina* could not grow on the aerated channel reactor effluent, a number of other known species and uncharacterised environmental isolates could, although at growth rates lower than in defined media.

Conclusions

While the CSTR with suspended culture is a useful research tool to provide excellent kinetic data, operating conditions are constrained by the maximum specific growth rate of the community members and washout occurs when the dilution rate exceeds this. This may be overcome by retaining or recycling biomass.

Biomass retention, by attachment to carbon microfibers, or recycling, using the crossflow microfiltration system, resulted in significantly higher volumetric sulphate reduction rates at low (12 hour) HRT. The maximum values, 47.5 and 65 mg/l.h respectively, were 20% and 50% higher than that achieved in a CSTR with no biomass retention.

The LFCR required no mixing or external energy input and is suitable for incorporation into a passive or semi-passive treatment system. the development of a floating sulphur biofilm at the air-water interface suggests the reactor could be optimised to integrate sulphate reduction and partial sulphide oxidation into a single unit.

The effluent from the anaerobic digestion of microalgae contained sufficient residual COD, primarily in the form of acetate and butyrate, to sustain efficient sulphate reduction. Blending the digestate and simulated AMD to maintain the desired COD to sulphate ratio of 0.7 resulted in sulphate reduction efficiencies similar to those achieved using defined media.

Decoupling the algal hydrolysis and acidogenesis stage from the sulphate reduction allowed a degree of control over the composition of the feed to the sulphate reducing reactor. In these systems an increased efficiency in sulphate reduction was observed.

Mechanical pre-treatment to rupture the algal cells enhanced the hydrolysis and acidogenesis during anaerobic digestion of biomass with cellulosic cell walls, but was not necessary in the case of *Spirulina*.

It was possible to cultivate certain algal species on simulated AMD that had been through the biological treatment process. the productivities were lower than on defined media, but could be improved by blending the effluent with freshwater on nutrient supplementation.

Further reading:
To order the report, ***Addressing the challenges facing biological sulphate reduction as a strategy for AMD treatment: Analysis of the reactor stage – raw materials products and process kinetics*** (**Report No. 2110/1/14**) contact Publications at Tel: (012) 330-0340, Email: orders@wrc.org.za or Visit: www.wrc.org.za to download a free copy.