BIOTECHNOLOGICAL SULPHIDE REMOVAL FROM EFFLUENTS

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ABSTRACT

A new system for sulphide removal is reported in which sulphide is converted to elemental sulphur using colourless sulphur bacteria. A 4 m^3 biorotor reactor has been tested using sulphide-containing anaerobically treated papermill wastewater. Sulphide removal efficiencies well above 90% were achieved at a hydraulic retention time of 19 minutes, using Pall rings of 2.5 cm or Bio-Net 200 as carrier materials.
It was also found that reticulated polyurethane is not suitable as carrier material for the sulphide removal process in the presence of fatty acids.

INTRODUCTION

The emission of sulphide is a major problem associated with anaerobic treatment of sulphate-containing waste waters. Sulphate is utilized by sulphur-reducing bacteria as an electron acceptor. Sulphide is the end product of the reduction. Also sulphite and organic sulphur compounds can be converted into sulphide. Release of sulphide into the environment should be controlled because of the following possible problems:

- toxicity; the limit values for H_2S are: TLV (threshold limit value), 10 ppm (14 mg/m^3) and STEL (short time exposure limit), 15 ppm (21 mg/m^3) (A.C.G.I.H., 1988). In high concentrations (500-1000 ppm) hydrogen sulphide acts primarily as a systemic poison, causing unconsciousness and death through respiratory paralysis. In lower concentrations (50-500 ppm) H_2S acts primarily as a respiratory irritant.
- corrosive properties; when present in the biogas, H_2S may cause corrosion problems in boilers and internal combustion engines; when sulphide is present in the effluent it may cause damage to concrete walls of reactors, sewer systems and steel pipelines as well.
- unpleasant odor; its characteristic rotten eggs odor is perceptible in fresh air in a concentration of 0.2 ppm.
- high oxygen demand; per mole of sulphide two moles of oxygen are required to form sulphate.

Based on the information available in the literature and the observations in
anaerobic treatment plants that elemental sulphur may accumulate in effluent
pipes, research on a new concept for sulphide removal was started. It should
be possible to convert the sulphide into elemental sulphur with bacteria. This
idea resulted in the present investigations.

The purpose of the research was to develop a high rate, effective and low-
cost biotechnological process for sulphide removal. The principle of the propo-
sed process is to convert sulphide by oxidation into elemental sulphur which
can be removed by sedimentation. The advantages of such a process are, (a). no
catalyst or oxidants (except air) are required,(b). no chemical sludge to be
disposed,(c).low energy consumption,(d). possible reuse of sulphur, and (e).little
if any sulphate or thiosulphate discharge.

Methods for sulphide removal in common use today are physical-chemical
processes which involve direct air stripping, chemical precipitation and oxidation.
However, the relatively high energy requirements or the high chemical and
disposal (chemical sludge like FeS and MnO_2) costs constitute important draw-
backs of these systems.
Direct air stripping leads to a voluminous air stream contaminated with H_2S,
which has to be treated. Chemical precipitation generates sludge (e.g. FeS) that
must be disposed.
Oxidation processes used for sulphide removal are aeration (catalyzed and
uncatalyzed), chlorination, ozonation, potassium permanganate treatment and
hydrogen peroxide treatment. In all these oxidation processes sulphur, thio-
sulphate and sulphate may be the end products.
Uncatalyzed oxidation of sulphide with oxygen is a very slow process (Chen &
Morris, 1972). Therefore either pure oxygen without catalysts or air with
catalysts is used. Table 1 gives a short overview of the relative costs invol-
ved in these methods.

Table 1. Difference in costs of sulphide removal methods as a percenta-
ge of the costs of hydrogen peroxide treatment

	Butler & Nadan (1981)	Tauw (1986)
H_2O_2	100	100
$KMnO_4$	1070[*]	-
Ozone	1514	-
pure oxygen	-	65
air with catalyst	-	47
Fe precipitation	-	87[*]

(* disposal costs of FeS and MnO_2 are not considered)

Very little useful information is available about the biological oxidation of
sulphide, especially for a process where sulphur will be the end product.
Therefore a considerable research effort was necessary to develop such a
process and to assess its feasibility. The fundamental microbial aspects are
currently being investigated by Kuenen and Stefess (Technical University Delft,
The Netherlands). The technological and engineering problems are subject of
research at the Department of Water Pollution control of the Agricultural
University Wageningen. The organisms that most likely will be present in the
aerobic sulphide removal reactors are bacteria of the group of colourless
sulphur bacteria (Table 2). The following (biological) overall reactions occur in
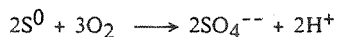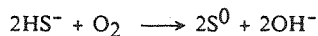an aerobic sulphide removal system (Kuenen, 1975):

$$2HS^- + O_2 \longrightarrow 2S^0 + 2OH^-$$

$$2S^0 + 3O_2 \longrightarrow 2SO_4^{--} + 2H^+$$

Table 2. Colourless sulphur bacteria oxidizing inorganic sulphur compounds

obligate chemolithotrophs	facultative chemolithotrophs	heterotrophs	unclassified
T.neapolitanus	T.intermedius	T.perometabolis	Thiovulum
T.denitrificans	T. A2	Pseudomonas	Thiophysa
T.thiooxidans	T.novellus	Beggiatoa	Thiothrix
T.thioparus	Thermothrix thiopara		Thiospira
T.ferrooxidans	T.acidophilus		Thioploca
Tms.denitrificans	P.denitrificans		
T.kabobis	S.acidocaldarius		
Tms.pelophila	S.brierleyi		

In a previous communication some lab studies were presented (Buisman et al., 1989a). It was found that an adapted biomass shows a satisfactory sulphide removal rate in the pH range 6.5 to 9.0. Above pH 9.0 sulphide removal deteriorates; pH values below 6.5 were not investigated. The optimal pH was found to be situated in the pH-range 8.0 - 8.5. The effect of the temperature on the sulphide removal capacity of the system was investigated using biomass adapted to a temperature of 20°C. The optimal temperature range is located between 25 and 35 °C, which was measured at a sulphide concentration of only 2 mg/l. At 5°C still 30% of the maximal sulphide oxidation capacity was reached. The concentrations of other sulphur compounds found in the effluent besides elemental sulphur, sulphide and sulphate were negligible.

The present publication deals with the feasibility of the biotechnological sulphide removal system. Experiments with anaerobically treated papermill wastewater using a lab-scale and a pilot-scale sulphide removal plant are described.
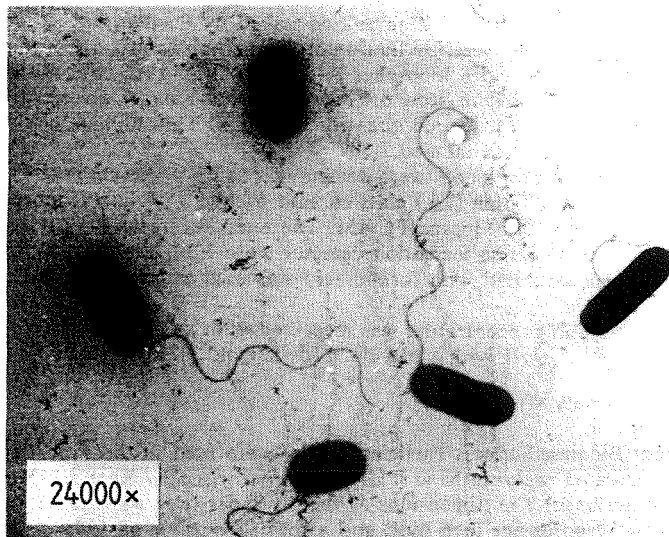

Figure 1. photograph of a *Thiobacillus* resembling bacteria isolated from a sulphide removal lab reactor by Stefess (Technical University Delft, The Netherlands)

MATERIALS AND METHODS

Composition of the papermill waste water

The removal plants are located at the wastewater treatment facility at Industriewater Eerbeek in the Netherlands. This plant treats the wastewater from three separate papermills with a total production approaching 300,000 tonnes p.a. Since 1985 an anaerobic (UASB) reactor is treating the wastewater (Habets & Webb, 1987). The composition of the effluent of the anaerobic reactor, used in this study, is shown in Table 3. There was little variation in the composition of the effluent in time (except at holidays). During the weekends the sulphide concentration increased slightly.

Table 3. Composition of the effluent of the anaerobic wastewater treatment at the plant Industriewater Eerbeek, The Netherlands

parameters		after 1/1'89	before 1/1'89
COD	(mg/l)	400	
N-kj	(mg/l)	10	
S^{--}	(mg/l)	35 - 70	140
SO_4^{--}	(mg-S/l)	0 - 20	
acetate	(mg/l)	30 - 350	15
propionate	(mg/l)	30 - 190	60
alkalinity	(meq)	18	
chloride	(mg/l)	50	

Analyses

Sulphide was determined photometrically by the method described by Truper and Schlegel (1964). Elemental sulphur was measured after extraction with acetone according to the method described by Bartlett and Skoog (1954). Sulphate was analyzed by liquid chromatography using a Chrompack HPLC column, packed with Ionospher A-5μ (dim: 10 cm x 3 mm; ID), eluent 0.027 M potassium biphthalate (flow 0.4 ml/min) and a Knauer differential refractometer as detector. The injection quantity was 20 μl. Thiosulphate could also be detected using this method.

Acetate and propionate were determined using a gas chromatograph equipped with a 2 m x 4 mm (i.d.) glass column packed with Supelcoport (100-120 mesh) coated with 10% Fluorad FC 431. The temperature of the column, the injection port and the flame ionization detector were 120, 220 and 240 °C, respectively. Nitrogen saturated with formic acid was used as carrier gas at a flow rate of 50 ml/min.

The oxygen concentration was measured with an O_2-sensor (WTW; DU 600 201 711) and the pH with a pH-electrode (Ingold, 425-60-s7).

Carrier materials

Different Biomass Support Particles (BSPs) were used in the experiments e.g.
- reticulated polyurethane (PUR) foam delivered by Recticel, Kesteren, The Netherlands. The dimensions of the PUR particles were 1.0x1.0x1.0 cm with 30 pores per inch (ppi) and a specific surface of 1375 m^2/m^3 (according to Recticel).
- reticulated polyurethane foam coated with PVC. The dimensions were 1.5x1.5x1.5 cm with only 10 pores per inch and a specific surface of 488 m^2/m^3.
- PVC Rasschig rings with a diameter of 5 cm at a height of 3 cm. The surface of one ring is approximately 180 cm^2.

- Polypropene Hiflow Pall rings (or Raflux rings) with a diameter and height of 9 cm and with a surface of 750 cm^2 per ring.
- Polypropene Hiflow Pall rings with a diameter and height of 2.5 cm and with a surface of 41.5 cm^2 per ring. The small Pall rings were placed in nets, in order to keep them inside the reactor. The diameter of the pores in the net were only 1 mm.
- Polyethene Bio-Net 200 carrier material, with a specific surface of 200 m^2/m^3

Table 4. Amounts of BSP's used in the lab-scale reactor

	number	total surface (m^2)
PUR 30 ppi	2100	2.89
PUR-PVC 10 ppi	640	1.05
Rasschig rings	35	0.63
Pall rings 2.5 cm	100	0.42
Bionet	-	0.68

Reactors

Two reactors were used , a lab-scale 3.0 litre (wet volume) Rotating Biological Contact (RBC) reactor and a 4 m^3 (wet volume) pilot-plant RBC reactor.

The BSPs were kept in a rotating cage. The diameter of the cage in the lab-scale reactor amounted to 13.3 cm, at a length of 30 cm. The pilot plant was divided into three compartments of equal size. In each compartment a cylindrical cage to hold the carrier material was placed. The cages in both reactors were 50% submerged. The lab-scale system was operated at a rotation velocity between 14 and 46 rpm and the pilot-plant reactor was operated at a rotation speed between 1.6 and 5.0 rpm.

The experiments were conducted at a process temperature of approximately 27 °C and the pH in both reactors remained between 7.7 and 8.2. The oxygen concentration in the gas phase of the lab-scale biorotor amounted to 20% (air) at an air flow of 22 liter/minute through the reactor. The oxygen concentration in the gas phase of the pilot plant could be controlled by changing the air flow through the reactor.

RESULTS

The experiments with the lab-scale reactor were conducted in order to assess the feasibility of different kinds of carrier material. Table 4 shows what amount of BSPs were used in the experiments. Table 5 summarizes the results of the experiments, which were conducted at a liquid residence time of 4.5 minutes.

Experiments with the pilot-plant biorotor reactor were conducted in order to optimize the sulphide removal process. Important parameters of the process are the flow rate of the wastewater (sulphide loading rate), the flow rate of the required air (oxygen concentration in the reactor), the rotation speed of the cage, the kind of carrier material and the H$_2$S concentration in the effluent air.

Table 5.   Sulphide removal rate and removal efficiency of different
            BSPs in the lab scale biorotor reactor

BSP	removal rate (mg/l h)	removal rate (mg/m^2 h)	removal efficiency (%)
after 1/1'89 (influent conc 45 mg/l; HRT 4.5 min)			
PUR 30 ppi	565	587	88
PUR–PVC 10 ppi	588	1680	82
Rasschig rings	536	2552	93
Pall rings 2.5 cm	306	2186	79
Bionet	484	2135	94
before 1/1'89 (influent conc 140 mg/l; HRT 13 min)			
PUR 30 ppi	710	737	87
Rasschig Rings	620	2952	96

In the pilot plant so far only the pall rings of 2.5 and 9.0 cm and Bio-Net have
been applied. Figure 2 shows the different removal efficiencies of the reactor
operated with the Pall rings of 2.5 and 9.0 cm and Bio-Net, at different
sulphide loading rates, at an oxygen concentration of the gas phase of 17% and
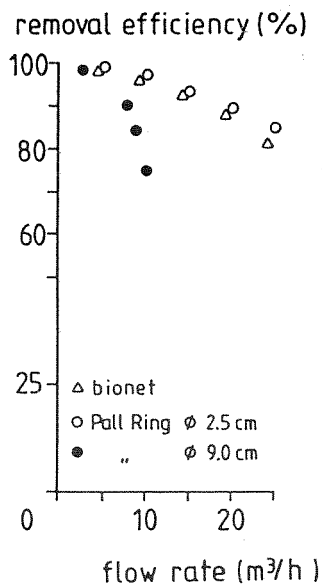a rotation speed of 3.2 rpm.

Figure 2. Comparison of the removal rates of the three different
kinds of carrier material (Pall rings of 2.5 and 9.0 cm and Bio-Net)
tested in the pilot plant. The rotation velocity of the cage was 3.2
rpm and the oxygen gas concentration was 17%.

Figure 2 shows that the smaller Pall rings have a much higher removal effi-
ciency than the bigger Pall rings and about the same as Bio-Net, therefore
more experiments were conducted with the smaller Pall rings. Figure 3 summa-
rizes the results of experiments conducted at different oxygen concentration,
rotation speed and sulphide loading rate, using the smaller Pall Rings. Before
the oxygen concentration and sulphide loading rate were varied, a steady state
was achieved at a flow rate of 12.5 m^3/h and an oxygen concentration (g) of
17%. The changes in oxygen concentration and sulphide loading rate were made
after four liquid residence times. The steady states at rotation velocities of 1.6
and 3.2 rpm are summarized in Table 6.

Table 6. Steady states of the pilot plant biorotor reactor at an oxygen gas phase
se concentration of 17%, at different rotation velocities of the cage.

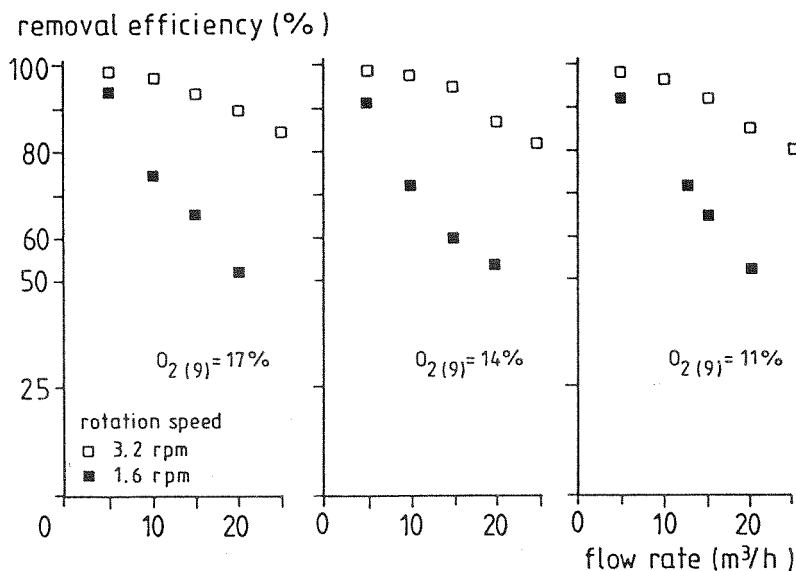| rpm	sulphide (mg/l) effl	acetate (mg/l) infl	acetate (mg/l) effl	propionate (mg/l) infl	propionate (mg/l) effl	SO_4 (mg-S/l) effl	S^0 (mg-S/l) effl
Pall rings 2.5 cm (flow rate of 12.5 m^3/h)							
1.6	17	208	214	170	109	3.4	26
3.2	3	335	334	185	147	9.6	27
Pall rings 9.0 cm (flow rate of 5.0 m^3/h)							
1.6	16	60	69	85	70	2.0	21
3.2	1	69	80	92	62	6.8	30
Bionet (flow rate of 12.5 m^3)							
1.6	15	94	90	77	56	2.0	31
3.2	2	70	60	51	26	5.8	31

Figure 3. Comparison of the removal efficiency at different rotation velocities.
Also the oxygen concentration and the flow rate were varied. The Pall rings of
2.5 cm were used as carrier material.

Another important parameter that will determine the feasibility of the process is the H_2S concentration of the gas effluent. The gas effluent must be treated because of the bad odour of sulphide, therefore the H_2S concentration should be kept low. It is obvious that the H_2S concentration of the effluent gas is dependent on the sulphide concentration in the liquid effluent. Figure 4 shows the H_2S concentration at different sulphide concentrations in the liquid effluent, for both types of carrier material and at different rotation speeds.
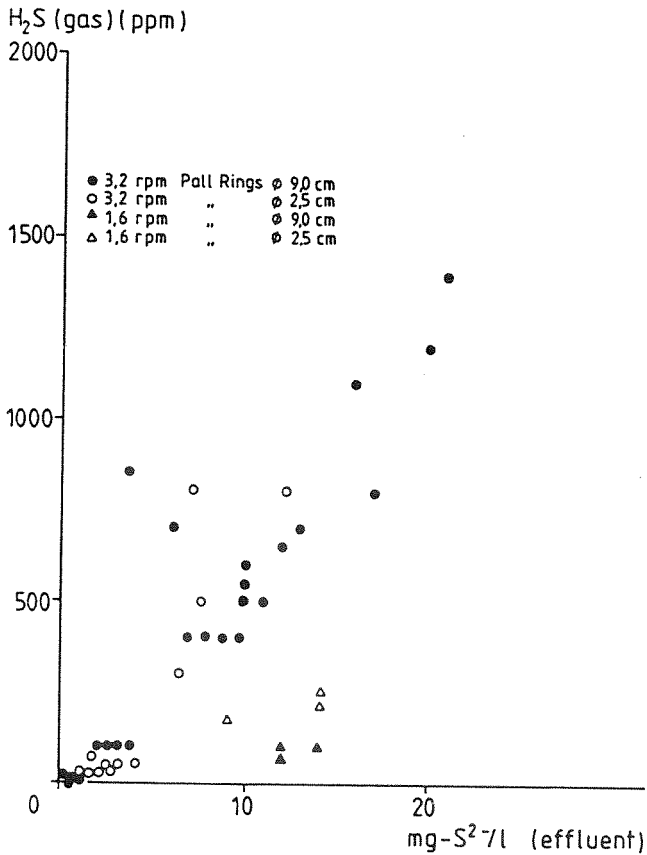

Figure 4. The H_2S gas concentration of the effluent gas of the pilot plant in relation with the effluent sulphide concentration, rotation velocity and kind of carrier material.

DISCUSSION

The results in Table 5 indicate that the activity per m^2 of the PUR foam is low compared to that of the rings. This is probably due to the larger anaerobic space inside the PUR particle. This anaerobic zone amounts to 50% of the total surface of the PUR particles with 30 pores per inch (Buisman et al., 1989b). With only 10 pores per inch less anaerobic space will be present. But the amount of anaerobic space still does not explain the large difference between the activity of the rings and the PUR particles. An additional explanation is the activity of the sulphide-producing bacteria, like Desulfuromonas acetoxidans (sulphur reduction) and Desulfobulbus propionicus (sulphate reduction (Buisman et al., 1989d,e). These bacteria will be able to produce much more sulphide in the large anaerobic space of the PUR particles than in the small anaerobic space in the biofilm on the rings. Therefore it seems obvious that PUR foam is not suitable for sulphide removal in the presence of fatty acids. From Table 5 it also can be inferred that the Rasschig rings achieve the highest removal rate combined with the highest removal efficiency.

The results presented in Figure 2 show that the application of the smaller Pall rings (2.5 cm) and Bionet results in a much higher removal efficiency than the larger Pall rings (9.0 cm). It is obvious that this is caused by the larger specific surface of the smaller Pall rings and Bionet.

Figure 3 shows the effect of the flow rate, the oxygen gas concentration and the rotation velocity. The results in Figure 3 indicate that the rotation speed is a more important factor for sulphide removal than the oxygen gas concentration.

The rotation velocity of the cage also is an important factor determining the H$_2$S concentration in the effluent gas. The results in Figure 4 show that there is hardly any difference between the two kinds of Pall rings. The rotation velocity and the sulphide effluent concentration determine the H$_2$S concentration of the effluent gas. It is important to note that at sulphide effluent concentrations below 3 mg/l the H$_2$S concentration will not exceed 100 ppm at pH levels around 7.5.

CONCLUSIONS

It was found that sulphide concentrations ranging from 30 to 150 mg/l could be removed very efficiently in lab-scale and pilot-scale modified RBC type of reactors at hydraulic retention times as short as 19 minutes.
Since more than 90% of the available sulphide could be converted into elemental sulphur, there is a real potential for sulphur recovery, i.e. from anaerobically treated effluent.

ACKNOWLEDGEMENTS

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