ANAEROBIC TREATMENT OF EVAPORATOR CONDENSATES FROM THE CHEMICAL PULP INDUSTRY

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Abstract

This paper describes the design and operation of two different full-scale anaerobic wastewater treatment plants treating evaporator condensates from the chemical pulping industry. The cases described comprise effluent treatment plants at a kraft based pulp mill and a sulphite based pulp mill. In both cases the IC expanded sludge bed reactor is the heart of the installation. As the internal circulation does not affect the upflow velocity in the upper part of the IC reactor and because of the two-stage separation system optimal sludge retention is ensured. Special attention is given to the typical characteristics of both types of condensates. The potential inhibiting effects of some components as also solutions to avoid inhibition and the necessity to add nutrients and essential (trace) metals are discussed. Kraft mill condensate is characterised by high concentrations of methanol (approx. 2500 mg/l). When operating the IC reactor at volumetric loading rates of 10-18 kg/m³.d removal efficiencies were as high as 80-85 % for COD and more than 99 % for methanol. Sulphite mill condensate is characterised by high concentrations of acetic acid (approx. 2000 mg/l). Operating at volumetric loading rates between 5 and 22 kg/m³.d the IC reactors realised removal efficiencies of more than 90 % on COD and more than 97 % on acetic acid.

Keywords

Acetic Acid, Anaerobic, Condensate, IC, Kraft, Methanol, Pulp mill, Sulphite

Introduction

Anaerobic effluent treatment using the UASB (Anaerobic Upflow Sludge Bed) process is well accepted within the pulp and paper industry. UASB reactors have been successfully applied for anaerobic treatment of recycled paper mill effluent (Habets & Knelissen, 1985) mechanical pulping effluents mills (Driessen & Wasenius, 1994), semi-chemical pulping effluents (Smith et al., 1994) and more recently also for treatment of evaporator condensates from chemical pulp mills.

Newly developed granular sludge bed reactors that allow for higher upflow velocities have been successfully introduced into the pulp and paper industry (Driessen et al., 1999; Wiseman et al., 1998, and 2000). An example of such a reactor is the IC reactor (Internal Circulation reactor). The IC reactor is an anaerobic sludge bed reactor constructed as a tall cylindrical vessel with a height up to 24 meters. The IC reactor is characterised by a two-staged separation system designed to provide optimal sludge retention. The first stage separates the majority of the biogas from the water, so that the second stage mainly separates the active biomass from the treated effluent. The name of the IC reactor has been derived from the gas lift (biogas) driven internal effluent circulation. The internal circulation provides optimal mixing conditions for the anaerobic sludge and wastewater at the bottom compartment of the reactor. The internal circulation is constructed in
such a way that it does not affect the upflow velocity at the top of the reactor. Because of this feature and because of the two-stage separation system the IC reactor is capable of ensuring good sludge retention at elevated upflow velocities and organic loading rates.

Chemical pulping accounts for approximately 2/3 of the world’s pulp production (James et al., 1999). Chemical pulp mills use chemicals for dissolving the non-cellulose fraction (especially lignin) from the wood. The two most commonly applied chemical pulping processes are sulphate pulping (so-called ‘kraft pulping’) and sulphite pulping. The kraft process involves cooking of the wood chips in a solution of sodium hydroxide (NaOH) and sodium sulphide (Na₂S). Kraft pulps are used to produce strong paper products (‘kraft is the German word for strong). In the sulphite process, often a mixture of sulphurous acid (H₂SO₃) and bisulphite (HSO₃⁻) is used to dissolve the lignin. In both chemical-pulping processes the active chemicals are recovered through a combination of multiple evaporation and subsequent burning of the pulp liquid (so called black liquor) containing the dissolved lignin and other extractives. The evaporation produces highly polluted condensates.

Condensates contain merely volatile organic compounds and practically no suspended solids and salts. Kraft condensates contain mainly methanol with remainders of terpenes, aldehydes, ethanol and reduced sulphur compounds. Kraft condensates are alkaline due to the presence of ammonia. Sulphite condensates contain mainly acetic acid, furfurals, methanol and sulphite. Due to the presence of sulphite and acetic acid sulphite condensates are acidic. Table 1 presents some typical composition of kraft and sulphite based evaporator condensates.
Table 1: Typical characteristics of chemical pulp evaporator condensates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Kraft Condensate</th>
<th>Sulphite Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>g/l</td>
<td>2.5 – 6.5</td>
<td>3 - 7.5</td>
</tr>
<tr>
<td>BOD</td>
<td>g/l</td>
<td>1.5 – 4.5</td>
<td>2 - 5</td>
</tr>
<tr>
<td>NH₄</td>
<td>mg/l</td>
<td>50 - 100</td>
<td>-</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/l</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PH</td>
<td></td>
<td>8 – 10</td>
<td>2 - 3.5</td>
</tr>
<tr>
<td>COD compounds</td>
<td></td>
<td>methanol, terpenes, aldehydes, hydrogen sulphide, mercaptanes</td>
<td>acetic acid, furfurals, methanol</td>
</tr>
<tr>
<td>Sulphur compounds</td>
<td></td>
<td>hydrogen sulphide (H₂S), (methyl) mercaptanes, DMSₐ, DDSₐ</td>
<td>sulphite (SO₂)</td>
</tr>
<tr>
<td>Nitrogen compounds</td>
<td></td>
<td>ammonia (NH₃)</td>
<td>-</td>
</tr>
</tbody>
</table>

ₐ DMS: dimethyl sulphide, ₐ DDS: dimethyl disulphide

Possible toxicity from kraft mill condensates might result from the terpenes, and high sulphide concentration (H₂S), whereas toxicity from sulphite mill condensates might result from the high concentration of sulphite (SO₂). At both pulp processes toxicity might result from the presence of the heavily polluted evaporator underflow (so-called “black liquor”). In case of process upset, black liquor might carry over into the condensate. Black liquor can be toxic to methanogens, mainly due to the presence of wood extractives. In this paper the feasibility of anaerobic treatment of chemical pulp mill condensates with the IC reactor is illustrated by one example at a kraft mill and one example at a sulphite pulp mill.

CASE: KRAFT MILL CONDENSATE

Process description

Having a total capacity of 950 tons per day, the kraft mill currently produces 820 tons of pulp per day. The pulp mill uses approximately 60 % hardwood and 40 % softwood (pine). The wastewater comprises various kinds of condensates among which blow heat accumulated condensate and foul evaporator condensate. The anaerobic treatment plant was designed to treat 3,078 m³ of kraft condensate per day and a COD load of 18,186 kg per day. In order to prevent possible inhibiting waste streams from entering the anaerobic treatment plant, conductivity measurements (to check for black liquor) and a fluorometer (to check for terpenes) were installed. As the common sulphide concentrations in the condensate showed not to be toxic during an extensive pilot trial, no special precautions were taken to reduce the hydrogen sulphide. The foul condensates are pumped into the buffer tank after which they are cooled before entering the conditioning tank. The wastewater is kept at around 35 °C. Phosphoric acid and trace elements are added into the conditioning tank. No nitrogen is added, as ammonia is present in sufficient quantity. Caustic as well as magnesium hydroxide can be added in order to correct the pH. From the conditioning tank the wastewater is pumped into the IC reactor, where COD is converted into biogas. In case of too high temperatures or extreme pH values the reactor is automatically shut down. The biogas produced is utilized in a combination boiler at the pulp mill. Part of the effluent from the IC reactor is recycled back to the conditioning tank. The anaerobically treated effluent finally flows to an existing lagoon system, where it is mixed with the other kraft mill wastewater and treated aerobically. A process flow diagram of the anaerobic treatment plant is shown in figure 2.
Operational results

Prior to start-up, the IC reactor was inoculated with approximately 6,000 kg VS of granular sludge from two UASB reactors at food processing plants. Within six weeks the original granular sludge was adapted to the condensate and all available condensate was treated. At the beginning the sludge bed became less dense and granular particles became smaller in size. Although the washout of sludge (< 100 mg/l) was lower than the expected biomass yield (150-300 mg/l) no accumulation was observed within the first half year. After approximately one year of operation, sludge growth was observed.

Analysis showed that 84 % of the COD consisted of methanol and that 99 % of the COD removed was due to removal of methanol. Unlike most other organic compounds, methanol is not acidified prior its conversion into methane and carbon dioxide. Under very specific (unfavourable) conditions, methanol can be converted into acetic acid prior methanogenesis (Florenceio et al., 1994). These conditions include simultaneous high concentrations of methanol, cobalt, CO₂ and undissociated VFA. Methanol analysis is the most important control parameter since the purpose of the treatment plant is to remove methanol, and more than 92 % methanol removal must be demonstrated to the authorities. Methanol was analysed twice per week, while COD was analysed on a daily basis. Concentrations and removal efficiencies of COD and methanol in time are presented in figures 3 and 4.
COD influent concentration averages 4568 mg/l, while the treated effluent averages 1121 mg/l. Average COD removal efficiency over the whole period is 75 %, although the last months COD efficiency exceeds 80 %. Methanol influent and effluent concentration averages 2571 mg/l and 166 mg/l respectively (including removal efficiency drops). During the last period methanol removal efficiency is almost complete resulting in methanol effluent concentrations of less than 5 mg/l.

Toxicity due to terpenes or black liquor was not observed so far during the full-scale operation. Low removal efficiencies of COD and methanol mostly resulted from the lack of micronutrients (even for one day). At times when micronutrient addition was minimized or when there were problems with nutrient addition, methanol concentrations in the reactor effluent increased. Florencio et al. (1994) reported the importance of certain micronutrients, especially cobalt, for the anaerobic conversion of methanol into methane.

Treating all the available condensate the IC reactor operated at volumetric loading rates at around 14-18 kg COD/m3.d. As the pulp mill already meets the legislation requirement by treating only a part of the waste streams, one waste stream (turpentine decanter underflow) has not yet been fed to the treatment plant. Furthermore the pulp mill operates at approximately 85 % of its projected capacity.

Figure 5 shows the methanol removal efficiency as a function the volumetric loading rate. The methanol removal seems to be independent of the volumetric loading rates applied. This is according to expectations as the IC reactor currently operates at volumetric loading rates that are below the projected design load.
Due to a relative low sludge concentration, the IC reactor has operated with F/M ratios as high as 3.0 kg COD per kg VS per day. Operating at such a high F/M ratio, without compromising the removal efficiency.

The specific gas production amounts approximately 0.39 m$^3$/kg COD removed. On average the biogas contains 85 % methane. The biogas contains hydrogen sulphide as well as other reduced sulphur compounds like mercaptanes, DMS and DDS.

**CASE: SULPHITE PULP MILL**

**Process description**

The mill described is an integrated pulp and paper factory. The sulphite pulp mill has a capacity of approximately 400 ton of pulp per day. The wood source used is softwood (pine). The used pulping process water is evaporated before it is burned for COD destruction and recovery of the reactive chemicals. The wastewaters produced are the condensates from the multiple evaporators. The anaerobic treatment plant is designed to treat 5300 m$^3$ of condensate per day and a COD load of approximately 24,500 kg/d. Extra capacity (25 %) was anticipate for, in order to allow for combined treatment of some of the pulp bleaching effluents. Prior to anaerobic treatment the condensate containing high concentrations of sulphite (500-400 mg/l) is treated in a steam stripper. The stripper reduces the sulphite concentration to less than 50 mg SO$_3$-S per litre. The stripped sulphite is returned to the mill, where it is reused in the pulping process. After the stripper the condensate is cooled to a temperature between 36 and 38 $^\circ$C and pumped into a conditioning tank. UV-measurement was installed to detect other possible inhibiting waste streams (e.g. “black liquor”) and prevent them from entering the anaerobic treatment plant. Due to the presence of acetic acid and sulphite the pH of the condensate is as low as 2.7. In the conditioning tank caustic is dosed for neutralization of the acid condensate. Urea (N) and phosphoric acid (P) are dosed to supply the necessary macronutrients. Furthermore in order to promote granulation and growth of the anaerobic sludge, hydrated lime (Ca(OH)$_2$) and essential trace elements (e.g. iron, cobalt, nickel etc.) are dosed. In the conditioning tank the wastewater is diluted with anaerobic effluent at a ratio of 1:1 before it is pumped into two anaerobic IC reactors each with a volume of 650 m$^3$. The biogas produced in the IC reactors is buffered and utilized in the steam boilers in the mill. The anaerobically treated effluent is fed by gravity into an aerobic polishing tank, where the hydrogen sulphide is oxidized in order to produce an odour free effluent. A process flow diagram of the anaerobic treatment plant is shown in figure 6.
Figure 6: Schematic process flow diagram of anaerobic treatment plant at sulphite pulp mill

Operational results

Prior to start-up, both IC reactors were inoculated with a total of approximately 50,000 kg VS of granular sludge originating from UASB reactors at recycled paper mills. After some weeks of operation, accidental spills of black liquor entered the anaerobic treatment plant, causing a part of the sludge to wash out. Approximately 40,000-45,000 kg VS biomass remained in the reactors. Since then, approximately one year of operation, the sludge amount almost remained the same.

The COD of the condensates contains for 50 % of acetic acid. As acetic acid is the main component VFA analysis in the anaerobic reactor outlet is the prime indicator for the performance of the anaerobic process. Concentrations and removal efficiencies of COD and VFA against time are presented in figures 7 and 8. It must be noted that VFA efficiencies are projected over the IC reactor, whereas COD and BOD efficiencies are projected over the complete treatment plant including the small post-aeration basin. As the retention time in the aeration basin is only about 2 hours and the VFA in the IC outlet are generally equal or less than 1 meq/l, very little COD conversion is expected to take place in this tank.

The average COD concentrations in the influent and final effluent were 4967 mg/l and 489 mg/l respectively. The average COD removal efficiency is 90 %. The BOD concentration averages 3983 mg/l, which is equal to 80 % of the COD. The average BOD removal efficiency is 98 % resulting in less than 75 mg/l of BOD in the outlet of the aeration tank. When black liquor entered the treatment plant, COD efficiencies went down to 50-60%, while VFA removal did not drop significantly. The IC reactor almost immediately recovered afterwards, and COD removal efficiencies came back to their regular level. No inhibiting effect was observed when the sulphite concentration in the condensate increased from an average of 50 mg SO₃-S/l up to 140 mg SO₃-S/l.

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**Figure 6: Schematic process flow diagram of anaerobic treatment plant at sulphite pulp mill**

- **NaOH**
- Urea
- H₃PO₄
- Ca(OH)₂
- Trace elements
- SO₂
- INFLUENT
- STRIPPING
- COOLING
- CONDITIONING TANK
- IC REACTOR: 2 x 650 m³
- AEROBIC POLISHING: 500 m³
- GAS BUFFER: 70 m³
- FLARE: 600 m³/h
- BIOGAS
- BOILER
- EFFLUENT
Figure 7: COD concentrations and removal efficiency

Figure 8: Acetic acid concentration and removal efficiency

Figure 9 indicates that acetic acid removal efficiency is not compromised by volumetric loading rates up to 22 kg/m³.d. The anaerobic treatment plant was designed for a volumetric loading rate on average of 19 kg COD/m³.d up to a maximum of 24 kg COD/m³.d. The IC reactors have been treating all the condensate available.

Figure 9: Volumetric loading rate and removal efficiencies

The actual sludge loading rate averages 0.5 kg COD per kg VS per day.
The specific gas production amounts approximately 0.36 m$^3$/kg COD removed. On average the biogas contains 82 % methane, 17 % carbon dioxide and 0.5 % of hydrogen sulphide.

Conclusions

In this paper long-term experience on anaerobic treatment of two different chemical pulp mill evaporator condensates are presented. The IC reactor successfully treats kraft pulping and sulphite pulping evaporator condensates.

Potential toxicity was prevented by a carefully designed pre-treatment in combination with installation of special detection measurements. The special features of the IC reactor ensure excellent biomass retention at elevated organic loading rates.

Kraft mill condensate is characterised by a high concentrations of methanol, while sulphite condensate contains mostly acetic acid. On kraft mill condensate the IC reactor achieved COD removal efficiencies as high and 80 % and methanol removal exceeded 99 %. On sulphite mill condensates the IC reactor achieved COD efficiencies of 90 %, whereas acetic acid removal was as high as 97 %.

References


