Anaerobic treatment for C and S removal in “zero-discharge” paper mills: effects of process design on S removal efficiencies

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Abstract
Stringent environmental laws in Europe and Northern America lead to the development towards closure of the process water streams in pulp and paper mills. Application of a “zero-discharge” process is already a feasible option for the board and packaging paper industry, provided in-line treatment is applied. Combining energy conservation inside the mill results in process water temperatures of 50–60°C. Thermophilic anaerobic treatment complemented with appropriate post-treatment is considered as the most cost-effective solution to meet re-use criteria of the process water and to keep its temperature. In the proposed closed-cycle, the anaerobic treatment step removes the largest fraction of the biodegradable COD and eliminates “S” as H₂S from the process stream, without the use of additional chemicals. The anaerobic step is regarded as the only possible location to bleed “S” from the process water cycle. In laboratory experiments, the effect of upward liquid velocity (V_upw) and the specific gas loading rate (V_gas) on the S removal capacity of thermophilic anaerobic bio-reactors was investigated. Acidifying, sulphate reducing sludge bed reactors were fed with partly acidified synthetic paper mill wastewater and were operated at 55°C and pH 6. The reactors were operated at organic loading rates up to 50 g COD·L⁻¹·day⁻¹ at COD/SO₄²⁻ ratios of 10. The effect of V_upw was researched by comparing the performance of a UASB reactor operated at 1.0 m·h⁻¹ and an EGSB reactor, operated at 6.8 m·h⁻¹. The V_upw had a strong effect on the fermentation patterns. In the UASB reactor, acidification yielded H₂, acetate and propionate, leading to an accumulation of reducing equivalents. These were partly disposed of by the production of n-butyrate and n-valerate from propionate. In the EGSB reactor net acetate consumption was observed as well as high volumetric gas (CO₂ and CH₄) production rates. The higher gas production rates in the EGSB reactor resulted in higher S-stripping efficiencies. The effect of V_gas was further researched by comparing 2 UASB reactors which were sparged with N₂ gas at a specific gas loading rate of 30 m³·m⁻²·day⁻¹. In contrast to the regular UASB reactors, the gas-supplied UASB showed a more stable performance when the organic loading rates were increased. Also, the H₂S stripping efficiency was 3–4 times higher in the gas-supplied UASB, reaching values of 67%. Higher values were not obtained owing to the relatively poor sulphate reduction efficiencies.

Keywords
Acidification; EGSB; granular sludge; gas loading rate; liquid upflow velocity; methanogenesis; paper mill; sulphate reduction; thermophilic; UASB; zero-discharge

Introduction
At present the world paper production is 300–320 million tons·year⁻¹. Cellular pulp, produced from wood or other agro-products, can be regarded as the most important raw material for paper production. Recycled paper, however, is a growing alternative having about 35% of the world market. In The Netherlands, about 65% of the produced paper originate from recycled paper. The pulp processes are the biggest polluters, discharging 50–500 kg COD per ton raw material, depending on the type of raw material (e.g. (pine)wood, straw) and type of pulping process, such as thermo-mechanical, semi-chemical, chemical. These pulping processes are concentrated in various pulp producing countries like Sweden, Finland, Canada, USA, Indonesia, Brazil, and Thailand. However, paper production occurs worldwide. Water pollution during the latter process varies from 10–50 kg COD per ton product for recycled paper and 5–10 kg COD·ton⁻¹ for cellular pulp processing.
At present, 55–60% of the worldwide produced paper consists of “low grade” products such as newspaper, packaging paper and board products. For these, slightly coloured products, recycled paper is often used as raw material, and “low quality” water can be used as process water. Within the pulp and paper industry, the board and packaging mills firstly started to reduce the water consumption from 80 to 20 m³·ton⁻¹ paper and currently towards “zero-discharge”. It must be noted that a decrease in effluent discharge of 10 m³·ton⁻¹ yields 1045 MJ·ton⁻¹, assuming a fresh water temperature of 10°C and an effluent of 35°C. Energy conservation by reduced water consumption automatically results in increased water temperatures inside the mill. The process water temperature in a zero-discharge mill may reach 55–60°C. The high temperatures are very beneficial for the paper production process due to: i) low liquid viscosity, i.e. higher run-ability of the paper machines up to 4–5%; and ii) less biological pollution (slime-forming bacteria) in the process water. Loop closure without process water treatment results in non-tolerable pollution of the process water, leading to severe odour problems in both the product (loss of economic value) and the factory including its neighbourhood. Therefore, a zero discharge set-up can only be applied when combined with an adequate in-line treatment system (Habets and Knelissen, 1997).

Because of the above-mentioned advantages, the paper producers want to keep the mill temperature in the thermophilic range. The latter calls for innovative thermophilic treatment systems since application of conventional moderate temperature treatment would lead to a valuable loss of energy. The energy costs for cooling and re-heating the process water of a moderate paper mill, i.e., 1,000 ton·day⁻¹, are about 500,000 Euro per year.

Polluting compounds
The closed water system of a paper mill can be regarded as a completely mixed tank reactor. During the pulping process, organic matter is dissolved in the process water. Working with recycled paper as raw material, about 75% of the COD derives from the starch, which had been used in the old paper as filling material. Under the mixed tank conditions, the starch is acidified to VFA (in the equation simplified to acetic acid), which in its turn dissolves the CaCO₃ filler from the old paper particles:

\[ 2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow 2\text{CH}_3\text{COO}^- + \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \]

The CO₂ may lead to foaming problems on the paper machine, while the dissolved Ca⁺ increases the water hardness and may cause problems related to unwanted precipitation in the production line.

Another unwanted biological reaction in the process water loop is the reduction of the available sulphate to sulphide that causes significant odour problems inside the mill as well as in the end product. In addition to VFA and sulphate, other compounds will also accumulate in the closed system until equilibrium with the end product is reached. Examples are paper chemicals, salts, anionic trash, stickies, coloured compounds etc. (Habets and Knelissen, 1997).

Process water treatment
Considering the composition of the process water, i.e., starch, volatile fatty acids (VFA), and cellulose, anaerobic treatment can be regarded as the most cost-effective treatment method for reducing the soluble COD content. Concomitantly, sulphate will be reduced under controlled conditions and removed from the process loop by biogas stripping. In general, an anaerobic reactor treating wastewater from a recycled paper mill degrades up to 80% of the available COD. The organic matter is either reduced to methane that can be
recovered for steam production inside the mill, or anaerobically oxidised to bicarbonate which is used in the subsequent stages for Ca removal (Figure 1.).

The combined C and S removal in the thermophilic anaerobic reactor constitutes the core of the inline treatment concept. Whether or not the treated water can be reused in the process after the aerobic stage depends on quality demands in the production line. For packaging and board mill, anaerobic treatment is complemented with aerobic treatment and sand filtration suffices. However, for the production of high quality paper a tertiary treatment step is required that is focussed on removal of (very) fine particles, colour and/or salts. The present research project also evaluates the existing physico-chemical treatment steps that can be combined with the proposed biological steps under high temperature conditions (to be presented elsewhere). Firstly, the research is focussed on the development of an adequate thermophilic anaerobic high-rate system.

Staged reactors improve the stability of thermophilic anaerobic high-rate treatment of partially acidified wastewater (Van Lier, 1996). For thermodynamic reasons, the first stage of such system will be characterised by a high acidifying activity. If combined with sulphate reduction, the first stage could represent an effective S-removal reactor since almost all of the available sulphide will be present as H2S and therefore, subjected to natural stripping. In addition, the subsequent methanogenic stages of the reactor will be safeguarded from high sulphide concentration, which could potentially inhibit the methanogenic conversions.

Previous results show that thermophilic (55°C) sulphate reduction proceeds well under acidifying conditions at pH 6.0 (Sipma et al., 2000). Under these conditions about 95% of the produced sulphide is present as non-ionised H2S and, therefore, relatively easy to strip. The dominant sulphate reducing sub-population used H2 as sole electron donor. The present paper discusses the effects of upflow gas and liquid velocities on the S removal capacity of the first stage of the anaerobic reactor, which is dedicated to complete acidification and concomitant sulphate reduction.

Materials and methods
Experimental set-up. The UASB (V=6.5 litre), and EGSB (V=4.3 litre) reactor set-up was previously described by Lens et al. (2000) and Sipma et al. (2000). The feed composition of all reactors was the same, having a COD/SO4 ratio of 10. Reactors were temperature and pH controlled at 55°C and 6.0 (± 0.2), respectively. The UASB reactors were operated at a liquid superficial upflow velocity (Vupw) of 1 m.h⁻¹ and the EGSB reactor at 6.8 m.h⁻¹. The Vupw was fixed by recirculating the effluent. The hydraulic retention time (HRT) in the reactors varied between 4.2 and 3.7 h. The gas in the N2-sparged UASB was introduced

![Figure 1](https://iwaponline.com/wst/article-pdf/44/4/189/430191/189.pdf)
below the sludge bed and distributed homogeneously as small bubbles (0.1 to 0.3 mm in diameter) over the reactor surface by using a sintered glass plate. The gas flow was controlled using a Brooks mass flow controller 58E (range 0–500 ml.min⁻¹), in combination with a Brooks microprocessor control and readout unit (541-C-052-AAG rev B, Fisher-Rosemount). The specific superficial gasflow (V_gas) was increased from 10 m³.m⁻².day⁻¹ at the start of the experiment until 30 m³.m⁻².day⁻¹ at the end of the experiment. Reactor numbers are: R1, UASB control V_upw; R2, EGSB; R3, UASB control V_gas; R4, N₂-sparged UASB (see also Table 1).

Inoculum. Reactors R1 and R2 were inoculated with mixed thermophilic, acidifying, sulphate reducing sludge from previous experiments (Sipma et al., 2000). Reactors R3 and R4 were inoculated with the sludge mixture coming from the reactors R1 and R2. The mixed inoculum contained about 100 mg total suspended solids (TSS) and 55 mg volatile suspended solids (VSS) per g wet sludge. All reactors were started-up with about 3.0 litres of inoculum sludge (165 g VSS per reactor).

Medium. All reactors were fed with a synthetic influent (pH 6.0; total COD 40 g.l⁻¹) containing (in g.l⁻¹): starch (6.00), sucrose (5.35), lactate (11.21), propionate (4.30) and acetate (9.35). The media were supplemented with nutrients and trace elements as described elsewhere (Lens et al., 2000). These concentrations were based on the average influent composition of a wastewater from a paper mill producing fluting and liner out of recycled wastepaper (Sipma et al., 2000). Sulphate was added as sodium sulphate in a COD/sulphate ratio of 10, as is the case for this wastewater type (Habets and Knelissen, 1997).

Analysis. All analyses were performed as described elsewhere (Sipma et al., 2000; Lens et al., 2000).

Results and discussion
The reactors R1 and R2 were operated at a hydraulic retention time of about 4 h. The imposed volumetric organic loading rates (OLR) ranged from 4.9 to 40.0 g COD.litre⁻¹.day⁻¹. When imposing an OLR of 40.0 g COD.litre⁻¹.day⁻¹, the acidification efficiency dropped to 80% and the sulphate reduction efficiency decreased to 50% in the UASB reactor (R1). In the EGSB reactor (R2), the sulphate reduction efficiency dropped to 30% directly following the OLR increase to 40 g COD.litre⁻¹.day⁻¹, but recovered rapidly to 100% (at an OLR of 35 g COD.litre⁻¹.day⁻¹) until the end of the experiment. A net acetate and propionate production occurred in R1. At the higher organic loading rates, propionate was converted to n-butyrate and n-valerate. These back reactions did not occur in R2, in which an active methanogenic population developed, leading to a net acetate removal (up to 50%) and a high gas loading rate (up to 8.5 litre.litre⁻¹.day⁻¹). See also Figure 2.

In reactors R1 and R2, the effluent sulphide concentration was always below 200 mg.litre⁻¹, of which about 90% were present as undissociated H₂S under the given conditions (pH 5.8–6.1 and temperature = 55°C). The biogas (CH₄ and CO₂) production rates in R1 were very low, i.e. < 3 litre biogas.litre⁻¹ reactor.day⁻¹, resulting in negligible amounts (<20%) of H₂S stripped from the reactor liquid. In R2, the biogas production rates reached up to 8.5 litre.litre⁻¹.d⁻¹, resulting in H₂S stripping efficiencies up to 75% (Table 1).

The effects brought about by an increased V_gas on the acidification pattern are comparable to the effects induced by a higher V_upw with a concomitant higher bio-conversion rate. Reactor R4, the N₂-sparged UASB, had a more complete and more stable acidification than
reactor R3 and both butyrate and valerate concentrations remained low or were even negligible. Very likely, the better contact between the sludge and the wastewater, induced by the gas sparging, prevented the (local) accumulation of reducing equivalents that may affect the fermentation pattern.

The effluent sulphide concentration of reactor R3 was always below 125 mg.litre$^{-1}$, of which about 90% was present as non-ionised H$_2$S under the given conditions. Similar to reactor R1, the biogas production rate in R3 was very low, i.e., < 3 litre biogas.litre$^{-1}$ reactor.day$^{-1}$, again resulting in negligible amounts (<20%) of H$_2$S stripped from the reactor liquid (Table 1).

The total H$_2$S concentration of the reactor R4 effluent was always below 25 mg.l$^{-1}$. However, it should be noticed that the sulphate reducing capacity of reactor R4 was significantly lower than that of reactor R2. Probably, the increased shear forces brought about by the increased gas load, led to a specific wash-out of sulphate reducing bacteria, limiting the

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**Figure 2** Evolution of the VFA concentration in the effluent of: A) the UASB (R1) and B) the EGSB (R2) reactor. Acetate (○), propionate (●), butyrate (○), n-valerate (●) and iso-valerate (□)
The overall S-removal efficiency to 67% (Table 1). The latter effect was also previously observed in a mesophilic sulphidogenic reactor (Omil et al., 1996). On the other hand, a satisfactory granulation of the acidifying, sulphate-reducing biomass was obtained, particularly in reactors R2 and R4. Likely, this can be attributed to the presence of non-acidified matter in the feed, which enhances the thermophilic granulation process (Van Lier, 1996). The sludge granules in reactors R1 and R3, however, developed a fluffy gel layer, a phenomenon often observed when the non-acidified fraction is too large and mechanical stress is absent (Lens et al., 2000).

Though the UASB control reactors only showed low “S” stripping efficiencies, the percentage of stripped “S” per unit of produced biogas was much higher than in the reactors R2 and R4. For the control reactors R1 and R3, a specific gas loading of about 2–3 m³.m⁻².day⁻¹ resulted in an H₂S strip factor of about 20%. However, reactors R2 and R4 needed a specific biogas load of 5–10 m³.m⁻².day⁻¹ to strip a similar percentage of H₂S. Very likely, this phenomenon can be attributed to differences in the driving force for H₂S liquid – gas mass transfer. Owing to the lower liquid and gas velocities in the UASB reactors, more H₂S will be stripped per litre of produced biogas.

None of the reactors suffered from inhibition due to the presence of relative high concentrations of non-ionised H₂S. Even in the control UASB reactors (R1 and R3), acidification of starch and sucrose prevailed at non-ionised H₂S concentrations up to 180 mg.litre⁻¹ (results not shown), which is in agreement with our previous results (Sipma et al., 2000). In the latter studies, which comprised thermophilic UASB reactors operating under similar operational and loading conditions, we did not find inhibition of sucrose degradation at undissociated H₂S concentrations up to 300 mg.litre⁻¹.

Conclusions

- Water closure in a board and packaging paper mill is a feasible option provided an inline wastewater treatment system is applied.
- A sequenced thermophilic anaerobic – aerobic treatment system is regarded as the most cost-effective solution to provide inline treatment.
- The anaerobic reactor converts organic matter in methane and carbon dioxide/bicarbonate alkalinity, meanwhile “S” is removed from the cycle via biogas stripping.
- Thermophilic (55ºC) sulphate reduction proceeds well during the acidification of synthetic paper mill process water at pH 6.0 up to an OLR of 35 gCOD.litre⁻¹.day⁻¹.
- Both the upward liquid velocity (R2) and an increased specific gas loading rate (R4) resulted in a more stable fermentation process. The acidification in these reactors remained at 80–100% throughout the study and there was no significant accumulation of propionate, n-butyrate and n-valerate in the effluent.
- An increased liquid upward velocity distinctly improved the sulphate reduction reach-

<table>
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<tr>
<th>Reactor</th>
<th>Description</th>
<th>Liquid upflow</th>
<th>OLR g COD. l⁻¹.day⁻¹</th>
<th>Gas flow m³.m⁻².day⁻¹</th>
<th>Acidification (%)</th>
<th>Sulphate red. efficiency (%)</th>
<th>S-stripping efficiency (%)</th>
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<td>&lt;2</td>
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<tr>
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<td>EGSB</td>
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<td>&lt;18</td>
<td>100</td>
<td>95</td>
<td>75</td>
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<tr>
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<td>UASB control</td>
<td>V&lt;sub&gt;gas&lt;/sub&gt;</td>
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<td>25</td>
<td>&lt;2</td>
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<td>60</td>
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<tr>
<td>R4</td>
<td>UASB N₂-sparged</td>
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<td>25</td>
<td>10–30</td>
<td>100</td>
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ing almost 100% in the EGSB reactor (R2). However, an increased gas flow limited the sulphate reduction rate, probably by selective wash-out of sulphate reducers.

- Increased gas loading rates resulted in significantly higher sulphide stripping efficiencies, up to 75%.
- The thermophilic, acidophilic, sulphidogenic EGSB, represents an effective anaerobic pre-treatment unit for S-removal in a closed process cycle of a pulp and paper mill.

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References


