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ANAEROBIC TREATMENT OF TANNERY WASTEWATER WITH SIMULTANEOUS SULPHIDE ELIMINATION

MATTHIAS WIEMANN, HARM SCHENK and WERNER HEGEMANN*Ⓜ
Technische Universität Berlin, Fachgebiet Siedlungswasserwirtschaft, Sekr. KF 7, Str. des 17. Juni 135, D-10623 Berlin, Germany

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Abstract—Sulphide is known as an inhibiting substance in anaerobic microbial processes. The objective of this research was to examine sulphide inhibition in batch and continuous culture experiments. A real wastewater of leather production was used which contained high sulphide and low sulphate concentrations. Thus the observed inhibition resulted from direct toxicity of sulphide on bacteria. Trace element precipitation and substrate competition between sulphate reducing and methane producing bacteria were of negligible influence. In batch experiments gas production was delayed with increased sulphide concentrations. A stripping system was integrated in a laboratory reactor to eliminate sulphide and to improve the efficiency of degradation. In a continuous flow fixed film reactor the concentration of 100 mg l^{-1} undissociated sulphide inhibited the efficiency and degree of degradation. This inhibition was eliminated by a simultaneous sulphide stripping system which reduced the concentration of undissociated sulphide to 30 mg l^{-1}. The efficiency of degradation was improved by 15% at a hydraulic retention time of 1.9 days. © 1998 Elsevier Science Ltd. All rights reserved

Key words—anaerobic wastewater treatment, sulphide toxicity, hydrogen sulphide stripping, tannery wastewater, fixed bed reactor

INTRODUCTION

In a lot of highly loaded organically wastewaters sulphur is a significant component. Sulphur can occur in different compounds, e.g. as organic or inorganic sulphur of various oxidation numbers. In the process of anaerobic wastewater treatment sulphur compounds are usually converted to sulphide due to biological reduction. Sulphide formation leads to problems of odour and corrosion. Sulphide is not only toxic for higher organisms, it is also known as inhibiting substance in anaerobic microbial processes.

Various publications quantify the inhibiting effect due to sulphide in anaerobic wastewater treatment. The results differ in a wide range. The following reasons can be responsible for this.

1. Three inhibiting effects of sulphide or sulphide reduction are known: (1) direct toxicity of sulphide (2) substrate competition between sulphate reducing and methanogenic bacteria and (3) precipitation of trace elements by sulphide. The extent of these three effects depends on the experimental system.
2. The direct toxicity, in particular, correlates exclusively with the undissociated amount of sulphide as hydrogen sulphide (H_2S) (Mudrack and Kunst, 1991). Because the degree of dissociation is substantially depending on the pH-value, this has to be known when sulphide toxicity is quantified.
3. The inhibition depends on the type of substrata (McCartney and Oleskiewicz, 1991) and has different effects on various bacteria groups (Shin *et al.*, 1995).

In this study inhibiting effects of sulphide were investigated using real wastewater from leather production. The effect of a simultaneous sulphide elimination on anaerobic processes was tested. In the complex composited tannery wastewater sulphur was present mainly as sulphide (> 50%) (see Table 1). Sulphate had only a low relevance (10%) as against organic sulphur compounds (40%). This indicates that substrate competition between sulphate reducing and methanogenic bacteria was of minor importance. Deficiency of trace elements could also be excluded for this investigation with tannery wastewater. Thus the resulting sulphide inhibition referred to direct toxicity of hydrogen sulphide.

Sulphide elimination integrated in the anaerobic wastewater treatment process renders possible the removal of both the sulphide contained in raw wastewater and the sulphide produced in the anaerobic process. Thus the inhibition of hydrogen

*Author to whom all correspondence should be addressed. E-mail: siwawi@ itu 402.ut.TU-Berlin.DE

Table 1. wastewater characteristics

Component	Unit	Concentration average	min–max
COD	(mg l^{-1})	6095	3980–7300
DOC	(mg l^{-1})	1870	1590–2070
TOC	(mg l^{-1})	2220	1910–2460
sulphide	(mg l^{-1})	360	250–525
sulphate sulphur	(mg l^{-1})	60	30–130
organic sulphur	(mg l^{-1})	270	—
orthophosphate–phosphorus	(mg l^{-1})	8	—
chloride	(mg l^{-1})	2600	900–6600
NH_4-nitrogen	(mg l^{-1})	385	180–480
depositable materials	(mg l^{-1})	0.65	—

sulphide is eliminated and the efficiency of wastewater purification is improved. Three techniques can be combined with anaerobic processes, such as biological oxidation, precipitation and stripping. *Stripping* can be integrated in the treatment systems without disturbance of the anaerobic process by applying a low volumetric flux of stripping gas. *Biological oxidation* however is an unreliable process which does not always results in sure and complete oxidation to elementary sulphur (Buismann *et al.*, 1990; Lee and Sublette, 1993). The *stripping* process does not create sludge and has no need of supplementary chemicals. *Precipitation* causes named disadvantages (Hellinger and Trommer, 1991). Comparing biological oxidation, precipitation and stripping Verink (1988) found stripping the most suitable technique for a combination of anaerobic wastewater treatment and sulphide removal. It has to be mentioned that stripping demands the purification of the stripping gas in a further treatment. Whether a sulphide elimination is of economical interest depends on the improvement of the anaerobic process and the possible renunciation of a re-treatment of the effluent and the biogas.

In this study the optimization potential for the simultaneous sulphide elimination was estimated. The effect of different sulphide concentrations on the anaerobic process was investigated in batch culture and continuous culture experiments. A sulphide stripping system was integrated in an anaerobic laboratory reactor. The practical application of this treatment concept was tested and an improve of decomposition efficiency was determined.

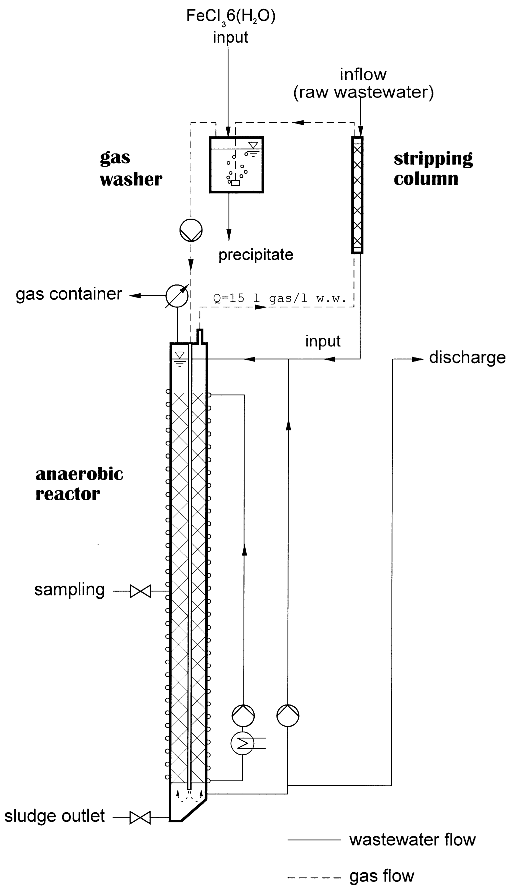

Fig. 1. Experimental plant, reactor 1.

MATERIAL AND METHODS

Wastewater characteristic

In this "Beamhouse"-wastewater study, which includes the first steps of leather tanning, was used. The wastewater is very alkaline and had to be neutralized to a pH-value of 7 by CO_2 before treatment. Further reduction of the pH-value would have been positive for stripping efficiency. Because of the great buffer capacity of the wastewater this was not practicable under laboratory scale conditions. After neutralization the wastewater showed the characteristics listed in Table 1.

Batch culture experiments

The effect of different sulphide concentrations on the anaerobic process was examined in batch culture experiments using a range of 20 to 260 mg l^{-1} sulphide (COD = 4000 mg l^{-1}, SO_4 = 116 mg l^{-1}). Different sulphide concentrations were obtained by mixing untreated and stripped wastewater, in which sulphide was completely removed by stripping with nitrogen, in different ratios. In this way samples of equal composition concerning all other parameters but sulphide were produced. Two hundred and fifty millilitres of these wastewater samples were inoculated with 100 ml excess sludge from a laboratory plant and filled with 150 ml oxygen-free dilution water. The mixture was incubated in 500 ml glass bottles covered with an eudiometer tube following DIN 38 414 S8. Starting at a pH-value of 7 the experiments were run for 54 days at a temperature of 35 ± 1°C. Five different sulphide concentrations were investigated in double experiments.

Table 2. dimensions and characteristics of reactors

	Reactor 1 fixed bed reactor with continuous fluid circulation	Reactor 2 fixed bed reactor
extents		
overall volume	7.85 l	7.85 l
used volume	7.60 l	7.60 l
liquid volume	7.30 l	7.00 l
overall altitude	125 cm	125 cm
inside diameter	9 cm	9 cm
fixed bed		
height	90 cm	100 cm
sort of particles	foamed plastic cubes	plastic raschig rings
dimensions of particles	1.0·1.0·1.0 cm	3.50·3.50·0.25 cm
specific surface area	600 $m^2 \cdot m^{-3}$	150 $m^2 \cdot m^{-3}$
operating temperature	35°C	35°C
pH–value	7.5	7.3
mixing	circulation	none
sulphide elimination	stripping in advanced stripping column and in reactor	none

Continuous culture experiments

In a continuously charged laboratory plant two reactors were run parallel. Reactor 1 was a fixed bed down flow reactor with continuous fluid circulation. Foamed polyurethane cubes were used as fixed bed material. The circulation was carried from the base to the top of the reactor (see Fig. 1). Thus a complete mixing was achieved. A stripping system was integrated in the reactor to remove sulphide continuously. The reactor was supplied with stripping gas at the base. Leaving the fixed bed the gas was conducted to a stripping column. The raw wastewater was transported in opposite directions, first through the stripping column, then into the reactor at its top. The stripping gas was purified in a gas washer with neutralized $FeCl_3 \cdot 6(H_20)$-solution and fed back into the reactor. A strip gas flow of 15-l gas per 1-l wastewater was kept constant during the experiment. Thus the negative influence of stripping on the process, due to foaming and increased shear stress, was constant in operating phases with the same hydraulic retention time. The reactor was temperated at 35°C using a warm water tube wrapped around the reactor jacket.

Operating conditions of the stripping system were varied to adjust different sulphide concentrations in the reactor. Stripping in the reactor and in the additional column resulted in the lowest sulphide concentrations. Stopping the operation of the stripping column resulted in higher sulphide concentration. Without washing the strip gas no sulphide elimination was possible; instead, the highest sulphide concentrations were produced. The reactor was run at each level of sulphide concentration until stationary conditions were reached.

A second reactor without sulphide elimination was run in parallel. This reactor 2 differed in the carrier material and the mixing conditions from reactor 1. During the experiments the hydraulic retention time of reactor 2 varied between 7.3 and 0.8 days. Dimensions and characteristics of the reactors are summarized in Table 2.

Analytic methods

In batch culture experiments the temporal gas production was a main parameter of evaluation. Each working day the produced gas volume was read from the eudiometer tube. In continuous culture experiments the produced biogas volume was measured with a gas meter (Ritter Gasuhr).

The wastewater was analyzed at the beginning and at the end of the batch culture experiments and continuously during the reactor experiments. COD was determined using a photometric cuvette test (Dr. Lange model LCK 314). Samples were acidified and stripped for 5 min with nitrogen to remove disturbing sulphide. TOC and DOC were measured using the TOC-analyser "TOCOR 100" and the CO_2-analyser "UNOR 600" (both Maihak) according to DIN 38409 with Na_2CO_3-solution and $C_8H_5KO_4$-solution as external standards. For DOC-measurement the samples were filtered with 0.45 μm cellulose acetate filters. Volatile fatty acids were analyzed by gas chromatography (Hewlett Packard model HP 5890 A) after filtration with 0.2 μm cellulose acetate filters. For

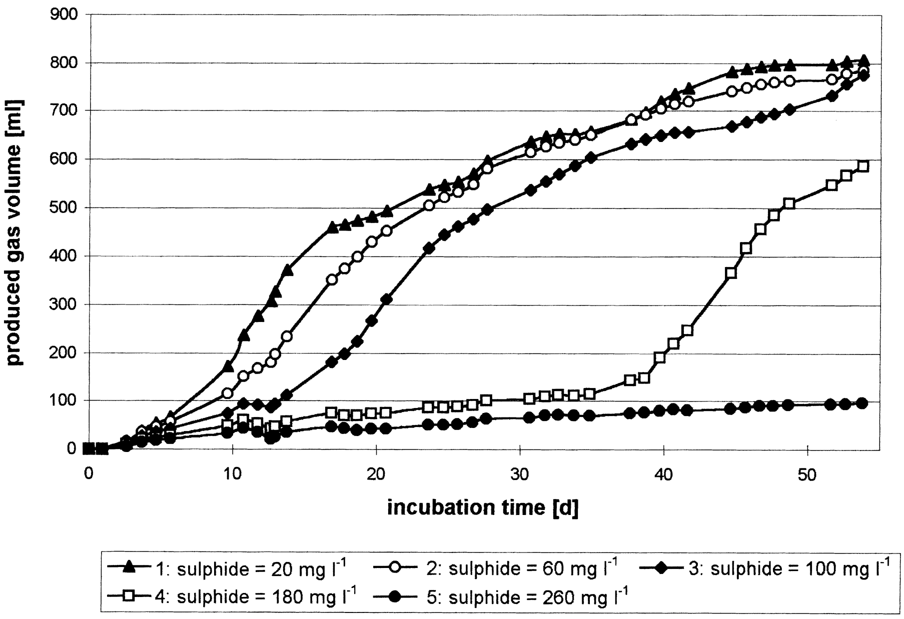

Fig. 2. Temporal development of the produced gas volume in batch experiments with different sulphide concentrations.

calibration an external standard containing acetic, propionic, butyric, isobutyric, isovaleric and valeric acid was used. The resulting concentrations of these acids were converted into COD-values using their specific oxygen demands. Afterwards they were added up to a theoretical COD of volatile fatty acids. For sulphide determination samples were fixed with a saturated solution of zinc acetate and measured with a photometric cuvette test (Dr. Lange model LCK 053). pH-value was measured with a pH-meter (WTW pH 323 SET) to calculate the concentration of undissociated sulphide (dissociation constants $pK_{S1} = 6.93$; $pK_{S2} = 11,96$). Sulphate was determined by ion chromatography (Dionex model DX-100).

RESULTS AND DISCUSSION

Batch culture experiments

Figure 2 shows the temporal development of the produced gas volume during incubation of batch cultures with different sulphide concentrations. The temporal gas production correlated directly with the sulphide concentration in wastewater. Culture 1, with the lowest sulphide concentration of 20 mg l^{-1}, showed a high gas production immediately. The velocity of gas production, which is proportional to substrate degradation velocity, is shown by the gradient of the curve. In culture 1 it reached its maximum on day 12 and afterwards slowed down. The total gas production was accumulated to approximately 800 ml after 54 days of incubation. With increasing sulphide concentration the cultures produced gas in temporal delay. A sulphide concentration of upto 100 mg l^{-1} produced 800 ml of gas was reached within 54 days. Culture 5, with the highest sulphide concentration of 260 mg l^{-1}, did not show any significant increase of gas production.

Figure 3 summarizes the delay of maximum gas production due to increasing sulphide concentrations. Furthermore the level of maximum gas production and the concentration of volatile fatty acids at the end of the experiment are shown. During batch experiments pH-values and sulphide concentrations were changing due to microbial processes, reduction of organic sulphur compounds and sulphate to sulphide and sulphide loss by biogas production. Because of that all data are correlated to the sulphide concentration at the start of incubation. Figure 3 indicates that methane production, in particular, is the step inhibited by hydrogen sulphide. The concentration of volatile fatty acids after 54 days of incubation increased significantly with the sulphide content. In culture 5 almost all the residual COD was acidified at the end of the experiment. This resulted in a pH-value of 6.8 at the end of incubation compared with a pH-value of 7.2 in all other cultures. The theoretical COD of volatile fatty acids was 85% of the total residual COD which was 3900 mg l^{-1}. Acetic acid had the predominant portion of 60% of the total residual COD. An extensive acidification was possible even with high sulphide concentrations whereas methane production was strongly inhibited. This explains why cultures with higher sulphide concentration showed an approximately equal maximum gas production velocity in spite of a delayed time of maximum gas production. Cultures with high sulphide concentration were acidified at the beginning

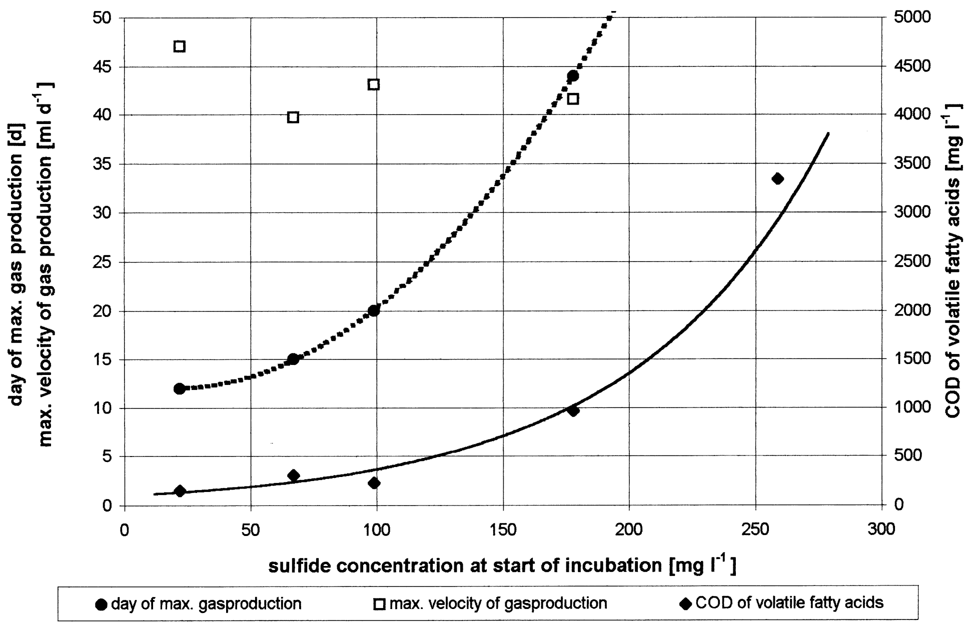

Fig. 3. Day and velocity of maximum gas production and COD of volatile fatty acids correlated with sulphide.

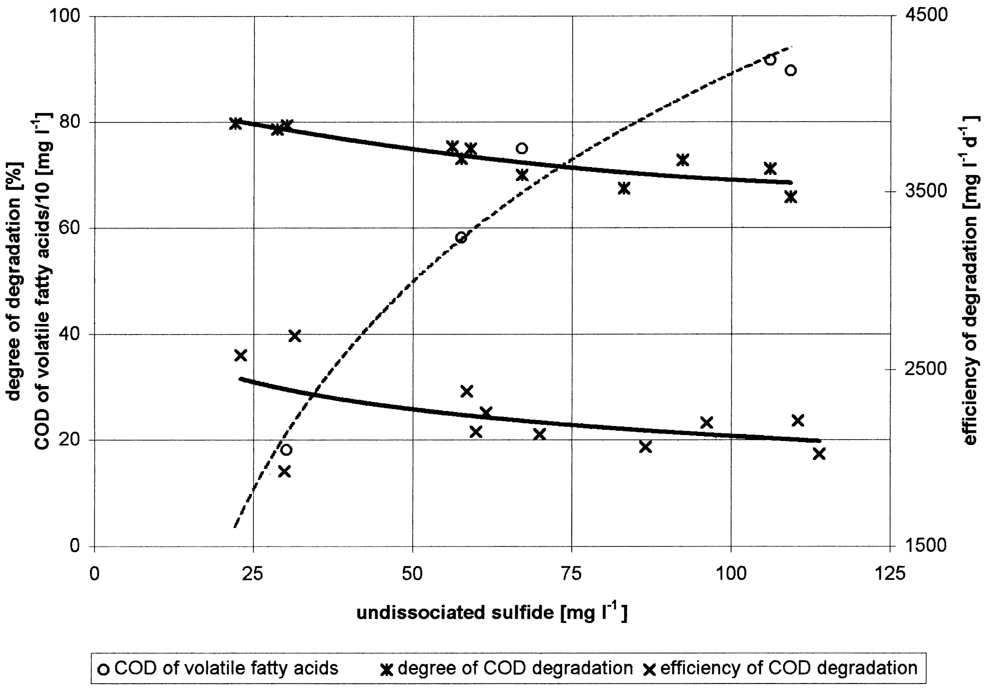

Fig. 4. Reactor 1—degree and efficiency of degradation and COD of fatty acids correlated with undissociated sulphide.

of incubation. This resulted in a very low gas production. Methane production was inhibited by sulphide. With increasing concentration of volatile fatty acids the substrate supply for methanogenic bacteria was improved and sulphide inhibition was largely compensated. In culture 5 a compensation of sulphide inhibition was not possible although acidification happened almost completely.

No inhibition of sulphate reduction due to increasing sulphide concentrations was found in the batch culture experiments. Even culture 5, with no significant gas production, realized 90% sulphate reduction, the same degree of degradation as in all other cultures.

Continuous culture experiments

In continuous culture experiments the effect of a simultaneous sulphide elimination was investigated in reactor 1. The suspension of sulphide inhibition was quantified. Figure 4 shows a correlation of the degree and efficiency of degradation with the hydrogen sulphide concentration. Only results with constant operation parameters like hydraulic retention time, strip gas volume or pH-value are shown in Fig. 4. Obviously an increasing degree and efficiency of degradation due to decreasing sulphide concentrations was found. Sulphide also had a significant effect on volatile fatty acid concentration in the effluent. At a concentration of 100 mg l^{-1} undissociated sulphide about 50% of the COD in the effluent was acidified. In contrast to the batch culture experiments in the continuously operated reactor 1 not only acetic acid had accumulated, but especially isobutyric and valeric acid were detected in increased concentrations. Under continuous conditions the inhibition of acetic acid producing bacteria and methanogenic bacteria decreased the efficiency of degradation.

The integrated sulphide stripping system made it possible to stop the inhibiting effect of sulphide in anaerobic wastewater treatment process. By reducing the content of hydrogen sulphide from 100 mg l^{-1} to 25 mg l^{-1} the degree of degradation was increased from 70 to 80% COD. It has to be mentioned that a degradation of 80 to 85% of COD was the maximum, which could be reached in all experiments. The residual COD of about 15 to 20% was not anaerobically degradable even at long retention times in continuous culture or at long incubation times in batch culture experiments. It has to be mentioned that for calculations of the stripping efficiency two effects have to be taken into consideration. On the one hand stripping is supported by biogas production; on the other, organic sulphur and sulphate, which are reduced in the anaerobic process, have to be eliminated by stripping as well.

The benefit of a simultaneous sulphide elimination in anaerobic wastewater treatment can be evaluated comparing the results of reactor 1 with data from literature and results from reactor 2, which was operated without a sulphide elimination.

Table 3. Anaerobic treatment of tannery wastewater

Author	Substrate	Treatment	hydraulic retention time (d)	COD inflow ($mg\ l^{-1}$)	COD-volumetric load ($mg\ l^{-1}\ d^{-1}$)	COD-degree of degradation (%)	COD-efficiency of degradation ($mg\ l^{-1}\ d^{-1}$)
1 Genschow and Hegemann, 1993	wastewater A	1. step: stirred reactor	4.2	8500	2030	76.7	1560
	wastewater B	2. step: fixed film	4.6	5250	1140	66.1	754
2 Carozzi *et al.*, 1990	total wastewater	fixed bed	2.44	4440	1820	66.2	1205
		contact process	2.45	4160	1700	68.6	1166
	laboratory scale	2-step	2.47	4100	1660	73.9	1227
		contact process	4.86	5990	1230	81.5	1002
		contact process	5.02	4860	990	66.4	657
	total wastewater	contact process	3.0	6535	1970	56.6	1115
			4.0	8080	1990	67.3	1340
	semi technical scale	fixed bed	3.0	6535	2185	71.8	1570
		reactor 1	4.0	8080	2030	71.0	1441
		fixed bed	3.0	6535	2185	70.2	1534
		reactor 2	4.0	8080	2030	72.9	1480
3 Young *et al.*, 1980	beamhouse	fixed bed reactor	1.0	3000	3000	51*	1530
		fixed bed reactor with circulation	1.0	3000	3000	39	1170
4 Tunik *et al.*, 1981	beamhouse	contact process	2.5	2000 to 15 000	1270 to 3890	62	787 to 1770†
5 Bai and Sivanthuanu, 1988	total wastewater	stirred reactor	15.0	4163	278	36.4	101
			25.0	4074	163	59.6	10
			30.0	4074	136	60.3	82
own results	beamhouse	reactor 1 (30 $mg\ l^{-1}\ H_2S$)	1.9	6100		80	2450
		reactor 1 (100 $mg\ l^{-1}\ H_2S$)	1.9	6100		70	2080
		reactor 2 (140 $mg\ l^{-1}\ H_2S$)	2.1	6100		58	1650

*soluble COD.
†original data corrected due to inconsistent results.

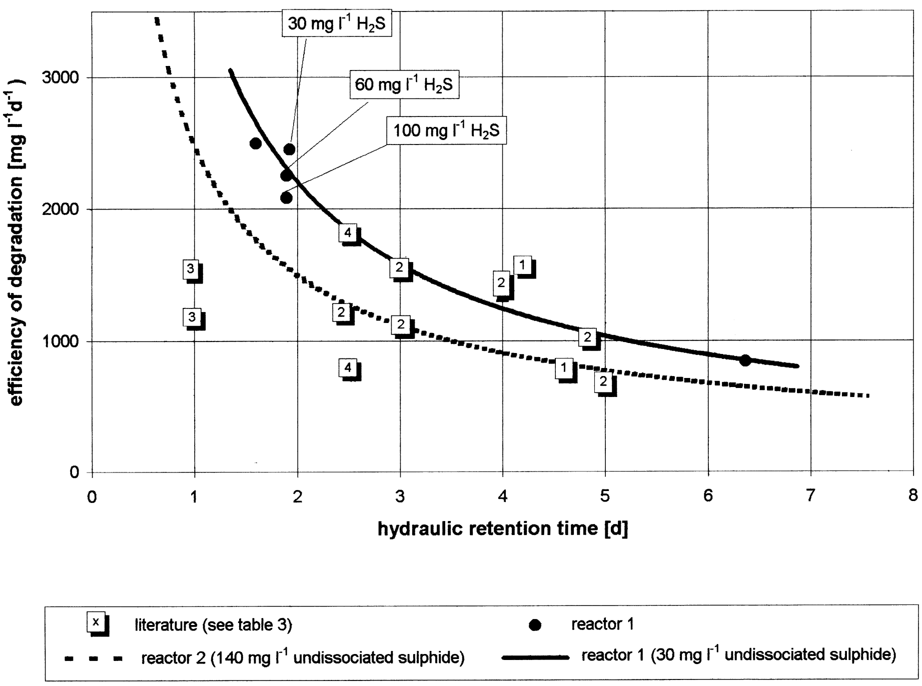

Fig. 5. Degradation efficiency of reactors 1 and 2 compared with literature.

Figure 5 shows the efficiency of degradation of these reactors compared with other studies on anaerobic treatment of tannery wastewater (see Table 3).

Reactor 2 had an average concentration of 140 mg l^{-1} hydrogen sulphide. Figure 5 shows the increase of the degradation efficiency with reduced retention times. At the same time the degree of degradation was decreasing. Compared to other studies reactor 2 reached an ordinary efficiency of degradation especially at low retention times.

The integrated sulphide stripping system in reactor 1 reduced the concentration of hydrogen sulphide to 30 mg l^{-1}. This clearly improved the efficiency of degradation compared to reactor 2. The sulphide elimination made it possible to establish both a high degree and a high efficiency of degradation at low retention times. In no other studies were degradation efficiencies, as high as measured for reactor 1, reached for low retention times.

Apart from sulphide elimination the reactors differed in other ways. Fixed bed material of reactor 1 had a greater specific surface area. The reactor was totally mixed so that an improved substrata transport can be supposed. The results of reactor 1 with higher sulphide concentrations, already described in Fig. 4, are also plotted in Fig. 5 at the average of three different phases of the experiment. It shows the increasing efficiency of degradation of reactor 1 by the reduction of undissociated sulphide from 100 mg l^{-1} to 60 mg l^{-1} and 30 mg l^{-1}, respectively.

CONCLUSIONS

In this study the inhibiting effect of sulphide on the anaerobic treatment of a complex wastewater from leather production was investigated. The inhibition resulted from direct toxicity of sulphide on bacteria. Trace element precipitation and substrata competition between sulphate reducing and methane producing bacteria were of negligible influence. Sulphide inhibition was examined in batch and continuous culture experiments. A stripping system was integrated in a laboratory reactor to eliminate sulphide and to improve the efficiency of degradation. Following results can be stated.

1. The anaerobic treatment of beamhouse wastewater was inhibited by sulphide.
2. In batch culture experiments gas production was delayed with increased sulphide concentrations.
3. In a continuously operated reactor a concentration of 100 mg l^{-1} hydrogen sulphide inhibited the efficiency of degradation of at least 15%.
4. The sulphide inhibition effected mainly the methanogenic bacteria, at a lower level also the acetic acid producing bacteria. For acidifying and sulphate reducing bacteria no inhibition was detectable.
5. An integrated stripping system made it possible to eliminate sulphide and to improve the anaerobic treatment process. The degradation efficiency of a reactor run at a hydraulic retention time of 1.9 days was improved by 15% because of hydrogen sulphide concentration decreasing from 100 mg l^{-1} to 30 mg l^{-1}.

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