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Sulphur Metabolism

PILOT PLANT STUDIES ON BIOLOGICAL SULPHATE REMOVAL FROM INDUSTRIAL EFFLUENT

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ABSTRACT

Sulphate-rich industrial effluents present a serious environmental pollution problem. A biological sulphate removal process has been developed for the treatment of such effluents. In this process, sulphate is converted to hydrogen sulphide in the anaerobic stage when an energy source, such as molasses, sugar or producer gas is added. The hydrogen sulphide is stripped off in a stripping stage, with a carrier gas such as nitrogen. The gas is recycled through a ferric solution where it is oxidized to elemental sulphur. In a subsequent aerobic stage, degradation of organic carbon residuals and calcium carbonate crystallization are achieved simultaneously. In this study the anaerobic stage of the process was evaluated on pilot scale. After the inoculation period, sulphate was removed continuously for a period of 100 days from 2200 mg/l to below 200 mg/l. For the first part of the study acetic acid served as energy source as the sugar content of molasses was allowed to ferment. Thereafter fresh molasses was supplied as energy source and the bacterial culture had to adapt to utilize sugar in molasses as energy source. A volatile suspended solids (VSS) concentration of 27 g/l was present in the packing material of the anaerobic reactor. With this VSS-value, a hydraulic retention time of 12 hours was needed for sulphate removal.

KEY WORDS

Sulphate reduction; molasses; acetic acid; mine water; anaerobic treatment.

INTRODUCTION

Environmental pollution can be caused by sulphur compounds which occur in the liquid, solid and gas phases. For example, sulphate-rich solutions are produced bacteriologically from pyrite during mining operations or from spent sulphuric acid where the latter is used in chemical or metallurgical plants. Mining effluents are major contributors to mineralization of receiving waters and may prove toxic to man, animal and plant due to unacceptably high concentrations of heavy metals and cyanide. Solid waste in the form of gypsum is produced by the fertilizer industry when phosphoric acid is leached from calcium phosphate rock with sulphuric acid, or by the mining industry when sulphuric acid containing effluents are neutralized with lime. Gaseous sulphur dioxide is produced by power stations when electricity is generated from coal and hydrogen sulphide gas by the coal-to-fuel industry. This paper deals with sulphate pollution in the liquid phase.

Various processes for the treatment of sulphate-rich effluents are being evaluated to determine the most feasible one. Among these are the slurry recycle and precipitation reverse osmosis (SPARRO) process (Chamber of Mines Research Organization, 1988), the barium sulphide and barium carbonate processes (Maree, et al., 1989), and the biological sulphate process (Maree and Hill, 1989). The latter offers the opportunity to recover re-usable water and elemental sulphur from sulphate-rich effluents or to neutralize acid water directly, saving pre-neutralization with lime. The process consists of anaerobic, stripping and sulphur production stages. In the anaerobic stage sulphate is reduced to H_2S when an energy source such as molasses, sugar or producer gas is added. In the stripping stage, H_2S is stripped from the water. In the last stage H_2S is converted to elemental sulphur. The technical feasibility of the process has been verified at laboratory scale.

The purpose of this study was to evaluate the anaerobic stage of the process at pilot plant scale and to determine:

* the suitability of unfermented and partially fermented molasses as substrates for biological sulphate reduction,

* the rate of biological sulphate reduction as a function of the biomass concentration,

* the ability of the process to treat acid water directly without pre-neutralization with lime, and

* the effect of H_2S on the rate of sulphate reduction.

EXPERIMENTAL

Pilot Plant Description and Operational Procedures

The anaerobic reactor (Fig. 1) was partially filled with 400 l pelletized ash (2-3 mm diameter, porosity 0.5) as bacterial support medium. Nitrogen was purged continuously through the medium at a rate of 6 l/h during the first 56 days to strip off hydrogen sulphide gas. Thereafter stripping was stopped in order not to disturb biomass growth on the medium. The nominal upflow velocity of fluid through the packed bed reactor was kept constant at 1 m/h by recirculation of the fluid. Provision was made for flushing out excessive sludge by increasing the recirculation rate to a fluid upflow velocity of 50 m/h. The plant was run in batch mode for the first 56 days. Thereafter, feedstock was introduced into the system at rates between 25 and 200 l/d to give corresponding hydraulic retention times between 8 days and 12 h in the active zone of the reactor. A multi-channel metering pump was used for feeding while a Germar pneumatic pump was used for recycling the fluid.

Feedstock consisted of partially neutralized underground water. Each litre of mine water was supplemented with 3 ml of molasses to serve as energy source for the sulphate-reducing bacteria. Fresh feedstock was prepared daily. The mine water/molasses feedstock was dosed as a mixture during the first 217 days. Thereafter, the mine water and molasses were dosed separately to prevent pre-fermentation of molasses in the dosing tank. The composition of the feedstock (fermented and unfermented) is given in Table 1. An active biological film was established on the support medium by inoculating the reactor with active sludge from a laboratory scale sulphate-reduction plant and waste sludge from an anaerobic digester at a sewage treatment plant.

Analytical

Samples of the effluent were taken daily for sulphate analysis and weekly for sulphide, alkalinity, chemical oxygen demand (COD), nitrate, ammonia, orthophosphate, total phosphate, heavy metals and pH. Samples of the support medium at various depths (200, 500 and 800 mm from the top respectively) were taken monthly to determine volatile suspended solids (VSS). VSS determinations

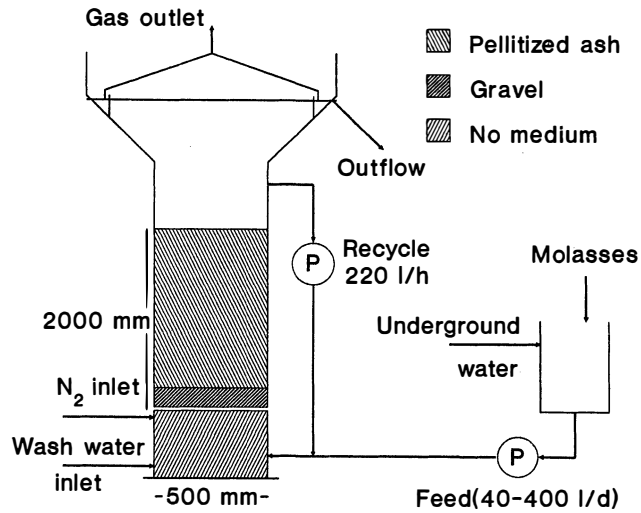

Fig. 1. Schematic diagram of the pilot plant used for biological sulphate reduction.

were done by calculating the mass difference per unit volume after heating the medium samples to 105 and 500 °C respectively. Determinations of sulphate, COD, alkalinity, sulphide and pH were carried out according to analytical procedures as described in Standard Methods (APHA, 1985). Direct-flame, atomic absorption, and automatic colorimetric techniques were used for the other chemical determinations.

RESULTS AND DISCUSSION

In the biological sulphate process, the following parameters require careful control to optimise process performance: nature of feed type substrate and the biomass, alkalinity, and sulphide concentrations.

In this section the influence on process performance of each of these parameters is discussed.

Feed substrate and minimum retention time

The performance of the pilot plant, feed with molasses fermented to acetic acid and unfermented molasses respectively, is shown in Fig. 2. The major reactions that take place in each case and the minimum retention time achieved are discussed.

Fermented feedstock. One of the main aims of this study was to determine the minimum retention time required for complete sulphate removal. The relationship between the degree of sulphate removal and retention time is shown in Fig. 2. The plant was operated in batch mode during the first 56 days. During the first 18 days of this period, sulphate decreased gradually to 266 mg/l. On day 19, a large amount of the biomass was lost due to an excessively high feed rate resulting from pump failure. After good sulphate reduction was restored on day 56, continuous dosing of feedstock was initiated.

Initially, the plant was operated at a nominal liquid retention time of 8 days (void volume in packed bed / influent flow rate). The retention time was subsequently reduced stepwise to 12 h (from day 186). The minimum achievable retention time is influenced mainly by the biomass concentration and type of feed substrate.

As the biomass concentration increased with time, it was possible to reduce the retention time accordingly. Each reduction had an impact on the degree of sulphate removal immediately thereafter. The sulphate concentration increased temporarily as seen on days 143 and 186 for example. On day 143, a reduction in the retention time from 3.3 to 2.5 days brought about an increase in the sulphate concentration from 127 to 755 mg/l, and on day 186, a reduction in the retention time from 18 h to 12 h brought about an increase from 100 to 500 mg/l. After sufficient time was allowed for further growth in biomass, good sulphate removal was restored after day 143. In the period following day 186, (retention time 12 h), the efficiency of sulphate removal decreased with time. This is because the specific culture in the plant, which utilized acetic acid as energy source, had reached its limit as far as the rate of sulphate reduction is concerned. A higher sulphate reduction rate could be achieved by changing the feed substrate in the plant from acetic acid to sugars. The results obtained when unfermented molasses was dosed will be discussed in the next section.

The chemical composition of the feedstock and treated water on day 167 is given in Table 1. The results show that sulphate was reduced from 2200 to 300 mg/l, while the COD value was simultaneously reduced from 3000 to 1500 mg/l, 200 mg/l in the feed tank and 1300 mg/l in the anaerobic reactor. The COD reduction in the feed tank is associated with the conversion of sugars in molasses (sucrose, glucose and fructose) to acetic and other fatty acids. This conversion occurred as a result of the open feed tank being stirred continuously. That a high bacterial activity developed in the feed tank is confirmed by a VSS value of 752 mg/l in the effluent of the feed tank.

The reaction whereby sulphate is reduced to H_2S when acetic acid is used as energy source is shown below:

$$8C_2H_4O_2 + 8SO_4^{=} \dashrightarrow 16CO_2 + 16H_2O + 8S^{=} \qquad [1]$$

(acetic acid biodegraded to carbon dioxide)

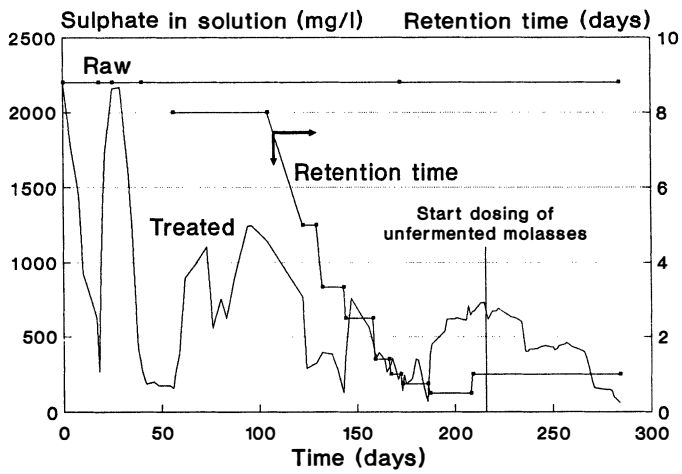

Fig. 2. Temporal variation of sulphate concentration during biological treatment in a packed bed reactor.

TABLE 1 Chemical Composition of Feedstock and Treated Water

Parameter	Units	Fermented feedstock*1	Treated effluent	Unfermented feedstock*2	Treated effluent
Sulphate	mg/l SO_4	2200	300	2200	300
Sulphide	mg/l SO_4	0	600	0	600
Sucrose	mg/l	20	0	940	20
Glucose	mg/l	4	0	340	0
Fructose	mg/l	10	0	320	0
Acetic acid	mg/l	930	50	120	1458
COD	mg/l O_2	2800*3	1500	3000	1500
Alkalinity	mg/l $CaCO_3$	-50	1100	-50	1100
Calcium	mg/l $CaCO_3$	1950	1200	1950	1200
Magnesium	mg/l Mg	135	135	135	135
Potassium	mg/l K	139	138	138	138
Sodium	mg/l Na	72	70	72	70
Ammonia	mg/l N	4	2	4	2
Nitrate	mg/l N	0.4	0.2	0.4	0.2
Orthophosphate	mg/l P	0.5	0.3	0.5	0.3
Chloride	mg/l Cl	250	250	250	250
pH		3.3	7.0	3.3	7.0
SS	mg/l	944	166	0	166
VSS	mg/l	752	32	0	32

VSS = 27 g/l

*1 Feedstock (mine water + molasses) after storage for 20 hours (Feedstock was stored under stirred conditions).

*2 Freshly prepared feedstock.

*3 COD loss due to fermentation was 200 mg/l (Compare with COD value under 'Unfermented feedstock').

Acetic acid produced in the feed tank had to be used as energy source for sulphate reducing bacteria during the experiment. The specific and volumetric sulphate reduction rates with acetic acid as energy source can be calculated from the following experimental data:

sulphate removed = 1.9 g/l
retention time = 1.4 days
VSS = 27 g/l

Specific sulphate reduction rate = (1.9 g/l) / (1.4 days x 27 g/l)
= 0.050 g SO_4/(g VSS.d)

Volumetric sulphate reduction rate = (1.9 g/l)/(1.4 days)
= 1.36 g SO_4/(l.d)

These results correspond with those of Middleton and Lawrence (1977) (Table 2) who observed a specific sulphate reduction rate of 0.03 g SO_4/(g VSS.d) for acetic acid, which is of the same order as the 0.05 g SO_4/(g VSS.d) obtained in this study.

Unfermented feedstock. Due to the inefficient utilization of molasses, the pilot plant was changed to prevent molasses conversion to acetic acid. This was done by feeding molasses separately from the mine water. After an adapted population, which utilizes sugar, had developed in the reactor, it was possible to reduce the retention time to 1 day. Table 1 shows that in this case sugar was degraded only to acetic acid as indicated by its high concentration of 1458 mg/l. These results could be represented by the following reactions:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3CHOHCOOH \quad [2]$$

(fermentation of sugar to lactate)

$$2CH_3CHOHCOO^- + SO_4^= \rightarrow 2CH_3COO^- + 2HCO_3^- + H_2S \quad [3]$$

(sulphate reduction and alkalinity production)

Figure 2 shows that sulphate removal improved gradually from day 216 when fermented molasses was replaced with unfermented molasses. At a retention time of 1 day, the sulphate concentration in the effluent decreased from 700 to less than 100 mg/l. The gradual improvement is due to the fact that a culture shift took place in the reactor. It is obvious that the retention time could be reduced to less than 1 day when unfermented molasses is dosed as energy source.

It is assumed that Desulfovibrio vulgaris dominated the system when acetic acid, the major component present in the fermented molasses, was the main energy source, while Desulfovibrio desulfuricans became the dominant micro-organism when unfermented molasses was dosed.

With this information it is possible to increase the efficiency of molasses when used for sulphate reduction by running two anaerobic reactors in series. In the first reactor, molasses will be fermented to lactate, which serves as carbon source for Desulfovibrio desulfuricans, while the acetate-rich effluent of the first reactor could be utilized for further sulphate reduction in the second reactor where Desulfovibrio vulgaris is the dominating organism.

TABLE 2 Summary of biological sulphate reduction rates obtained by various researchers (Adapted from Olthof et al., 1985)

Reference	Reduction rate $\frac{g\ SO_4}{g\ VSS.d}$	$\frac{g\ SO_4}{l.d}$	Temp. °C	Carbon source
Burgess and Wood (1961)	-	4.50	35	primary sewage sludge
Maree (1988)	0.11	6.40	24	molasses; packed bed reactor
Maree and Hill (1989)	0.20	0.80	27	molasses; complete mix reactor
Middleton and Lawrence (1977)	0.03	-	-	acetic acid
Obarsky et al.(1978)	-	0.24	35	rubber waste effluent
Oleszkiewicz and Hilton (1986)	-	10.20	35	cheese whey with gas stripping
Oleszkiewicz and Hilton (1986)	-	1.50		cheese whey without gas stripping
Pipes (1960)	0.11	1.20	35	waste activated sludge
Rabolini (1971)	-	2.79	-	sewage sludge
Sadana and Morey (1962)	0.08	2.40	35	primary sewage sludge
Smith and Middleton (1980)	0.15	-	35	primary sewage sludge

Biomass

Biological reaction rates are directly proportional to biomass concentration. Therefore, the reactor should be operated to maximize biomass concentration as measured by volatile suspended solids (VSS). Table 3 shows the VSS (biomass) and SS (suspended solids) concentrations in the reactor on day 214 at different depths. SS values represent biomass and chemical precipitation products in the water and VSS the biomass. The biomass concentration on the stone medium remained at 23 g/l through the depth of the reactor, while in the liquid phase it increased with depth from 3.3 to 5.1 g/l. The uniform distribution of the biomass through the depth of the reactor on the stone medium is due to the recirculation of water. It is clear that the major fraction of biomass (about 85 %) was attached to the stone medium, while the balance was present in suspended form in the liquid phase.

TABLE 3 SS and VSS concentrations at various depths of the packed bed reactor

Depth (mm)	SS Liquid phase (g/l)	VSS Liquid phase (g/l)	VSS Solid phase (g/l)
200	15.2	3.3	24.6
500	24.4	4.5	
800	67.7	5.1	22.1

The increase in VSS concentration with depth results because biomass settles at a higher velocity than the 1 m/h upflow velocity of the water through the reactor. An increase in SS values with depth occurs for the same reason. The difference between SS and VSS values indicates the presence of inorganic salts in suspension, such as calcium carbonate. The change in the calcium and alkalinity values through the anaerobic reactor (Table 1), suggests the presence of calcium carbonate in suspension. The results show that 750 mg/l of calcium carbonate had precipitated. The alkalinity increased by only 1150 mg/l which is less than the expected increase of 1979 mg/l (calculated from equation 3 for the reduction of 1900 mg/l sulphate). This is due to alkalinity losses as a result of calcium carbonate crystallization.

In order to remove the calcium carbonate precipitate in the reactor, and to maintain a biomass sludge age of, say 30 days, the reactor needs to be backwashed regularly. This is done by increasing the upflow velocity through the reactor from 1 to 50 m/h. At 50 m/h, the stone medium will fluidize and the resulting abrasion will erode some of the sludge. By recycling the water through a clarifier, the solids and water can be separated.

Alkalinity production

Alkalinity is produced according to reaction 3 when sulphate is reduced to H_2S and when an organic carbon source is supplied as energy source. For each gram of sulphate reduced, 1.042 g of alkalinity (as $CaCO_3$) is produced. This reaction makes the direct treatment of acid water possible as shown in Table 1. Water, with a pH of 3.3, was neutralized to pH 7.0 when mixed with the highly buffered water in the reactor. It is noted in Table 1 that the untreated water had an alkalinity of -50 mg/l $CaCO_3$ (acidity of 50 mg/l $CaCO_3$) and that, after treatment, it had an alkalinity of 1100 mg/l (as $CaCO_3$). These figures indicate that water with a much higher acid content could be treated with the biological sulphate process.

H_2S stripping

Due to the probable toxicity of H_2S in solution towards micro-organisms, it is expected that the rate of sulphate reduction will be faster when H_2S is stripped off than when no stripping is applied. This point was not confirmed during this study. It was, however, determined that sulphate reduction occurs under both situations. During the period when the plant was operated under batch conditions, good sulphate removal was achieved when H_2S was stripped off completely by bubbling nitrogen gas through the reactor. Sulphate was removed equally well afterwards when no sulphide stripping was applied.

It is noted in Table 1 that less sulphide was detected in the effluent than expected from the stoichiometric amount of sulphate reduced. Only 600 mg/l H_2S (as SO_4) was present in the effluent while 1900 mg/l sulphate had been reduced. The difference could be explained as follows:

* A large fraction of the sulphide was stripped off automatically as a result of the low solubility of H_2S gas in solution.
* A small fraction of the sulphide was converted to elemental sulphur due to the activity of photosynthetic sulphur bacteria in the perspex chambers of the recirculation pump.

CONCLUSIONS

* Both acetic acid and sugar are suitable substrates for biological sulphate reduction. The specific sulphate reduction rate when acetic acid is used as energy source is 0.05 g SO_4/(g VSS.d). This value is four times less than when molasses is used as energy source. A biomass (VSS) concentration of 27 g/l developed in the packed bed reactor. Of this amount, 23 g/l was attached onto the stone medium while 4 g/l was suspended in the liquid.

* As alkalinity is produced in the biological sulphate process, acid water was neutralized directly from a pH value of 3.3.

* The H_2S concentration in solution has no or little effect on the efficiency of sulphate reduction.

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