

Application of anaerobic biological treatment for sulphate removal in viscose industry wastewater

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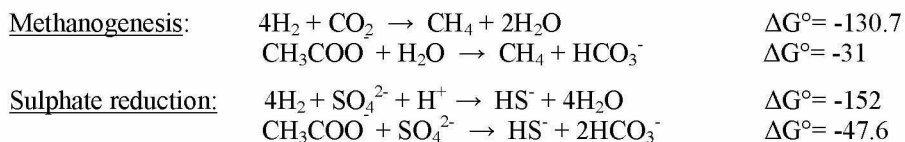
Abstract Long term lab-scale and bench-scale experiments were performed to investigate the feasibility of the anaerobic process to treat wastewater from a pulp and viscose fibre industry. Anaerobic wastewater treatment enables an advantageous combination of COD, sulphate and zinc removal from viscose wastewater. The aim of the investigations was to evaluate the influence of the free sulphide concentration on COD and sulphate removal efficiency and on the substrate competition between sulphate reducing and methanogenic bacteria. Since the wastewater did not contain enough COD for complete sulphate removal it was of main interest to determine favourable process conditions to steer the substrate competition in favour of sulphate reduction. Further experiments in bench-scale permitted to evaluate applicable COD-loading rates and gain fundamental information about process stability and optimization for large-scale implementation. The present work will deal with the most relevant experimental results achieved and with important technological aspects of anaerobic treatment of viscose wastewater.

Keywords anaerobic wastewater treatment, hydrogen sulphide inhibition, sulphate reduction, viscose wastewater

Introduction

The wastewater generated by the viscose production process is generally characterised by a high concentration of sulphate and zinc and medium strength of organic carbonaceous matter. Sulphate does not represent a direct threat for the aquatic environment because of its low toxicity and reactivity. For this reason sulphate emissions in wastewater generally do not undergo strict regulations. In Austria, however, sulphate concentration in the receiving water bodies is regulated by limit values (AImVF, 1994). In this way direct inhibiting effects of high sulphate concentrations on aquatic biological processes as well as indirect problems caused by the formation of hydrogen sulphide can be prevented. Under anaerobic conditions in the natural environment sulphate reducing bacteria (SRB) use sulphate as terminal electron acceptor for the degradation of organic matter. H₂S which results from dissimilatory sulphate reduction is toxic, malodorous, corrosive and can cause severe damages e.g. to concrete structures.

During anaerobic treatment of sulphate rich wastewater SRB compete with methanogenic bacteria (MB) for the available organic substrate. MB and SRB both utilized as substrate hydrogen and acetate, the main intermediate products of the anaerobic degradation of organic matter:



ΔG° : Free enthalpy in kJ/mol by 25°C, 1 atm und pH 7 (calculated according to Thauer *et al.*, 1977).

Substrate competition will play a significant role during anaerobic treatment of viscose wastewater, since in this case the COD source for sulphate reduction is limited. Considering the thermodynamic (e.g. free enthalpy ΔG°) and kinetic (e.g. specific growth rate μ_{max} , substrate affinity k_s) properties of SRB it can be expected that sulphate reduction will outcompete methanogenic consortia. Several studies on anaerobic reactors at different scale have already confirmed the predominance of SRB on substrates like hydrogen, propionate and butyrate with pure or mixed culture (e.g. Stams *et al.*, 2004; Colleran *et al.*, 1995). On the contrary, substrate competition seems to be very intensive during the mesophilic degradation of acetate (Omil *et al.*, 1998; Visser *et al.*, 1993) and methanol (Weijma, 2000; Greben *et al.*, 2000). In addition to growth kinetics, also many other factors like the type of seed sludge, H₂S inhibition,

pH-value and temperature were found to influence the outcome of the competition between SRB and MB (Hulshoff Pol *et al.*, 1998).

Anaerobic treatment of viscose wastewater has already been studied in previous research works in lab-scale, thus with emphasis on zinc removal (Kroiss *et al.*, 1985). The H₂S produced by sulphate reduction precipitates zinc ions as zinc sulphide:



As zinc sulphide has a lower solubility than zinc hydroxide, sulphate reduction would be advantageous in regards to effluent concentrations as compared to the frequent applied zinc precipitation with lime. Furthermore, zinc precipitation as zinc sulphide opens new challenges for the reuse of zinc in the viscose production.

Thus anaerobic treatment of viscose wastewater allows an advantageous combination of COD, sulphate and zinc removal. Due to viscose wastewater composition H₂S production during anaerobic treatment aiming for sulphate removal will exceed the H₂S needed for Zn precipitation. For this reason a further treatment step for H₂S elimination has to be foreseen for effective sulphate removal. Excess H₂S has to be removed from the anaerobic reactor on one hand to avoid its re-oxidation to sulphate during aerobic post-treatment, on the other hand to reduce its inhibiting effect on SRB. H₂S inhibition is detrimental for process efficiency and can lead to process failure (Kroiss & Plahl-Wabnegg, 1983). Considering that H₂S will be distributed in the anaerobic reactor over the gas phase and the liquid phase according to the Henry-Dalton's law:

$$\text{H}_2\text{S}_{\text{liq.}} = K_{\text{H}} \cdot \text{H}_2\text{S}_{\text{gas}}$$

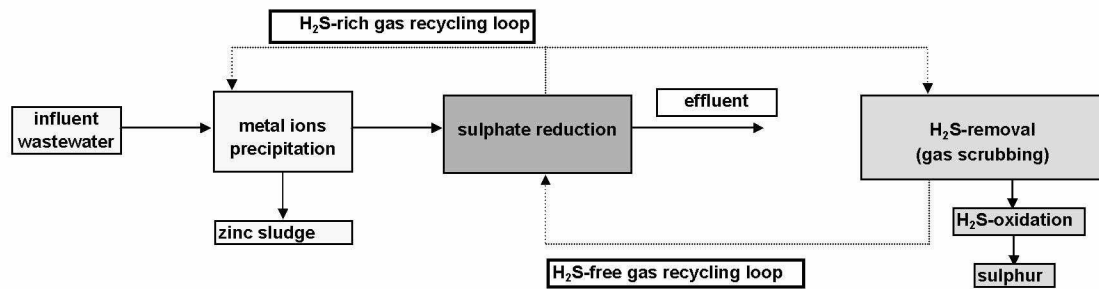
H₂S_{liq.}: H₂S concentration in the liquid phase (mol/m³)

H₂S_{gas.}: H₂S partial pressure in the gas phase (bar)

K_H: Henry's constant, depending on temperature (mol/m³.bar)

H₂S removal can proceed either in the gas or in the liquid stream (Figures 1a and 1b). For this purpose several technologies based on chemical/physical or biological H₂S removal processes (Claus process, biological sulphide oxidation, etc.) have already been applied in large scale (Janssen *et al.*, 2000). H₂S is recovered in the most cases as elemental sulphur and according to the purity obtained it can be reused in different applications (e.g. fertiliser industry, sulphuric acid production).

a) H₂S and heavy metal ions removal in the gas phase



b) H₂S and heavy metal ions removal in the water phase

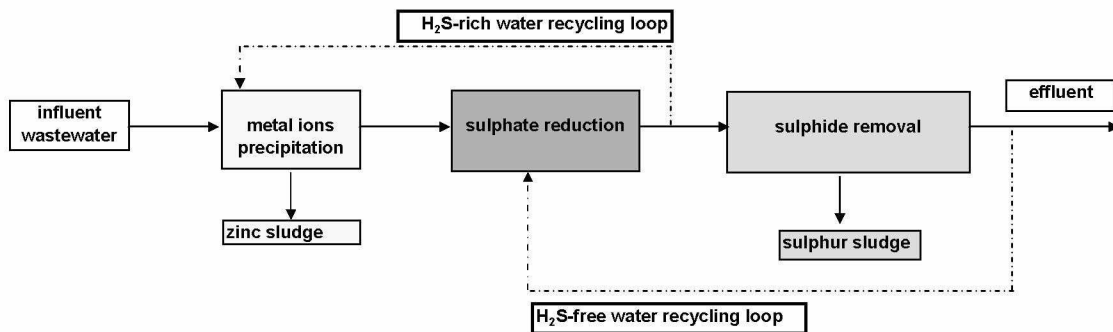


Figure 1. Two examples of process configurations integrating sulphate, COD and heavy metals removal in industrial wastewaters (Lens *et al.*, 2000).

In the liquid phase, depending on the pH-value, H_2S_{liq} will be present in the unionised (free) form H_2S_{free} and as ion HS^- and S^{2-} (Helgeson, 1967):



In the usual pH-range applied during anaerobic treatment the concentration of ions S^{2-} can be neglected. According to the current knowledge H_2S inhibition is related to H_2S_{free} concentration, as only unionised H_2S -molecules can pass the cell membrane by diffusion (Speece, 1983). H_2S inhibition is therefore strongly dependent on pH-value, as it governs the dissociation equilibrium.

In the present study long term lab-scale and bench-scale experiments were conducted to investigate the feasibility of the anaerobic treatment process of wastewater from a pulp and viscose fibre manufacture. In particular, the aim of the investigations was to gain fundamental information about process stability, H_2S inhibition and competition between SRB and MB on the available substrate, leading to the optimization of the operational conditions for large-scale implementation.

Methods

Lab-scale experiments

Three mesophilic up flow sludge bed lab-scale reactors (4 litres volume) were operated in parallel over a period of four years treating wastewater from a viscose fibre industry. A second wastewater stream from pulp production was used as supplemental COD source. The pH-value in the influent was increased to 8-8.5 using an alkaline rich wastewater stream, also from the viscose production. COD sources in the wastewater consisted mainly of acetic acid (20-30% of COD_{tot}), methanol (10-15% of COD_{tot}), hemicellulose and lignocellulosic compounds. As the S/COD-ratio in the wastewater shows (table 1), COD availability was not sufficient for a complete reduction of sulphate (stoichiometrical value: 0.5). Ammonium and phosphate were added to prevent nutrient limitation.

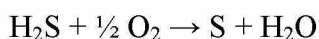
Table 1 Influent wastewater specifications

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
COD	4,500-5,500	Sulphate (as S)	3,000-3,500
TOC	1,600-1,900	S/COD	0.6-0.7
COD/TOC	2.8-2.9	Zinc	150-250

Anaerobically digested sewage sludge from a municipal wastewater treatment plant was used as inoculum. Process temperature was kept at 38°C. Two reactors (1 and 2) were additionally equipped with a gas scrubbing system ($CuSO_4$), in order to reduce the H_2S concentration in the gas phase respectively to 1 and 5 vol%. One part of the desulphurised gas was reused in the reactor as stripping medium. A third reactor (3) was operated without removal of H_2S resulting in concentrations of 10 to 15 vol%. The COD loading per unit reactor volume ($B_{v,COD}$) was increased step-wise from 0.75 to 2 kgCOD/m³.d during the experimental period. In addition one reactor was exposed to higher $B_{v,COD}$ up to 5.5 kg COD/m³.d. COD loading per unit of volatile suspended solids ($B_{x,COD}$) varied between 0.2 and 2.8 kg COD/kgVSS.d.

Bench-scale experiments

By bench-scale experiments on site of the factory with online wastewater supply a different process configuration was applied (Figure 2). A mesophilic (36°C) anaerobic continuously stirred tank reactor (CSTR) with external settling tank was coupled with a micro-aerophilic stage for biological sulphide removal. Biological sulphide oxidation is based on the conversion of sulphide to elemental sulphur by the colourless sulphur bacteria (e.g. genera *Thiobacillus*):



Sulphide complete oxidation to sulphate can be minimized by imposing proper operating conditions, such as oxygen supply and sulphide loading rate (Buisman *et al.*, 1990). One part of the H_2S -free effluent water stream was recycled to the anaerobic reactor to reduce H_2S concentration (2 to 4 vol%). Zinc in influent wastewater was removed as zinc sulphide before entering the CSTR using a part of the effluent of the anaerobic settler. The new process configuration for full scale application was developed together

with Paques B.V. (www.paques.nl). Influent wastewater composition was the same as for the lab scale experiments. $B_{v,COD}$ varied between 2 and 5.5 kgCOD/m³.d, $B_{x,COD}$ between 0.2 and 0.5 kgCOD/kgVSS.d.

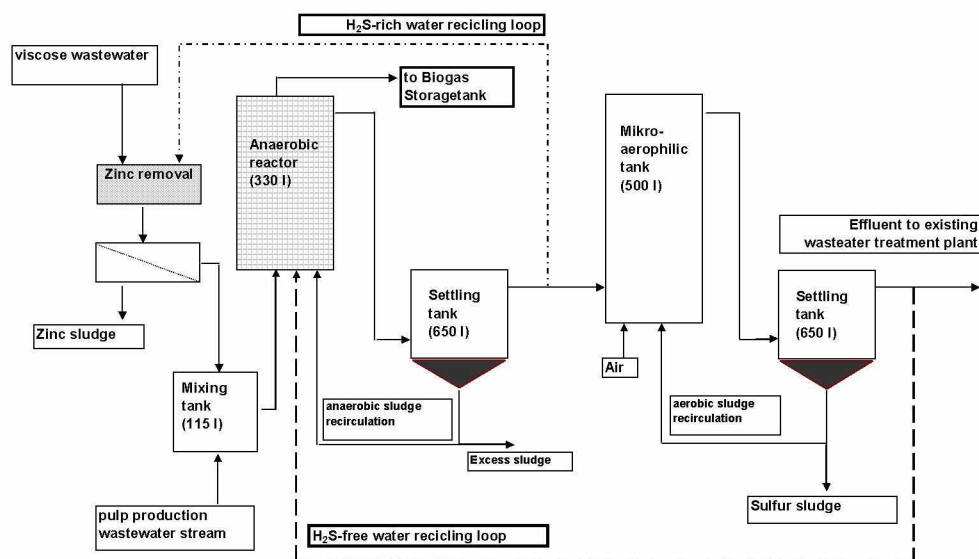


Figure 2 Flow sheet of the bench-scale treatment plant

Analytical Methods

All analyses were carried out according to German Standard Methods for water, wastewater and sludge analysis (DIN). Effluent samples were filtered through paper filters (white ribbon) and stored at 4°C until analysis. Samples for total sulphide (H_2S , HS^- and S^{2-}) were collected with pipettes directly from the reactors and immediately displaced in the reagent solution (Methylene-blue method). Concentration of H_2S and carbon dioxide (CO_2) in the biogas was determined using short-term test tubes (Dräger). During bench-scale experiments gas composition was analysed additionally by gas chromatography.

Results and Discussion

COD removal efficiency and sulphide inhibition

Figure 3 shows the COD removal efficiency of the three lab-scale reactors calculated using mass balances for experimental periods with steady state conditions. COD and sulphate mass balances were applied to check the reliability of the analytical results. COD removal (%) was referred to the corresponding $B_{x,COD}$ in order to make results comparable. In this regards it has to be noted that also the applicability of process parameter related to VSS is in general restricted by the unknown amount of active biomass in the reactor. It can vary consistently under the different H_2S concentrations applied.

During the lab-scale experiments the anaerobic process was stable at H_2S concentrations in the gas phase ≤ 1 vol.% (30 mg H_2S_{free}/l in the liquid phase) and reached a maximum removal efficiency of 70% at $B_{x,COD}$ of 0.4 kgCOD/kgVSS.d. About 80% of the residual COD in the effluent consisted of acetic acid (500-700 mg CH_3COOH/l). The pH value was about 7.2. COD removal efficiency decreased with increasing loading rate as well as with higher H_2S concentrations (Figure 3). Inhibition of COD removal showed a good correlation with the concentration of the unionized H_2S , which is in equilibrium with the H_2S concentration in the gas phase. At H_2S concentrations higher than 3% (80 mg H_2S_{free}/l) the process was characterized by an increasing intrinsic instability in the form of accumulation of acetic acid (1,000-1,500 mg CH_3COOH/l). As a consequence, the pH-value in the process decreased below 7, thus increasing the inhibiting effect of H_2S and of acetic acid.

SRB and MB present in the seed sludge were similarly inhibited by H_2S concentrations between 3 and 10 vol.% (see next paragraph, figure 4a). Acetotrophic micro-organisms turned out to be strongly affected by the inhibition. The higher sensitiveness of acetate degradation compared e.g. to hydrogen uptake has been already reported by previous studies (O'Flaherty *et al.*, 1998) and can be related to the lower specific growth rate of acetotrophic micro-organisms (Gujer & Zehnder, 1983). 50%-inhibition of the COD removal was reached at a H_2S concentration in the gas phase of about 9 vol.% (230 mg H_2S_{free}/l),

which agrees well with values for mixed cultures and flocculent sludge reported by O'Flaherty & Collieran (2000). According to Parkin & Speece (1982) process inhibition in anaerobic reactors can be counterbalanced by an increase of sludge age. This was confirmed during the further experiments in bench-scale (Parravicini, 2005).

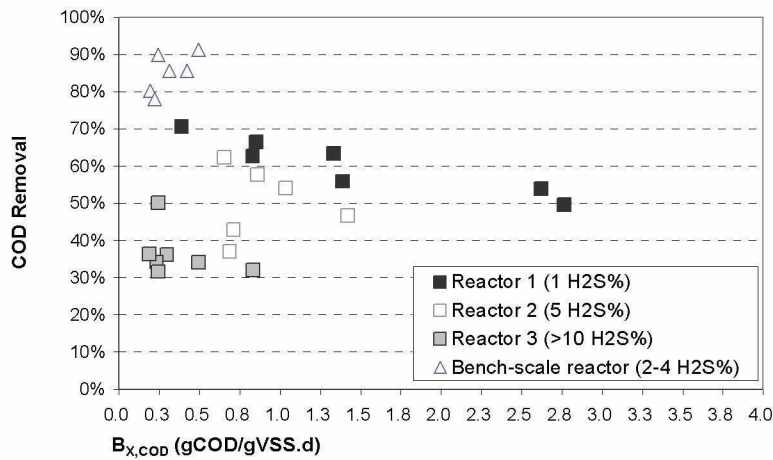


Figure 3 COD removal (%) in function of the influent $B_{x,COD}$ for the lab- and bench-scale experiments

During the bench-scale experiments process efficiency could be increased through the daily dosage of thickened activated excess sludge (TAS) of the annexed industrial wastewater treatment plant (dosage: $0.3 \text{ kgCOD}_{\text{sludge}}/\text{m}^3.\text{d}$). TAS acted as COD and trace elements source, seed sludge and flocculation agent, thus improving sludge retention in the system. COD removal at $B_{x,COD}$ between 0.3 to 0.5 $\text{kgCOD}/\text{kgVSS}.\text{d}$ and H_2S concentrations between 2 and 4 vol.% averaged 85%. A complete acetate conversion was achieved under these conditions. About 65% of the VSS in TAS were anaerobically degraded. The result agrees with the usual VSS removal during anaerobic digestion of sewage sludge.

B_v in the start-up phase could be gradually raised from 2 to 5.5 $\text{kgCOD}/\text{m}^3.\text{d}$ by daily increases of 2.4% and 1.3%, respectively with or without TAS dosage. The observed growth rate with TAS dosage was therefore slightly higher than the values observed in similar anaerobic reactors (Kroiss & Svardal, 1988).

Substrate competition between SRB and MB

Competition between SRB and MB on the available COD was evaluated using the ratio between reduced sulphate (as S) and removed COD ($S_{\eta}/\text{COD}_{\eta}$). Substrate competition was intensive in a H_2S range between 1 and 10 vol%. In this concentration interval even after four years of operation MB were still responsible for the reduction of 30% of the removed COD ($S_{\eta}/\text{CSB}_{\eta}=0.35$) (Figure 4a and 4b).

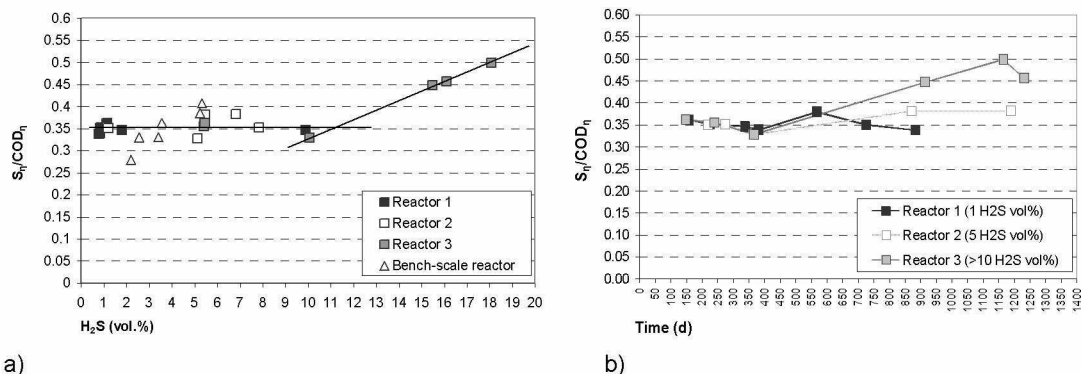


Figure 4 $S_{\eta}/\text{CSB}_{\eta}$ ratio calculated out of mass balances for the three lab scale reactors for different experimental periods in function of the H_2S concentration in the gas phase a) and of the time b).

A good correlation was found between the methane production and the methanol fraction in the influent (Parravicini, 2005). This confirms experimental results of previous studies on mesophilic degradation of methanol in sulfidogenic anaerobic reactors (Weijma, 2000). MB could not adapt to higher H_2S concentrations. During the lab-scale experiments at $\text{H}_2\text{S} \geq 10 \text{ vol.}\%$ complete sulfidogenic conditions

could be established after three years of operation (Figure 4b). The S_{η}/CSB_{η} ratio slowly rose to 0.45-0.5. However under these extreme conditions sulphate removal efficiency and stability was strongly affected by H_2S inhibition.

50% of the influent sulphate load was reduced under optimised process conditions (bench-scale experiments). For higher removal efficiency supplemental COD source is required. Among the substrates tested as external COD sources, ethanol and sucrose were found to be appropriate for sulphate reduction. The suitability of ethanol and sucrose as substrate for SRB has been already reported by previous studies (e.g. Greben et al., 2000). Municipal anaerobically digested sewage sludge showed to be a suitable inoculum for sulphate reduction in lab-scale as well as in bench-scale experiments. Sulphate reduction accounted already after two weeks operation for 50% of the COD removal.

Impacts of anaerobic sulphate removal at the existing activated sludge treatment plant

Since 1987 the wastewater of the pulp and viscose fibre industry has been treated biologically in the industrial wastewater treatment plant on site, based on a two stage activated sludge process. The specific effluent of the pulp and viscose fibre production is 96 m³ per ton of produced viscose. The specific COD load accounts for 108 kg/ton viscose. Zinc is removed from the wastewater as zinc hydroxide with lime dosage. Emitted sulphate load is reduced below regulation limits by dosing lime for gypsum precipitation.

Due to an increase of the pulp and viscose fibre production capacity, the manufacture had to face the problem of additional sulphate, COD and zinc loads in the wastewater. After several years of investigations in lab-scale and bench-scale, finally anaerobic biological treatment of viscose wastewater for sulphate removal was selected for a large-scale installation. January 2004 the large-scale treatment plant was ready for start-up. The selected process configuration consists of a combination of UASB-reactors followed by a micro-aerophilic reactor for biological sulphide oxidation (Paques B.V.).

The introduction of the new plant for sulphate removal in the existing wastewater treatment plant has following main impacts considering the whole operational costs of the plant:

- The degradation of the additional COD load by SRB prevents the existing activated sludge plant from overloading. An enlargement of the plant is therefore no longer necessary. Furthermore, less excess sludge is produced during anaerobic wastewater treatment, due to the lower yield of anaerobic micro-organisms. The removal of zinc as zinc sulphide reduces significantly the amount of inorganic sludge to be disposed. However, if sulphur sludge withdrawn in the aerophilic stage is also considered, overall sludge reduction is less significant. Possibilities for reusing the sulphur sludge in future would allow for a reduction in sludge to be disposed of.

- The removal of COD under anaerobic conditions allows energy savings by the aeration in the activated sludge tanks. The advantage is however consistently lower if the additional operational costs of the new plant are considered (e.g. heating, pumping, etc.). The cost/benefit balance would get more efficient if zinc was reused during the viscose production. Recycling sulphur for sulphuric acid production is currently not profitable due to low prices of the raw stock.

Technological aspects of anaerobic biological sulphate removal in viscose wastewater

There are some particular aspects that should be considered while designing technologies for anaerobic treatment of viscose wastewater:

- According to the experimental results inhibition of SRB by H_2S can be counterbalanced to some extent by an increase of sludge age, as dictated by the well known relationship between bacterial growth rate, decay and sulphate effluent concentration. This aspect should be taken into account while choosing the configuration of the anaerobic reactor (Parkin & Speece, 1982). Besides an adequate large reactor volume also suitable sludge retention efficiency has to be ensured. For the same reason, precipitation of zinc sulphide in a pre-treatment stage prior to the anaerobic reactor should be preferred. The increased amount of inorganic sludge in the anaerobic reactor can result in a drastic reduction of the sludge age due to the necessary higher surplus sludge withdrawn (Särner, 1986).

- Several literature sources report experiences in lab-scale as well as in bench-scale with mesophilic as well as with thermophilic anaerobic reactors for sulphate removal. The choice of the process temperature mainly depends on wastewater influent temperature and specifications. A mesophilic process is preferable when content of calcium ions in the wastewater is high, due to e.g. gypsum pre-precipitation treatment. Anaerobic thermophilic processes are known to be more sensible to temperature changes (Bischofsberger et al., 2005). This would also increase the numbers of parameters needed to be controlled for stable process conditions. Additionally, corrosion becomes a more acute problem at higher temperatures.

- Because of the much higher solubility of H_2S and CO_2 in water compared to methane less gas is set free for mixing during sulphate reduction compared to fully methanogenic reactors. This can lead to decreased substrate mass transfer efficiency and therefore needs to be considered by selecting proper

reactor technology (Lens *et al.*, 2000). In most cases the required mixing has to be ensured through supplemental mechanical devices (e.g. recirculation loop, mixer, gas injection). Values for specific energy density between 2 and 6 Watt/m³ reactor volume are considered to be sufficient for a good mixing in anaerobic reactors (Bischofsberger *et al.*, 2005).

-Experimental results showed that for stable process operation H₂S concentration in the gas phase in the anaerobic reactor must be kept below 3 vol. %. H₂S removal can proceed either a) in the gas phase or b) in the liquid phase (Figure 1a and 1b).

a) The first option enables the production of higher quality sulphur in respect of organic and inorganic residuals through the uncoupling of wastewater and gas treatment. However, due to the low gas production by sulphate reduction an extra carrier gas (e.g. N₂) is required for efficient H₂S stripping. Additionally, losses of CO₂ within the stripping step must be minimised to avoid disturbances in the alkalinity equilibrium (van Groenestijn *et al.*, 1995). Several well-established physical/chemical or biological technologies are available on the market for the removal of H₂S in gas streams (Janssen *et al.*, 2000). The application of the processes mainly depends on the amount of H₂S to be treated. In the case studied biological sulphide oxidation and Claus process were considered among others for large scale implementation.

b) The removal of dissolved sulphide in the effluent of the anaerobic reactor offers the advantage of an easier operation, in exchange for less valuable sulphur sludge. For this application, biological sulphide oxidation to elemental sulphur was successfully developed as a cost-effective method for the removal of sulphur from wastewater streams compared to chemical processes (Janssen *et al.*, 2000; Lens *et al.*, 2000). It must be considered, that the higher alkalinity present in the H₂S-free effluent recycle loop will raise the pH-value in the anaerobic reactor. This will exert on one hand a positive effect on H₂S and acetic acid inhibition, on the other hand may result in higher precipitation of calcium carbonate. Additionally, it must be ensured that sludge retention efficiency will not be affected by the higher hydraulic load applied, leading to a considerable loss of biomass in the anaerobic reactor with consequent depletion of the sludge age (Kroiss, 1985).

-Viscous wastewater is poor in nutrients. Nitrogen and phosphorous were added to the wastewater for efficient treatment. At a specific load B_{x,COD} between 0.3 and 0.5 gCOD/gVSS.d the COD:N ratio for nitrogen consumption in the pilot scale was in average 1000:7. The ratio agrees well with the values given by Henze & Harremoës (1983) for methanogenic reactors at a similar organic loading. A phosphorus dosage of COD:P=1000:2 was found appropriate. Lack of micronutrients was not observed within the experiments. As already mentioned the addition of TAS to the anaerobic reactor also accounted for a sufficient pool of trace element.

Conclusions

Anaerobic biological treatment showed to be a feasible option to treat wastewater from the viscose industry for sulphate, COD and zinc removal. In this way it was also possible to prevent overloading of the existing wastewater treatment plant and avoid its enlargements. Furthermore, sulphate reduction opens new challenges for the reuse of zinc and sulphur in the viscose production.

Experimental results showed that for high process efficiency the concentration of the produced H₂S in the gas phase in the anaerobic reactors must be kept below 3 vol% (< 80 mg H₂S_{free}/l). Sludge age, pH-value and acetic acid concentration are further key parameters for stable operation. The COD in the wastewater was easily biodegradable (85%) and a suitable substrate for sulphate reduction. By H₂S concentrations ranging from 1 to 10 vol% about 70% of the degraded COD was used by SRB. On the contrary, methanol in the influent was found to be primarily a substrate for mesophilic MB. Methane production ceased only at H₂S concentrations ≥10 vol%. Sulphate reduction accounted for 50% and was COD limited.

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