Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process

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Abstract

A novel chemical/biological process is described in which sulphate and sulphide are removed simultaneously during biological treatment. Partial sulphate removal is achieved during chemical pre-treatment. In the biological stage sulphate is reduced to sulphide in a complete-mixed reactor through addition of sucrose or ethanol as a carbon and energy source. Sulphide is oxidised by allowing oxygen to enter the system in a controlled way. The experimental investigation of the process showed that sulphate and sulphide could be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria. The volumetric sulphate reduction rate in a complete-mixed reactor, with sucrose as an organic carbon and energy source, amounts to 12.4 g SO_4/(ℓ.d). The rate of biological sulphate removal was found to be directly related to the square root of sulphate, COD and VSS concentrations respectively, and inversely proportional to sulphide concentration. The practical value of simultaneous sulphate and sulphide removal is that only one stage is required for removal of both sulphate and sulphide; a conventional complete-mixed reactor can be used; and sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO_4) due to the stability of the process.

By combining the biological stage with $CaCO_3$-neutralisation and/or lime pre-treatment, the chemical cost can be reduced. Sulphate, associated with the over-saturated fraction after treatment with $CaCO_3$ or lime, can be removed through gypsum crystallisation. In the integrated sulphate removal process ($CaCO_3$-neutralisation, lime treatment and biological stages), sulphate can be removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the various stages respectively. The chemical cost with the integrated process amounts to R2.94/m³, versus R12.44/m³ when all the sulphate is removed using the biological stage only. Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m³ for the integrated process, versus R3.11/m³ for biological treatment only.

Keywords: acid mine water; ethanol; kinetics; sulphate reduction; sulphide oxidation; sucrose

Introduction

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites are oxidised due to exposure to the atmosphere, e.g. in the mining industry. Acidic industrial effluents require treatment prior to discharge into sewage networks or into public watercourses. In water-rich countries, the main causes of concern are the low pH and metal content of acidic effluents. Salinity is not a problem due to dilution with surplus capacity of surface water. In semi-arid countries like South Africa, the high salinity associated with acidic industrial effluents is an additional concern.

Biological sulphate removal can be used to treat industrial effluents to achieve, in addition to sulphate removal, metal removal and neutralisation. Sulphate can be removed as elemental sulphur via sulphide as an intermediate product when an energy source is provided. Desalination is achieved by effecting calcium carbonate crystallisation after sulphate removal. Metals are completely removed by precipitation as sulphides. Alkalinity is generated in quantities stoichiometrically equivalent to the amount of sulphate removed, which allows direct treatment of acid water.

The biological sulphate removal process has been developed over the past 15 years to the stage where it can compete successfully with other sulphate removal technologies for full-scale treatment of mine and other industrial effluents. Maree and Strydom (1985) showed that sulphate could be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as a carbon and energy source. Metals like nickel, cadmium and lead were completely removed due to precipitation of metal sulphides. Maree and Hill (1989) showed that a three-stage process could be applied for sulphate removal, using molasses as the carbon and energy source in an anaerobic packed-bed reactor. Sulphide can be stripped with a mixture of CO_2/N_2 from the effluent of the anaerobic reactor in an H_2S-stripping stage, and residual COD and $CaCO_3$ can be removed in an aerobic final treatment stage. Maree et al. (1991) showed that when molasses is used as a carbon and energy source it could either be utilised in the fermented or unfermented form. When molasses is allowed to ferment, acetic acid is the main carbon and energy source for the sulphate-reducing bacteria. When molasses is kept sterile in the storage tank, sucrose is the main carbon and energy source with acetic acid as the metabolic end product.

With this information, it was concluded that by running two anaerobic sulphate removal reactors in series, sucrose could be fermented to lactate in the first reactor and, via acetate, to CO_2 in the second reactor. Du Preez et al. (1992) were the first to demonstrate that producer gas (mixture of H_2, CO and CO_2) can be used as a carbon and energy source for biological sulphate reduction. Both H_2 and CO were utilised as the carbon and energy source. Visser (1995) investigated the competition between sulphate-reducing bacteria (SRB) and methanogenic bacteria (MB) for acetate as the carbon and energy source in an up-flow anaerobic sludge blanket (UASB) reactor. He found that at pH values less

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than 7.5, SRB and MBs are equally affected by the presence of H_2S, while at higher pH values SRB out-compete MB. Van Houten (1996) showed that sulphate could be reduced to H_2S at a rate of 30 g $SO_4/(\ell.d)$ when H_2/CO_2 is used as the carbon and energy source and pumice or basalt particles are used to support bacterial growth in a fluidised-bed reactor. The sulphate reduction rate was not inhibited at H_2S-concentrations less than 450 mg/ℓ (as S).

The aim of this investigation was to further improve the biological sulphate removal process by achieving simultaneous removal of sulphate and its product, sulphide. Specific aims of the investigations were to demonstrate the symbiosis between SRB and sulphide oxidising bacteria (SOB) and to determine the kinetics of simultaneous sulphate and sulphide removal.

Materials and methods

Two experimental set-ups were operated in parallel. One system comprised a complete-mixed reactor (15 ℓ) and a clarifier (15 ℓ), while the other system comprised a column reactor (20 ℓ) and a clarifier (15 ℓ). The reactors and the clarifiers were open to the atmosphere to allow air contact. Sulphate-rich water (1 500 mg/ℓ $CaSO_4$ as SO_4) was fed to both systems. This water was supplemented with sucrose and/or ethanol as the carbon and energy source, and with the macro-nutrients (75 mg/ℓ ammonia-N and 15 mg/ℓ ortho-phosphate-P). The following micro-nutrients (100 μg/ℓ Fe, 210 μg/ℓ Co, 0.28 μg/ℓ Mn, 0.44 μg/ℓ V, 0.25 μg/ℓ Ni, 0.48 μg/ℓ Zn, 0.40 μg/ℓ Mo, 0.18 μg/ℓ B, 0.37 μg/ℓ Cu) were added as well. The reactors were inoculated with anaerobic sludge obtained from a sewage treatment plant. Sludge was recycled from the bottom of the clarifier to the complete-mixed reactor, or from the bottom to the top of the column reactor, at a rate of 50 ℓ/d. The performance of the systems was monitored by operating the two systems in either continuous or batch mode. During continuous operation, water was fed at a rate between 20 and 100 ℓ/d. Batch studies were carried out as follows: Feed water to the system was stopped, recycle pumps were stopped and sludge was allowed to settle. Clear water was decanted and replaced with fresh feedstock, where-after the recycle pumps were started again. Filtered samples were collected on a regular basis and analysed for various parameters (sulphate, sulphide, COD, alkalinity, pH and Eh). Additional batch studies were carried out similarly in 1 ℓ beakers by mixing biomass (obtained from one of the systems described) with fresh feedstock. Continuous studies were executed to determine the effect of hydraulic retention time on the chemical composition of the feed water and the volumetric and specific sulphate reduction rates. Batch studies were carried out to determine the effect of a number of parameters on the kinetics of sulphate reduction. The parameters are: sulphate concentration (1.1 - 3.5 g/ℓ); sulphur concentration (0 - 5 g/ℓ); sulphide concentration (0 - 1 g/ℓ); alkalinity (0 - 1 g/ℓ); $CaCO_3$ solids concentration (0 - 1 g/ℓ); COD (0.5 - 2 g/ℓ); VSS concentration (1.7 - 12.1 g/ℓ); stirring rate (20 - 265 r/min).

Analytical

Samples were collected and filtered through Whatman No. 1 filter paper. Sulphate, sulphide, MLSS and VSS determinations were carried out manually (*Standard Methods*, 1985)). Calcium and magnesium concentrations were determined using atomic absorption spectrophotometry. Alkalinity was determined by titrating the solution to pH 4.3 using HCl.

Results and discussion

Symbiotic activity of SRB and SOB

Figures 1a, 1b, and Table 1 show the performance of the single-stage sulphate removal process operating continuously during the period from start-up until steady-state conditions were attained. The complete-mixed reactor was used with sucrose (1.5 g/ℓ) as the carbon and energy source. The feed rate increased gradually from 15 to 130 ℓ/d. This corresponded with a reduction in the hydraulic retention time (HRT) from 48 to 5.5 h in the system, based on the combined volume of the reactor and clarifier. The volume of the clarifier was included as it was partially filled with biomass.

Sulphate reduction rate

The volumetric sulphate reduction rate increased during the experimental period of 78 days from 0.2 to 12.4 g $SO_4/(\ell\cdot d)$, while the specific sulphate reduction rate increased from 0.09 to 1.06 g $SO_4/(gVSS\cdot d)$ (Fig. 1b). The increase in the volumetric sulphate reduction rate was ascribed to the increase in the biomass concentration with time, adaptation of the biomass to its environment, suitability of the complete-mixed reactor for simultaneous removal of sul-
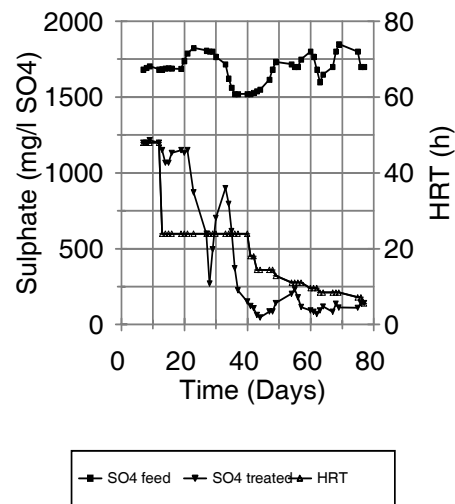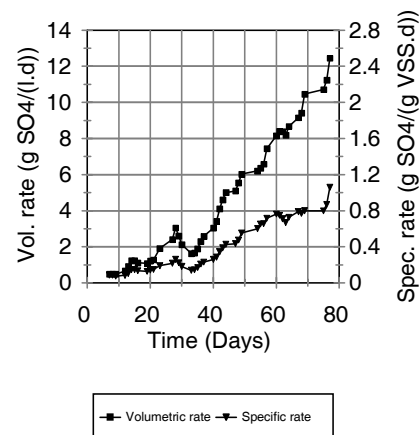

Figure 1a
The sulphate removal at different HRT

Figure 1b
The sulphate removal rates

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TABLE 1
Chemical composition of feed and treated water during simultaneous biological sulphate and sulphide removal

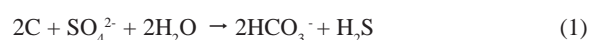| Parameter	Quality	
	Feed	Treated
pH	4.3	7.2
Sulphate (mg/ℓ SO_4)	1672	123
Sulphide (mg/ℓ S)	0	162
COD (mg/ℓ O_2)	1781	733
Acidity (mg/ℓ $CaCO_3$)	335	
Alkalinity (mg/ℓ $CaCO_3$)		834

phate and sulphide, and the suitability of sucrose as the carbon and energy source. The increase in the specific sulphate reduction was ascribed to improved performance of the micro-organisms due to adaptation to their environment. Like sugar, ethanol can also be used as carbon and energy source for sulphate removal with the single-stage sulphate/sulphide removal process. Greben et al. (2000a) reported sulphate removal rates of 6.6 g SO_4/(ℓ·d) using ethanol as the carbon and energy source. Improved sulphate reduction rates were obtained when using ethanol as the carbon and energy source, to which a small amount of sugar (0.25 g/ℓ) was added (Greben et al., 2002a). It was reported (Greben et al., 2002b) that methanol was not effectively utilised by SRB at ambient temperatures, possibly because it was out-competed by methanogenic bacteria. Weijma (2000) however, showed the use of methanol at themophilic temperatures.

Simultaneous sulphate and sulphide removal

Sulphate removal to less than 250 mg/ℓ (as SO_4) was achieved after 37 days of continuous operation and remained at this level for the rest of the experimental period (until day 77) (Fig. 1.a). Sulphide was also partially removed. Of the 1 549 mg/ℓ sulphate (as SO_4) that was removed, only 162 mg/ℓ sulphide (as S) was measured in the effluent (Table 1). A distinct characteristic of the process is its stability. Any deterioration in the quality of the effluent was due to plant failure (e.g. loss of sludge at day 28) or change in experimental conditions (e.g. reduced HRT at day 50) (Fig. 1a). This stable performance was achieved with a complete-mixed reactor. Preliminary studies with column up-flow sludge blanket reactors showed that simultaneous sulphate/sulphide removal could also be achieved in a sludge blanket column reactor. It appeared, however, that sulphate removal is more stable in a complete-mixed reactor than in a packed-bed reactor. A possible reason why the complete-mixed reactor could be more suitable for simultaneous sulphate/sulphide removal than the column reactor, is the way in which oxygen enters the water through diffusion at the air–liquid interchange High numbers of sulphate reducers are present in the oxic zones and near the oxic-anoxic boundaries of sediments and in stratified water bodies, microbial mats and termite guts (Cypionka, 2000). Due to continuous mixing in a complete-mixed reactor, the total content of the reactor is in more direct contact with the atmosphere than in the column reactor where water comes into contact with the atmosphere only periodically. In a packed-bed reactor sulphate was not consistently removed to less than 120 mg/ℓ and a longer acclimatisation period was required for start-up.

Sulphide$_{produced}$/Sulphate$_{removed}$-ratio

A large portion (59%) of the sulphate that was converted to sulphide (Reaction 1) was converted to elemental sulphur due to the activity of sulphur oxidising bacteria (Reaction 2) and photosynthetic sulphur bacteria (Reaction 3). This shows the symbiotic existence of SRB and SOB. It is assumed that aerobic sulphur oxidising bacteria dominated the activity of the photosynthetic sulphur oxidising bacteria. Sulphide oxidation rates as high as 17 g S/(ℓ·d) have been reported for aerobic systems with reticulated polyurethane foam as support medium for bacterial growth (Buisman, 1989), compared to only 1.92 g S/(ℓ·d) for photosynthetic sulphur oxidising bacteria (Cork et al., 1986). This finding was confirmed by Greben and Maree (2002b), who showed that the sulphide oxidation is mainly a biological process under the influence of air. Elemental sulphur accumulated on the surface of the water in the clarifier. This finding shows that SRB can tolerate low levels of oxygen entering the water, if it is immediately taken up for sulphide oxidation (Cypionka et al., 1985). Greben et al. (2000) showed that the sulphide oxidation rate is a function of the sulphate reduction rate and the retention time.

$$2C + SO_4^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \qquad (1)$$

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \qquad (2)$$

$$4H_2S + 2CO_2 \rightarrow 4S + CH_3COOH + 2H_2O \qquad (3)$$

Alkalinity$_{produced}$/Sulphate$_{removed}$-ratio

The Alk$_{produced}$/SO$_{4removed}$-ratio was measured to be 0.99, which corresponds well with the theoretical ratio of 1.04 (Reaction 1).

Similar observations were made from batch studies. The results reported in Fig. 2 were obtained when 1.19 g/ℓ sucrose, 1.5 g/ℓ Na_2SO_4 (as SO_4) and 4.81 g/ℓ VSS were stirred in a 1 ℓ beaker. It shows the relative behaviour between the following parameters as a result of various reactions: COD and sulphate is removed in the ratio 0.81 g O_2/g SO_4 which compares with the theoretical ratio of 0.67 (Reaction 1); sulphide produced from Reaction 1 is removed due to Reaction 2. Alkalinity increased initially because of alkalinity production (Reaction 1), but thereafter decreased due to $CaCO_3$-precipitation. The Alkalinity$_{produced}$/SO$_{4removed}$-ratio of 0.83 compares with the theoretical value of 1.04. The pH increased slightly with increased reaction time. The E_h value remained constant at -140 mV while the sulphide concentration was greater than 90 mg/ℓ sulphide (as SO_4) and increased to 6 mV when the sulphide concentration was less than 90 mg/ℓ. The sulphide concentration decreased from 432 to 144 mg/ℓ sulphide (as SO_4). The pH increased slightly from 7.3 to 7.8.

Sulphate is reduced via intermediate products (valence of S species in brackets), such as SO_3^{2-} (+4), $S_2O_5^{2-}$ (+4), $S_2O_3^{2-}$ (+2) and S^{2-} (-2) to sulphur. During batch studies, similar to that shown in Fig. 2, the concentrations of various S-compounds were monitored. It was noted that:

- SO_4^{2-} (sulphate) (+6) was removed gradually with time over a 24 h period (from 1080 to less than 100 mg/ℓ as SO_4), while SO_3^{2-} (sulphite) (+4) and $S_4O_6^{2-}$ (tetrathionate) (+2.5) were not detected.
- $S_2O_3^{2-}$ (thiosulphate) (+2) was formed in small quantities with a maximum level of 38 mg/ℓ (as S) reached between 4 and 6 h.
- Sulphide increased to an intermediate level of 130 mg/ℓ (as S) between the time interval 2 and 10 h, whereafter it was removed completely.
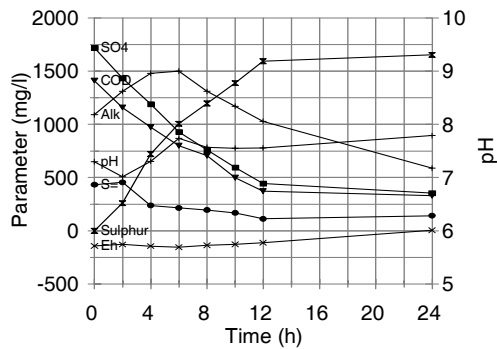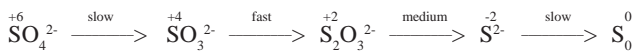
Figure 2
*Relationship between various parameters during batch studies.
Intermediate products*

- The amount of sulphur increased gradually (calculated from other S species).

By taking the intermediate concentrations of S^{2-} (highest), $S_2O_3^{2-}$ (low), SO_3^{2-} (zero) and $S_4O_6^{2-}$ (zero) into account, it was concluded that under the specific experimental conditions, SO_4^{2-} is converted to sulphur via the various intermediate compounds at the following relative reaction rates:

$$\overset{+6}{SO_4^{2-}} \xrightarrow{\text{slow}} \overset{+4}{SO_3^{2-}} \xrightarrow{\text{fast}} \overset{+2}{S_2O_3^{2-}} \xrightarrow{\text{medium}} \overset{-2}{S^{2-}} \xrightarrow{\text{slow}} \overset{0}{S_0}$$

Effect of different parameters on the SO_4 reduction rate

The kinetics of biological reactions can be explained by the Monod and Haldane equations. The Monod equation shows the relationship between the specific growth rate constant, μ, and the substrate concentration, [S]. The Haldane equation, similarly, shows the relationship between the reaction rate, R, and the substrate concentration, S. The latter makes provision for the inhibitory effect of the substrate. The purpose of this section of the research was to determine the effects of various parameters on the rate of biological sulphate removal. For the purpose of this investigation, it was assumed that the reaction rate equation had the following functional form:

$$-d[SO_4^{2-}]/dt = k.[SO_4^{2-}]^{n1}.[S^{2-}]^{n2}.[COD]^{n3}.[VSS]^{n4} \quad (4)$$

where:

$-d[SO_4^{2+}]/dt$ or R = rate of sulphate reduction
k = reaction rate constant
n_i = reaction order constants
$[SO_4^{2-}]$ = sulphate concentration (moles/ℓ)
$[S^{2-}]$ = sulphide concentration (moles/ℓ)
[COD] = carbon oxygen demand (mg/ℓ)
[VSS] = volatile suspended solids concentration (g/ℓ).

By varying the value of only one parameter in a series of experiments, say $[SO_4^{2-}]$, Eq. (4) can be written as:

$-d[SO_4^{2-}]/dt = K.[SO_4^{2-}]^{n1}$ or
$\log(-d[SO_4^{2-}]/dt) = \log K + n_1.\log[SO_4^{2-}] \quad (5)$

where:
$K = k.[S^{2-}]^{n2}.[NO_3]^{n3}.[COD]^{n4}.[VSS]^{n5}.M^{n6}$

The contribution, n_1, of sulphate, to the overall reaction rate was determined from the slope of the graph when log R vs. log $[SO_4^{2-}]$ was plotted. The data in Table 2 shows that the sulphate reduction reaction in respect of SO_4 (COD not limiting), VSS, S^{2-}, COD and stirring rate (O_2), had kinetic order constants of 0.55 (~0.5), 0.6 (~0.5), -0.8 (~-1), 0.42 (~0.5) and -0.34 (~-0.5) respectively. The empirical reaction can thus be written as:

$$-d[SO_4^{2-}]/dt = k.[SO_4^{2-}]^{0.5}.[COD]^{0.5}.[VSS]^{0.5}/[S^{2-}]^1 \quad (6)$$

The reaction rate was zero order with respect to sulphate when the substrate was dosed in limiting concentrations, in contrast to 0.5 order, when the substrate was unrestricted. The reaction rate was also affected by stirring rate and temperature. At high stirring rates (265 r/min) the reaction rate was inhibited by too high oxygen concentrations, while at too low stirring rates (20 r/min) the sulphate reduction rate was inhibited by too high sulphide concentrations. Thus, an optimum oxygen dosage is required to control the sulphide concentration at minimum levels in solution. The finding that the rate is inversely related to the sulphide concentration is in line with the finding of Hilton et al. (1985) who demonstrated that sulphide inhibits biological processes.

General

This investigation showed that sulphate-reducing bacteria do not require strict anaerobic conditions in the bulk of the water, only in their micro-environment. They can tolerate oxygen, as long as other organisms present in the system consume it. The practical value of simultaneous sulphate and sulphide removal is that, during full-scale application, only one stage is required for removal of sulphate and partially sulphide; a conventional complete-mixed reactor can be used; sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO_4) due to low sulphide concentrations in the water.

Pre-treatment combined with biological sulphate removal

Biological sulphate removal can be used for removal of sulphate from water, both under-saturated and over-saturated with respect to gypsum, as well as for treatment of acid water direct. It is, however, more cost-effective if sulphate, associated with the over-saturated fraction of gypsum, were removed through pre-treatment with $CaCO_3$ or lime in the CSIR integrated sulphate removal process (Fig. 3). This process comprises the following stages:

$CaCO_3$-neutralisation/Iron(II)-oxidation
Powder $CaCO_3$ is used to raise the pH to 7. Iron(II)-oxidation is achieved through aeration in the same tank where neutralisation is applied, or biologically in a separate stage, up-steam of neutralisation, at low pH (2 to 3) (Eq. 7). Free acid in the feed water is neutralised, as well as free acid that is released when metals (Fe^{3+} and Al^{3+}) are precipitated as hydroxides. CO_2 generated during $CaCO_3$-neutralisation is utilised downstream for pH adjustment from 12 to 8 of the lime treated water, $CaCO_3$-precipitation and stripping of residual H_2S in the biological sulphate removal stage.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad (7)$$
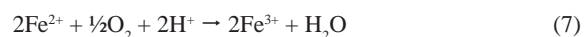
Lime treatment/gypsum crystallisation/ $CaCO_3$-precipitation
Lime is used to raise the pH to 12 for precipitation of metals, such

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Figure 3
CSIR integrated process for step-wise sulphate removal

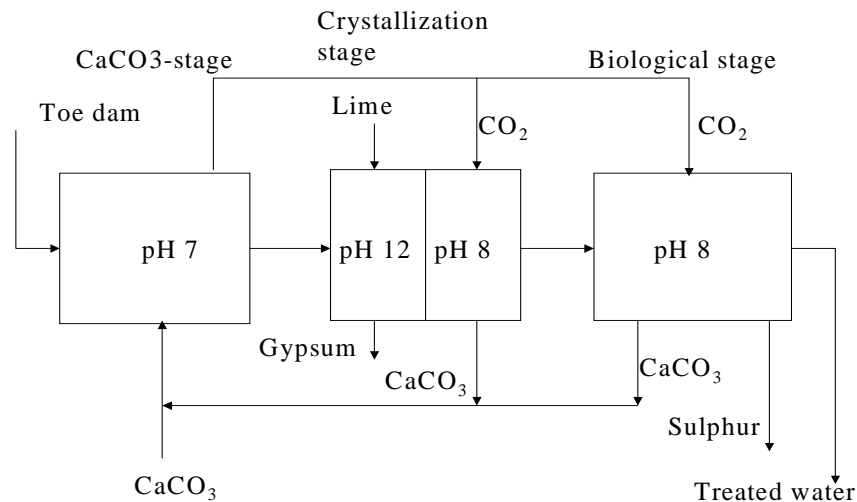| Parameter	Stage				
	Untreated	**CaCO₃**	**CaOH**	**CaCO₃**	**Biol.**
pH	2.2	7.1	12.0	8.3	8.1
Sulphate (mg/ℓ SO₄)	9200	2410	1230	1220	205
Alkalinity (mg/ℓ CaCO₃)	0	0	1000	100	150
Calcium (mg/ℓ Ca)	377	639	903	543	140
Magnesium (mg/ℓ Mg)	202	200	3	3	3
Manganese (mg/ℓ Mn)	20	20	0	0	0
Aluminium (mg/ℓ Al)	106	3	2	0	0
Iron (II) (mg/ℓ Fe)	3040	4	0	0	0
Free acid (mg/ℓ CaCO₃)	1740	30	0	0	0
Total dissolved solids (mg/ℓ)	12945	3276	2738	1826	438

TABLE 2
Chemical composition when coal discard leachate is treated with the integrated sulphate removal process

as magnesium and manganese, which do not precipitate in the CaCO₃-stage. Sulphate is also partially removed (to less than 1 200 mg/ℓ) due to gypsum crystallisation. Upon completion of gypsum crystallisation, the pH is adjusted with CO₂-gas, as described above. The produced CaCO₃ can be recycled to the first stage for neutralisation of the free acid, or sold as a by-product (such as a filler in various industrial applications).

Biological sulphate removal
The biological sulphate removal process forms an integral part of the integrated process. It also produces CaCO₃ (Eq. 8), which can be recycled to the CaCO₃-neutralisation stage. Residual H₂S, that is not converted to sulphur in the anaerobic reactor, is stripped off and converted to sulphur by contacting it with an iron (III)-solution. Iron (III) is produced biologically from iron (II) as described under the CaCO₃-neutralisation/Iron (II)-oxidation-stage.

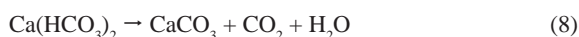$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \quad (8)$$

Table 3 shows the chemical composition when leachate from a coal discard dump is treated with the integrated sulphate removal process. It is noted that:

- Sulphate is removed from 9 200 mg/ℓ to 2 410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO₄) in the CaCO₃-neutralisation,

gypsum crystallisation and biological sulphate removal stages, respectively.
- Free acid, iron and aluminium are completely removed in the CaCO₃-neutralisation stage.
- Magnesium and manganese removal and sulphate removal to less than 1250 mg/ℓ is achieved in the lime treatment/gypsum crystallisation stage.
- Sulphate can be removed to 200 mg/ℓ in the biological sulphate removal stage.

Table 3 shows the chemical cost when coal discard leachate is treated with various combinations of the stages of the integrated process. In Option A, only biological treatment is applied, while in Option B lime treatment and biological treatment is applied, and in Option C CaCO₃-treatment, lime treatment and biological treatment is applied. It is noted that the total chemical cost for Options A, B and C amount to R12.44/m³, R4.69/m³ and R2.94/m³ respectively. It is therefore cost-effective to remove as much as possible sulphate through gypsum crystallisation during pre-treatment with CaCO₃ and/or lime. Similarly, Table 4 shows the cost when magnesium-rich mine water, with a neutral pH, is treated with Options A and B. It is noted that the total chemical cost for Options A and B amount to R3.11/m³, R1.92/m³ respectively.

TABLE 3
Chemical cost when coal discard leachate is treated with various combinations of the stages of the integrated process

Stage	SO₄ conc. mg/ℓ	Dosage mg/ℓ	Price R/t	Cost R/m³	Purity %	Utilis. %	Usage g/g SO₄
Option A Untreated	9 000						
Biological (EtOH)	200	4 444	2 800	12.44	90	70	0.32
Total cost				**12.44**			
Option B Untreated	9 000						
CaOH	1 200	5 948	550	3.27	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**4.68**			
Option C Untreated	9 000						
CaCO₃	2 400	10 185	100	1.02	75	90	1.04
CaOH	1 200	915	550	0.50	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**2.93**			

TABLE 4
Chemical cost when magnesium sulphate-rich water is treated with various combinations of the stages of the integrated process

Stage	SO₄ conc. mg/ℓ	Dosage mg/ℓ	Price R/t	Cost R/m³	Purity %	Utilis. %	Usage g/g SO₄
Option A Untreated	2 400						
Biological (EtOH)	200	1 111	2 800	3.11	90	70	0.32
Total cost				**3.11**			
Option B Untreated	2 400						
CaOH	1 200	915	550	0.50	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**1.91**			

Conclusions

The following conclusions were drawn from this study:

- Sulphate and sulphide (partial) can be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria.
- The volumetric sulphate reduction rate in a complete-mixed reactor with sucrose as an organic carbon and energy source amounts to 12.4 g SO_4/(ℓ.d). The corresponding specific sulphate reduction rate was 1.06 g SO_4/(gVSS.d).
- The removal rate of sulphate is influenced by the removal rate of the intermediate products. SO_4^{2-} (+6) is reduced to SO_3^{2-} (+4) at a slow rate, the latter to $S_2O_3^{2-}$ (+2) at a fast rate, the latter to S^{2-} (-2) at a medium rate and the latter to S (0) at a slow rate.
- The rate of biological sulphate removal is directly related to the square root of sulphate, COD and VSS concentrations and inversely related to the sulphide concentration.
- Sulphate, associated with the over-saturated fraction after treatment with $CaCO_3$ or lime, can be removed more cost-effectively through gypsum crystallisation, than biologically. In the integrated sulphate removal process ($CaCO_3$-neutralisation, lime treatment and biological stages), sulphate can be removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2 410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the various stages respectively. The chemical cost with the integrated process amounts to R2.94/m³ versus R12.44/m³ when all the sulphate is removed biologically.

Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m³ for the integrated process, versus R3.11/m³ for biological treatment only.

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