Biological sulphate reduction of acid mine drainage using primary sewage sludge

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Abstract

Acid Mine Drainage (AMD) waters pose a significant environmental threat to the quality of surface and underground water resources. This paper describes a novel system for the biological sulphate reduction (BSR) of acid mine drainage using primary sewage sludge (PSS) as carbon source in an upflow anaerobic sludge bed (UASB) reactor. PSS is available as a by-product at municipal wastewater treatment plants and its co-disposal proposes an elegant solution to BSR. A laboratory-scale UASB reactor, operated at 35°C, was inoculated with sulphate reducing bacteria, and operated for over 250 days with a sulphate-rich feed of concentration 1800 mg/L. PSS was added to the feed as substrate source for BSR. A biomass recycle stream from the top to the bottom of the sludge bed was introduced to enhance sulphidogenic activity at the bottom of the reactor bed. In this study, the effects of various operational parameters were investigated. It was found that the UASB reactor achieved a sulphate reduction of around 92% at a hydraulic retention time as short as 18h. In the UASB system, significant alkalinity was generated as a consequence of BSR. This is a major advantage in the treatment of low pH and alkalinity AMD waters. The effect of the biomass recycle line was found to initiate rapid BSR from the bottom as soon as the influent entered the reactor. It was concluded that the AMD water has been successfully treated using PSS as carbon source. The experimental observations indicate that the UASB configuration offers significant advantages in BSR for AMD remediation and that this novel technology has considerable potential for full-scale implementation. In fact, based on the results of this investigation, a 2 ML/d pilot plant using PSS for BSR at the Grootvlei Mines Ltd (South Africa) was operated and thereafter scaled up to 10 ML/d.

Keywords: Acid mine drainage, biological sulphate reduction, primary sewage sludge, UASB reactor

Introduction

Acid Mine Drainage (AMD) waters originate from both surface and underground mining activities either through intentional pumping to prevent mine flooding or through unintentional seepages. AMD is characterised by a low pH (2-3), elevated concentrations of heavy metals, sulphate and total dissolved solids (Christensen *et al.*, 1996). During mining activities, large surface areas of rock which often contain iron disulphide (FeS2) are exposed to air and water. Iron disulphide, commonly known as Pyrite, is oxidised to soluble iron complexes and sulphuric acid, catalysed by the sulphur oxidising bacteria (Davison *et al.*, 1989). The resulting highly acidic water dissolves a large variety of heavy metals into solution as long as the pH remains very low (<3.5). Because of these characteristics, mine waters pose a significant environmental hazard. The negative impacts of AMD are both short and long term and are very well documented in the literature. In addition, the liabilities as a result of AMD pollution can attain astronomical figures because of the large volumes (scores of ML/d) of mine water generated at the mine sites. For instance, the Canadian liability is estimated to C$ 2-5 billion/year while the Australian liability is estimated to be around A$60M/yr (Anon., 2005).

In view of the above, considerable effort has been made in the treatment of AMD with regard to the high acidity and heavy metals content. However, little attention has been focused on the mitigation of dissolved sulphate because of its lower toxicity compared with acidity and heavy metals. Nonetheless, there is a growing concern about high dissolved sulphate concentrations and more stringent effluent sulphate standards are enforced by regulatory agencies. As a result, sulphate remediation is now required at many mine sites around the world.

Acid Mine Drainage (AMD) treatment

Several physical and chemical processes have been developed for AMD remediation, such as the high density sludge (HDS) (Pulles *et al.*, 1995), neutralisation (Maree *et al.*, 1996) or seeded ambient temperature ferrite (Morgan *et al.*, 2004) systems to remove iron and heavy metals, and gypsum ($CaSO_4.2H_2O$) precipitation to remove sulphate. However, the high costs of chemicals involved and large sludge volumes generated make the treatment of AMD via these processes disadvantageous. As supplement or alternative to the chemical/physical processes for AMD remediation, biological treatment would seem an attractive option for chemically pre-treated or relatively low sulphate (<2000 $mgSO_4^{2-}/L$) mine water. Biological treatment usually forms one unit process in a treatment train encompassing additional chemical and/or physical treatment (Rose *et al*., 2002; Maree, 2002) but can sometimes stand alone.

Biological sulphate reduction (BSR), mediated by sulphate reducing bacteria (SRB), requires an organic substrate as electron and carbon source. Conventionally, organic substrates such as molasses, ethanol, acetate or lactate have been used as energy source (Herlithy *et al.*, 1987). Although all these pure substrates have been effective for BSR, they are expensive thereby making AMD treatment costly. As a consequence, BSR via these organics have in general been restricted to lab-and/or pilot scale levels.

Since the economics of BSR are steered by the economics of the organic source, the BioSURE® process has been developed as a low-cost effective system where BSR is achieved using primary sewage sludge (PSS) as energy source for the central BSR unit process (Rose *et al.*, 2002). PSS is available as a by-product at municipal wastewater treatment systems, and therefore co-treating this waste with AMD proposes an elegant solution to BSR. In its initial conception for BSR, the Rhodes BioSURE® process made use of a Recycling Sludge Bed Reactor (RSBR), which is a down-flow based configuration. However, the RSBR configuration has a number of disadvantages: (1) it requires a long hydraulic retention time of approximately 48h and a second post treatment step (Rose *et al.*, 2002) which demand relatively large reactor volumes with significant capital cost; (2) dissolved sulphate can "short-circuit" to the effluent requiring downstream BSR as proposed in the BioSURE® process and (3) BSR systems with PSS tend to produce higher nonsettleable solids concentrations than equivalent methanogenic systems (Ristow *et al.*, 2005), which in the RSBR configuration would cause high suspended solid concentrations in the effluent. As alternative, the use of an upflow configuration, based on the upflow anaerobic sludge bed (UASB) reactor has been proposed. This scheme should improve and maximise the contact between the PSS and the sulphate where all the sulphate would in effect flow through the entire sludge bed.

Conceptual process design

Biological sulphate reduction and heavy metal precipitation of AMD using biogenic H_2S can be applied in separated unit processes (Figure 1).

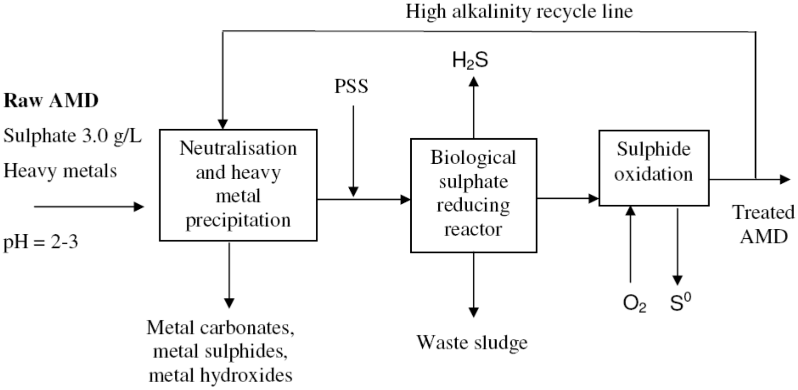

***Figure 1** Conceptual process for biological sulphate reduction of AMD using primary sewage sludge.*

The conceptual unit process train (as illustrated in Figure 1 above) would consist of a number of unit processes where heavy metals can be precipitated prior to the biological sulphate reduction. The reduced aqueous sulphide is oxidised to elemental sulphur either biologically or chemically. Part of the treated effluent, which would contain bicarbonate species, residual sulphide and a relatively high pH (7-8), is recycled to blend with the raw AMD. This would result in metals precipitation and neutralising the pH.

Aim of the study

The aim of this study was the viability of PSS to serve as an energy source in BSR in an UASB reactor. To achieve this, the minimum values of the operating parameters, such as hydraulic retention time (HRT), bed hydraulic retention time (BRT) and sludge age, for maximum sulphate reduction were determined from the performance of the UASB reactor. Further, the effect of introducing a sludge mass recycle line from the top to the bottom of the reactor bed was studied, by conducting profile tests along the axis of flow through the UASB reactor.

Methodology

Experimental set-up

A laboratory-scale UASB reactor (Figure 2) was operated for 250 days to investigate the system. The reactor had a total volume of 9.1 L with an internal diameter of 93 mm and height 1330 mm. It was sealed and mixed by a vertical rod fixed to a central shaft and set to rotate for 5 revolutions every 5 minutes. Effluent draw-off was subsurface via an inverted "U"-tube which was adjusted to control the reactor liquid volume. Sampling ports were set at 10 cm height intervals from bottom to top of the reactor for the bed profile studies. The reactor was heated to approximately 35^{o}C with heating wires wrapped around the column, with a thermocouple inserted into one of the sample ports of the reactor and connected to a temperature controller.

The UASB reactor was inoculated with stored sulphate reducing bacteria, and operated with a synthetic sulphate rich feed similar to low sulphate AMD, except for the deliberate omission of heavy metals. PSS was added to the feed as substrate (carbon and electron) source for BSR. In order to close the sulphur loop and do a sulphur mass balance around the system, hydrogen sulphide gas was collected from the headspace (gaseous phase) of the reactor and bubbled through ferric solution. Analyses of the ferric solution were conducted with the Phelanthroline method (Morgan, 2003) to determine the concentration of ferrous iron (Fe^{2+}) formed from the reduction of ferric iron (Fe^{3+}) with hydrogen sulphide as reductant as per the following equation.

$$2Fe^{3+}\ (aq) + H_2S\ (gas) \rightarrow 2Fe^{2+}\ (aq) + S^0(s) + 2H^+\ (aq)$$

Reactor Operation

The reactor was seeded with 6 L of sulphate-reducing sludge from previous sulphidogenic studies stored at 4^{o}C. The system was given a start-up period to allow the SRB to acclimatise and to accumulate a sludge bed. The sludge bed was then maintained at a constant volume of 7.1 L in the reactor column, by withdrawing excess sludge from the top of the sludge bed via a sampling port. A biomass recycle line was introduced withdrawing sludge from the UASB reactor just below the 7.1 L volume and returning it to the bottom of the reactor, at half the feed flow rate. It was envisaged that this recycle line would initiate rapid BSR from the bottom of the bed and thus was worthwhile investigating. A schematic representation of the lab-scale UASB reactor is shown in Figure 2 below.

The hydraulic retention time (HRT) was reduced stepwise by increasing the feed flowrate to obtain the minimum value for stable operation and low effluent sulphate concentration (<250 mg/L SO_4^{2-}). After each stepwise change, the system was allowed to stabilise, indicated by measured effluent alkalinity, volatile fatty acids (VFA) and sulphate concentrations and pH remaining constant for a period of about 5-7 days. The minimum stable HRT was accepted as the shortest HRT where the effluent VFA (<100 mgHAc/L) and effluent sulphate (<250 mg/L SO_4^{2-}) were low, and the measured alkalinity and pH were almost constant. When the minimum stable HRT was reached, bed profiles along the sludge bed were done to gain insight into the process behaviour inside the reactor bed.

Results and Discussions

From the experimental data of this detailed investigation, a summary of the performance, design and operating parameters of the BSR UASB system using PSS as carbon source is listed in Table 1. The UASB reactor measured effluent alkalinity concentration increased significantly while the VFA concentration remained low, indicating high sulphate reduction into hydrogen sulphide and bicarbonate. These two species contribute to the production of a highly alkaline effluent. The pH increased from 5.9 to 7.1 with this production of alkalinity and effluent sulphate concentration averaged 146 mg/L (representing a reduction of 92%).

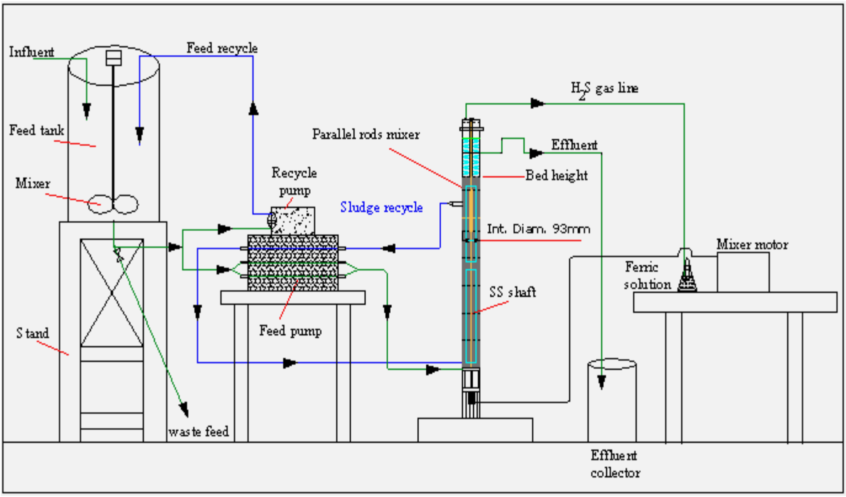

Figure 2 *Schematic diagram of the lab-scale UASB reactor.*

Conclusions

The results obtained in this study show that sulphate is successfully reduced under complete sulphidogenic conditions in UASB reactors using PSS as carbon source and electron donor. The UASB reactor was operated for 250 days with an influent sulphate concentration of 1800 mg/L and COD 1875 mg/L. The minimum HRT was found to be around 18h with low effluent sulphate and VFA. Solid-liquid separation in the system was very good, achieved even at a HRT of 18 h, with very low solids content in the effluent. The PSS, which has a good settleability, appears to enmesh and entrap fine solids arising from biodegradable particulate organic breakdown. Sludge bed granulation in the system was observed, which further enhances solid/liquid separation. At HRT lower than 18h and maintaining the sludge bed height constant, the effluent quality deteriorated. This deterioration could be ascribed to the reduced sludge bed biomass caused by sludge bed expansion, greater sludge mass removal via wastage and sludge loss to the effluent as a result of the increased upflow velocity.

The introduction of a biomass recycle line from top to bottom of the reactor bed effectively distributed the active biomass throughout the bed, facilitating sulphate reduction as soon as the feed enters the reactor. This recycling of the sludge bed offers two advantages: (i) introducing BSR biomass to initiate rapid sulphate reduction and (ii) adding alkalinity to buffer pH changes due to possible build up of VFAs. It was concluded that the AMD water has been successfully treated using PSS as carbon source. The experimental observations indicate that the UASB configuration offers significant advantages in BSR for AMD remediation and that this novel technology has considerable potential for full-scale implementation. In fact, based on the results of this investigation, a 2 ML/d pilot plant using PSS for BSR at the Grootvlei Mines Ltd (South Africa) was operated and thereafter scaled up to 10 ML/d.

Table 1 *Summary of the performance, design and operating parameters of the BSR UASB system using primary sewage sludge.*

Parameters	**Units**	**Influent**	**Effluent**
Total organic COD	mgCOD/L	1880	454
Organic soluble COD (mgCOD/L)	mgCOD/L	337	225
Particulate COD (mgCOD/L)	mgCOD/L	2249	229
VFA (or SCFA) (mgCOD/L)	mgCOD/L	158	72
Sulphate	mgSO_4^{2-}/L	1800	146
Free and saline ammonia (FSA)	mgN/L	10	46
pH	-	5.9	7.1
Sum carbonate and sulphide alkalinities	mg/L as $CaCO_3$	22	1855
Total carbonate alkalinity	mg/L as $CaCO_3$	22	1358
Design and operating parameters			
Volume of reactor bed/digester after wastage	L	7.1	
Feed flow rate	L/d	10.4	
Hydraulic retention time (HRT)	h	18	
Sludge age	d	21	
Waste flow rate	L/d	0.34	
Upflow velocity	m/h	0.10	
Sulphate reduction achieved	%	92	

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