BIOLOGICAL MINE WATER TREATMENT OPERATING A ONE STAGE REACTOR SYSTEM

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ABSTRACT

Mine drainage arises from oxidation of pyrites, due to exposure to air and water. Acid mine drainage normally contains high concentrations of sulphate, metals and acidity. These pollutants can be reduced applying the biological sulphate reduction technology.

The aim of the study was to investigate whether rumen bacteria can degrade cellulytic material to produce the fermentation products, such as Volatile Fatty Acids and other intermediates), which can be used by sulphate reducing bacteria as the carbon and energy source for biological sulphate reduction, operating a one stage reactor system.

A 20 ℓ reactor was used, which was operated as a "hybrid" reactor at temperature of 39 °C. The fermentation products of cellulose degradation, using rumen fluid as source of the fermentation organisms, were utilised as electron donor when sulphate, as the electron acceptor, is converted to sulphide. The feed water entered the reactor at the top, to allow the water to get in contact with grass cuttings, the source of cellulose. The total experimental period was 113 days, which was divided over 4 periods resulting from the addition of fresh grass cuttings and the feed water flow rate.

It was concluded from this study that the microorganisms from rumen fluid can degrade t cellulose in grass cuttings to the preferred substrates for biological sulphate removal. The results indicated that butyrate and propionate were utilized for the biological sulphate removal process, producing acetate. The advantage of this technology is that the fermentation and utilization of the fermentation products for sulphate removal can be executed, operating a one stage reactor, which has potential for a cost effective AMD treatment.

Keywords: Acid mine drainage; single stage; sulphate reduction, rumen bacteria, grass cuttings

INTRODUCTION

South Africa is a scarce water country. Acid Mine Drainage (AMD) caused by mining activities accelerates the water shortage problem. AMD from abandoned coal mines affects the quality of both ground and surface water, due to seepage and to the discharge to the water receiving bodies, respectively. Mine effluents can have a detrimental effect on aquatic plant and fish life, because of its acidity and salinity characteristics. In addition AMD poses the problem of introducing iron and potentially other metals to local watercourses, since the mining process exposes pyrite (FeS_2) to air and water (1). AMD needs to be treated to prevent the pollution of water courses with iron precipitates. Currently, treatment for acidic industrial effluents consists of either the chemical treatment systems, such as lime neutralization or the biological sulphate reduction, while the integrated treatment method (chemical treatment, followed by the biological) might be the most cost effective (2).

In this study the focus is on the biological treatment of AMD. In order to achieve this treatment method, a carbon and energy source is needed. A bio-waste product, such as grass cuttings, which consist of cellulose and hemicellulose, forming hexose and other sugars through a fermentation process, can provide cost effective carbon and energy sources   Cellulose degradation can be carried out by bacteria isolated from compost or from the rumen of fistulated ruminants. Rumen bacteria (RB) are important cellulose degradation bacteria, responsible for polymer and monomer fermentation, producing volatile fatty acids (VFA's). Sulphate reducing bacteria (SRB) utilize a number of fermentation products from cellulose mineralization, especially hydrogen, propionate and butyrate. These processes convert sufficient sulphate to sulphide when these produced intermediates are used by SRB as energy sources. In addition to sulphide generation, the biological sulphate reduction technology produces alkalinity, which results in pH increase of treated AMD (3, 4).

MATERIALS AND METHODS

Feed water

Artificial sulphate water

Synthetic sulphate rich (SO_4≈2500 mg/ℓ) feed water to which macro nutrients (6.5% N, 2.7% P, 13.0% K, 7.0% Ca, 2.2% Mg and 7.5 % S) and micronutrients (0.15% Fe, 0.024% Mn, 0.024% B, 0.005% Zn, 0.002% Cu and 0.001% Mo) were added functioned initially as feed water to the reactor.

Acid mine water (AMD)

Seepage from an abandoned coal mine in the Witbank area, South Africa, was used as feed water to the reactor during the second period of the study. The chemical composition of the seepage water is presented in Table 1. Due to the acidic character of this AMD, the feed water was pre-treated with the alkalinity and sulphide rich effluent of the biological reactor in a 1:1 ratio.

Table 1: The chemical composition of AMD

Parameter	Units (mg/ℓ, except for pH)
pH	2.5
Acidity	1 200
SO_4	2 600
Cu	0.75
Total Fe	76
Pb	0.25
Mg	77
Mn	9.3
Ni	0.61
Zn	4.0
Na	19
K	7

Reactor system

The anaerobic bioreactor, FR (Figure 1), with an active volume of 20 ℓ was operated as a "hybrid" reactor. The bottom part (2/3) of the reactor contained ceramic rings as packing material for biofilm formation of the SRB. The upper part of the reactor was initially fed with 1000 g grass cuttings (BWC), which, there after were added regularly as indicated in Table 2. Fermenting microorganims (250 mℓ, of which the (VSS) was 10604 mg/ℓ), occurring in rumen fluid acquired from fistulated ruminants (Pretoria University) were added to the BWC. The pH of FR was maintained between 6.6 and 6.9, to accommodate the rumen bacteria (RB). Although the SRB prefer a reactor pH of 7.5, these bacteria can operate at the lower pH of about 7 as well.

Table 2: Amount of grass added during indicated periods

Periods (days)	Grass added
1 – 24	100 g/w
25 – 33	1000 g/w
34 – 40	100 g/w
41 – 61	20 g/d
62 – 72	40 g/d
73 – 76	500 g/w
77 – 113	40 g/d

Carbon and energy source

The fermentation products of grass cuttings (collected from the CSIR garden service) served as the carbon and energy source for the biological sulphate removal process.

Biomass

SRB
The reactor was seeded with 250 mℓ, of which the Volatile Suspended Solids (VSS) was 9692 mg/ℓ adapted to sulphate removal biomass, obtained from the CSIR demonstration reactor in Witbank, South Africa.

RB
Rumen fluid (250 mℓ: VSS of 10604 mg/ℓ), obtained from fistulated ruminants (Experimental Farm, University of Pretoria, South Africa) was added to the grass at the fermentation stage of the reactor.

Experimental

The feed water entered FR at the top, to allow the water to get in contact with the grass cuttings. A recycle (360 ℓ/d) was installed from the bottom of the grass section to the top of the reactor, for mixing purposes and for further fermentation of the partially degraded grass. Initially synthetic sulphate rich water was used as feed water at 5 ℓ/d. Thereafter, the feed rate was increased to 10 and 15 ℓ/d. Later, pre-treated AMD was used as feed water at feed rates of 15 and 30 ℓ/d. The different feed waters and feed rates resulted in 4 experimental periods (Table 3). The fermentation products of grass cuttings produced in the top part of FR served as electron donor for the sulphate reduction in the bottom part of FR.

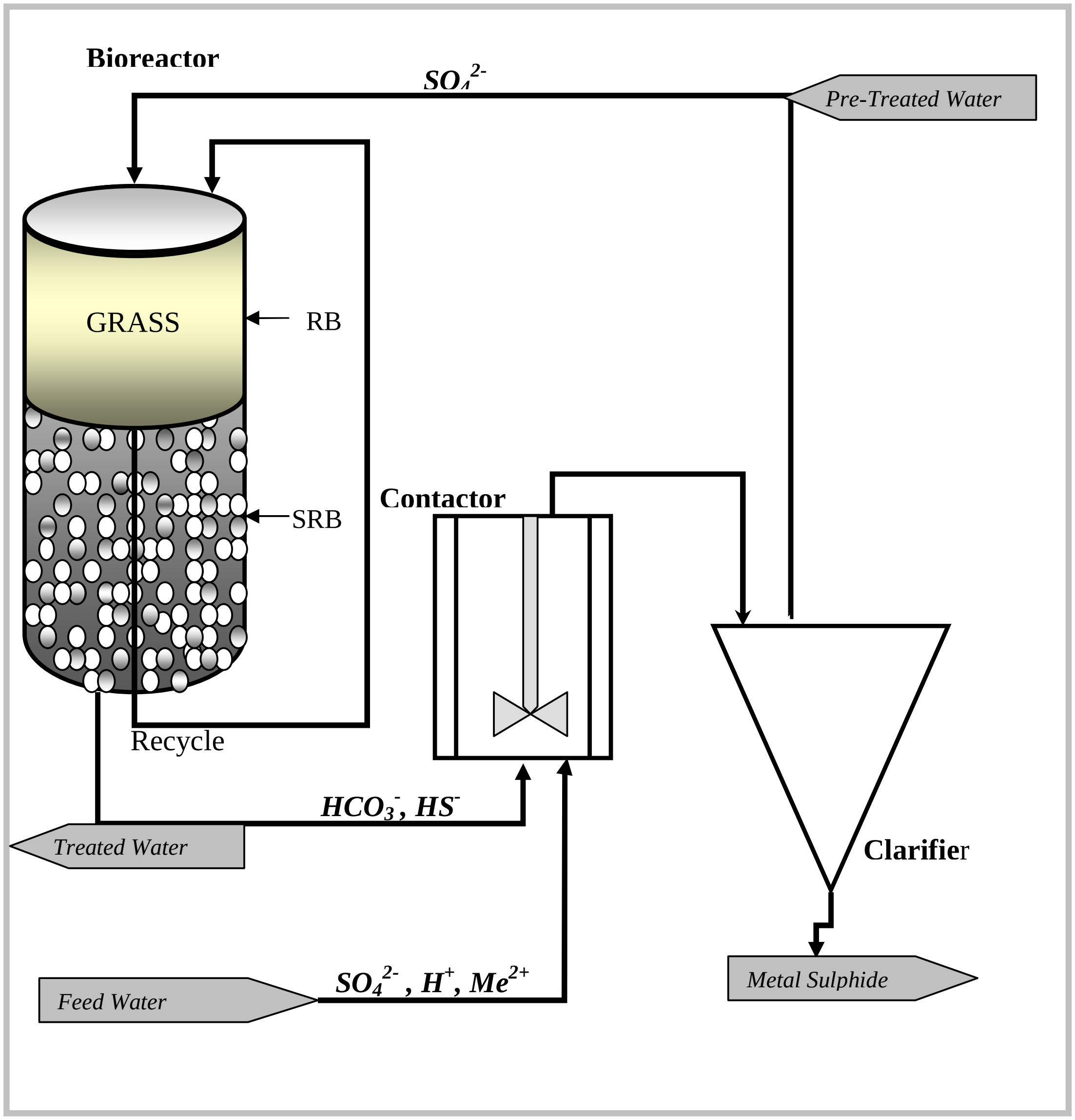

Figure 1: A one-stage fermentation and SO_4 reduction reactor system

Table 3: Experimental periods determined by feed composition and rates

	Synthetic feed water		**AMD**	
Exp. Period	1	2	3	4
Flow rate (ℓ/d)	10	15	15	30
HRT	2 d	32 h	32 h	16 h

<u>Analytical methods</u>

Chemical analysis

The sulphate, sulphide, alkalinity, COD, and pH were manually determined according to the analytical procedures as described in Standard Methods (APHA, 1985). The analyses were all carried out on filtered samples, except for the sample for redox potential and the sulphide samples. The redox potential of the samples was calculated from the mV and stabilization temperature measured with a 744 pH meter (Metrohm). The alkalinity of the samples was determined by titrating with 0.1N HCl to a pH of 4.3. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 gas to correct for the COD value caused by the sulphide concentration.

VFA analysis
All VFA analyses were done using a gas chromatograph (Hewlett Packard. HP 5890 Series II) equipped with a flame ionisation detector (GC/FID), while the data analyses were done using the Chem Station software package, supplied by Hewlett Packard. The column used was a HP-FFAP, 15 m x 0.530 nm, 1 micron. An outline of the GC/FID programme used is depicted in Table 4. The N_2 flow rate was set at 1 mℓ/min.

Table 4: The GC/FID programme for the detection of VFA

Parameter	Setting
Initial oven temperature (℃)	30
Initial time (Min)	2
Temperature programme: (℃)	80
Rate (℃/min)	25
Final temperature (℃)	200
Final time (min)	1
FID temperature (℃)	240

RESULTS AND DISSCUSSION

<u>Sulphate removal</u>

The graphs in Figure 2 showed the sulphate concentration in the influent and effluent as well as the COD concentration, when feeding synthetic feed water. It can be observed that when the feed rate was 10 ℓ/d, during period 1, almost complete sulphate removal was achieved. During that period, the COD concentration increased from 300 to almost 2000 mg/ℓ in the reactor. This result demonstrated that grass cuttings can be degraded by rumen bacteria to short chain VFA and other fermentation products, which are utilized for the sulphate removal. The sulphate removal during the second period, feeding 15 ℓ/d was less remarkable, which can be ascribed to the lower COD concentration in the reactor. The feed rate had increased from 10 to 15 ℓ/d, however the amount of grass per addition had not increased.

The sulphate concentration in the feed and treated water when feeding pre-treated mine water during a continuous period of 113 days is illustrated in Figure 3. It can be seen from the graphs (Fig. 3) that the COD concentration was mainly < 1000 mg/ℓ, except for a short period from day 27 to day 29 where 1000 g/d of grass was added eliminate the COD concentration depletion. Weekly addition of grass (100 g/w) did not seem sufficient as the sulphate concentration of the treated water was >1000 mg/ℓ. Thereafter the reactor was seeded with grass on a daily basis (20 g/d) (Fig.3). After daily grass addition, the sulphate concentration in the treated water varied from 50 to 500 mg/ℓ. However, when the flow rate was increased to 30 ℓ/d the reactor performance declined again due to low COD concentration. Due to increased flow rate, a higher SO_4^{2-} concentration entered the reactor, which implies that more COD, thus more grass is required. Therefore the amount of grass was doubled (Table 2) and the sulphate concentration in the treated water was < 800 mg/ℓ, which indicated an improvement compared to the previous period, but was not satisfactory. Improved sulphate reduction could possibly be achieved through the addition of more grass. These results indicate the narrow relationship between grass addition and fermentation and sulphate reduction.

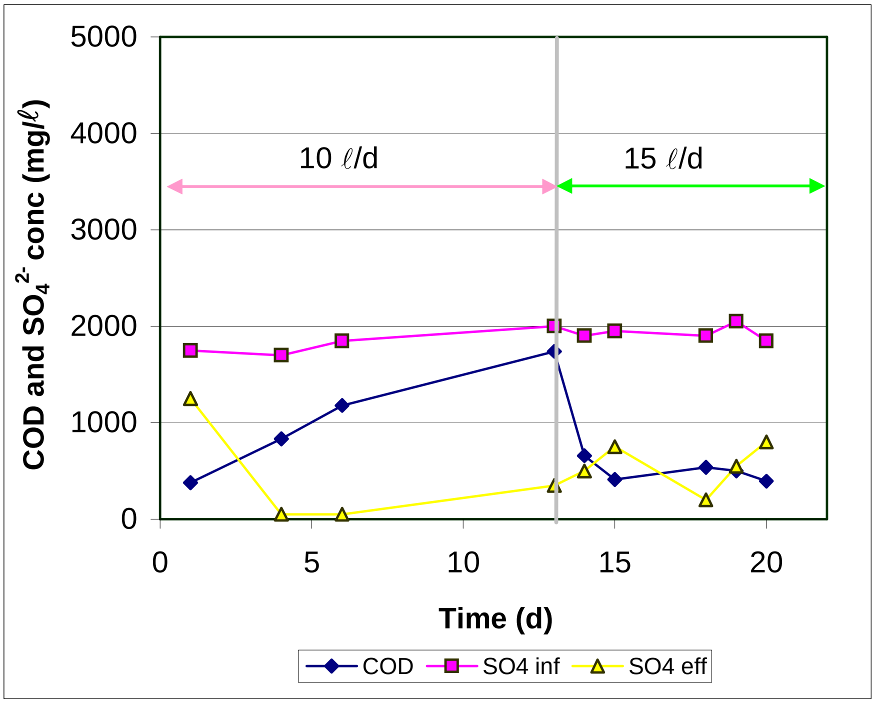

Figure 2: Sulphate and COD concentrations feeding synthetic feed

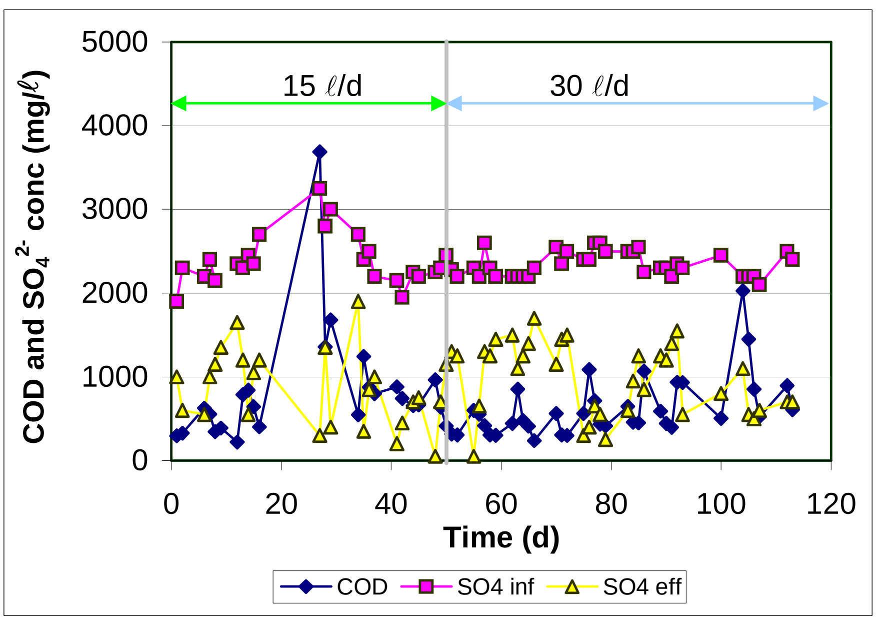

Figure 3: Sulphate and COD concentrations feeding pre-treated mine water

VFA concentration

The results (Figure 4) show that during the total experimental period of 113 days, the butyric and propionic concentrations in the reactor were very low and that the acetate concentration increased. When sulphate is reduced, utilising one mole of butyrate and one mole of propionate, two and one mole(s) of acetate are produced, respectively, [Equations 1 and 2]. The increased acetate concentrations agreed with the higher propionate and butyrate in the reactor (days 27 and 106). The higher VFA concentrations correspond with the higher COD values in the reactor (Figures 2 and 3), which in turn can be related to grass addition (Table 2).

$$CH_3CH_2COO^- + \tfrac{3}{4}\,SO_4^{2-} \rightarrow CH3COO^- + HCO3^- + \tfrac{3}{4}\,HS^- + \tfrac{1}{4}\,H^+ \qquad [1]$$

$$CH3CH2CH2COO^- + \tfrac{1}{2}\,SO42^- \rightarrow 2\,CH3COO^- + \tfrac{1}{2}\,HS^- + \tfrac{1}{2}\,H^+ \qquad [2]$$

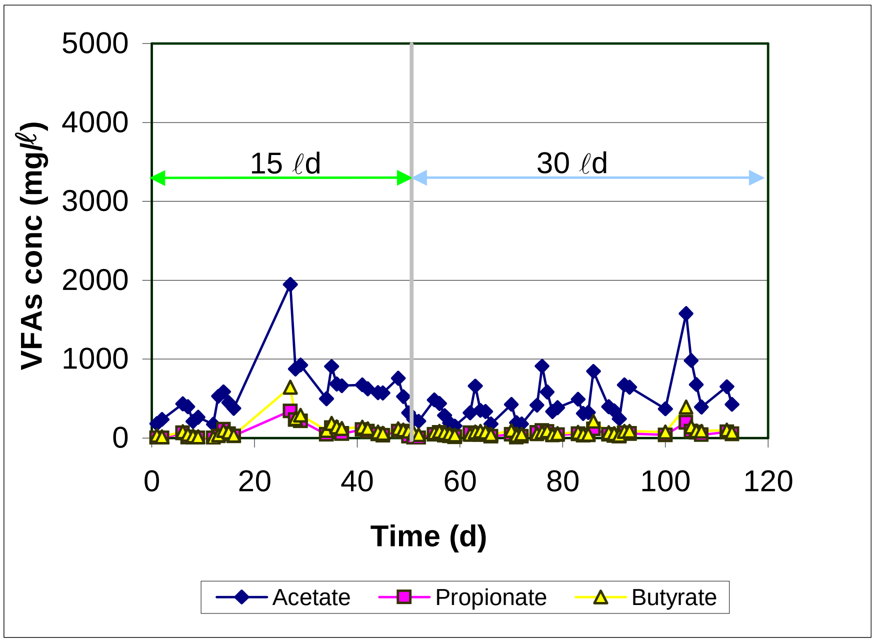

Figure 4: VFA concentration in the reactor.

Fermentation

Due to the fermentation of cellulose, utilising the microorganisms obtained from rumen fluid, the degradation products to be used as substrate for the biological sulphate reduction, are formed. These rumen microorganisms consist of a complex and dense population of bacteria and protozoa, which convert plant material to volatile fatty acids, methane, carbon dioxide, hydrogen, ammonia and microbial cells. The major types of rumen bacteria are cellulose digesters, which produce sugars (e.g. hexose) from carbohydrates. Hexose is broken down by the rumen bacteria mainly by glycolytic pathway, which converts glucose to pyruvate. Glucose is fermented to formate, butyrate, lactate, succinate and ethanol. Pyruvate, a key intermediate product, is metabolized by a variety of mechanisms to yield propionate, which, as shown in this study can be used by SRB to reduce sulphate (2).

Metal precipitation of acid mine drainage

The metal concentrations of the AMD and the treated water are given in Table 4. The Aluminium, lead, zinc and iron concentrations were reduced to value less than 0.5 mg/ℓ after treated with the effluent water (ratio 1:1). Manganese was reduced to 4 mg/ℓ. All metals precipitated as metal sulphide except, aluminium, which is precipitated as $Al(OH)_3$(REF). Biogenically-produced sulphide was used to precipitate metals that have a low metal sulphide solubility product, where Me^{2+} symbolizes a divalent metal with a low metal sulphide solubility product [Equations 3]. (REF) The two protons released by this reaction were neutralized by the alkalinity produced during the treatment.

$$Me^{2+} + H_2S \rightarrow MeS_{(s)} + 2H^+ \quad [3]$$

Table 4: Metals composition of AMD, pre-treated AMD and treated AMD

Sample Id	**Units**	**AMD**	**Pre-treated AMD**	**Treated AMD**
Aluminium	mg/ℓ Aℓ	122	11	<0.07
Aluminium (total)	(mg/ℓ Aℓ)	128	10	0.12
Copper	(mg/ℓ Cu)	<0.04	<0.04	<0.04
Iron	(mg/ℓ Fe)	64	2.2	0.22
Iron - total	(mg/ℓ Fe)	86	14	0.49
Lead	(mg/ℓ Pb)	0.25	<0.07	<0.07
Manganese	(mg/ℓ Mn)	10	6.8	3.8
Manganese - total	(mg/ℓ Mn)	8.7	6.8	4.0
Zinc	(mg/ℓ Zn)	1.7	<0.07	<0.07

CONCLUSIONS

The results of the study shown that

- Cellulose in grass cuttings can be degraded to VFA and other fermentation products.
- The produced degradation products can function as substrate for the biological sulphate removal technology
- Propionate and butyrate were utilised by SRB to reduce sulphate
- Acetate was the fermentation product of the sulphate reduction, when propionate and butyrate were used as the carbon and energy source.
- There seems to be a strong relationship between the amount of grass added to the reactor, the produced COD and the sulphate removed
- The higher the COD concentration in the reactor, the better the sulphate reduction.

REFERENCES

Drury W.J. (1999). Treatment of acid mine drainage with anaerobic solid substrate reactors. A research note prepared for: Water Environment Research. February 19.

Findlay A.L.R. Microbiology of rumen and small and large intestines. Physiological Laboratory, University of Cambridge, CB2 3EG. Revised: February 1998.

Holmer M. and Storkholm P. (2001). Sulphate reduction and sulphur cycling in lake sediment: a review. *Freshwater Biology*, **46**, 431-451

Maree, J.P., Greben, H.A. and M de Beer (2004) Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process, *Water SA*, **30:** (2), 183-189.

McGinness S. (1999). Treatment of acid mine drainage. Science and Environment section, House of Commons Library. *Research paper* 99/**10**. February 2.