Spectral Absorption Coefficient (SAC) measurement for controlling an ozone system in the paper industry

Advantages

• Cost savings due to specific ozone metering
• Reduction of the COD load in the effluent at the wastewater treatment plant
• Possible reduction in the COD threshold values
• Increase in the BOD₅/COD ratio, increasing the bioavailability
• Removal of coloration from the paper wastewater

Background

Paper mills often have large amounts of wastewater contaminated with high organic loads (COD) and strong coloration. To tackle these elevated pollutant loads and quantities of wastewater, further treatment using ozone has become an important process in addition to conventional biological treatment. Here the term “Biology-Ozone-Biology” combination is used.

Biology-Ozone-Biology

The “Biology-Ozone-Biology” combination is a more extensive wastewater treatment process using ozone. Two-stage biological treatment cannot adequately tackle a higher COD load, as lignin and lignin derivatives form a low-activity residual COD that cannot be broken down biologically. Here ozone treatment as a third treatment stage can be used for further COD elimination. While the complete breakdown of the low-activity COD using ozone is possible in principle, it can be expensive. Conversely, a low ozone dose to increase the bioavailability (BOD₅/COD) is cost-effective. The substances produced are broken down using a subsequent aerobic low load process (e.g. bio-filtration). In this way a COD reduction of 25–90% can be achieved.

The Action of Ozone on Paper Wastewater

Ozone acts in various ways on paper wastewater. The reduction in the COD and the increase on the BOD₅/COD ratio are of primary importance. However, the coloration of the wastewater cannot be neglected. The brown coloration is largely caused by lignin derivatives with double-bonded carbons that are attacked and destroyed by ozone. If the treated wastewater is to be returned to the manufacturing process, color removal is critical.

Aspects that Effect the Action of an Ozone System

The action of the ozone on the treated wastewater depends on a number of factors. Primarily these are the organic load (COD), feed flow rate and reaction time in the ozone reactor. The performance of the treatment can be controlled in relation to the feed load using the specific ozone dose.

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Parameters for Controlling an Ozone System

As an increase in the BOD$_5$/COD ratio is the prerequisite for further residual COD elimination, the online measurement of these two parameters would be optimal for controlling the ozone system. Because both parameters cannot be measured reliably online, it is necessary to find a parameter that can be measured. To identify correlations with the BOD$_5$/COD ratio, a wide range of parameters were compared in a research report by the PTS-Papiertechnisches Institute in Munich (Figure 1).

Based on the trend line produced, SAC can be used in appropriate software for control purposes. Correlations and parameters that can be used for control are dependent on the wastewater. For this reason, a dedicated strategy must be prepared for each type of wastewater.

Regulation of the ozone dose to be used by means of SAC

In this pilot study it was investigated how quickly and precisely a previously defined target for the SAC or BOD$_5$/COD ratio is reached when the composition of the wastewater changes. The flow rate remains constant at 600 l/h.

The wastewater has a load with a SAC = 400 m$^{-1}$. Within two hours the ozone reduces the SAC to a target of approximately 150 m$^{-1}$. The ozone system is loaded alternately with pure wastewater and mixtures of wastewater and tap water. The target for SAC of approximately 150 m$^{-1}$ is achieved within a maximum of two hours. A newly defined target for SAC of approximately 200 m$^{-1}$ is achieved in less than two hours (Figure 2).

A further pilot study investigated how the irregular addition of fresh water to the wastewater affects the desired result. In this pilot study the feed quality is changed continuously by the irregular addition of fresh water once the target was reached. Once the disturbance is over, the target is reached again in approximately one hour (Figure 3).

Fig. 1 shows the correlation determined between the BOD$_5$/COD ratio and the Spectral Absorption Coefficient (SAC), with a correlation coefficient of 0.82.

Fig. 2 shows an ozone control system that is achieving a defined BOD$_5$/COD ratio based on a defined SAC value.

Fig. 3 shows the ozone control system with continuously changing feed quality.
Commercial Significance

The following table shows the estimated operating costs for an ozone system with and without direct control of the ozone dose to be applied. The comparison of the operating costs for a manually controlled ozone system and an automatically controlled ozone system are based on the research report published by the PTS-Papiertechnisches Institute in Munich. The trials were performed in a paper mill in Bavaria.

<table>
<thead>
<tr>
<th>COD wastewater O₃ feed</th>
<th></th>
<th>COD treated wastewater</th>
<th></th>
<th>Manual regulation of the O₃ dose to be used</th>
<th></th>
<th>Automatic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>223</td>
<td>mg/L</td>
<td>137</td>
<td>183</td>
<td>137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water flow rate m³/h</td>
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<td>100</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Ozone dose g/m³</td>
<td>135</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ozone concentration (gas) g/m³</td>
<td>150</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Necessary ozone mass kg/h</td>
<td>13.50</td>
<td>8.00</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Operating costs

| Spec. energy demand kWh/kg O₃ | 10.00 | Energy demand kWh/h | 135.00 | 80.00 |
| Spec. energy costs $/kWh | $0.04 | Energy costs per h $/h | $5.67 | $3.36 |
| Oxygen demand m³/h |  |
| Spec. oxygen demand $/Nm³ | $0.07 |
| Oxygen costs per h $/h |  |
| Total energy costs $/h | $11.97 | $7.09 |
| Total energy costs $/m³ | $0.12 | $0.07 |

Table 1: Estimated operating costs for an ozone system.

Basis for the data

The data in Table 1 is based on a pilot study (Figure 4) during which a COD of 135 mg/L was established in the outlet from the ozone system. The COD in the feed was initially 223 mg/L. To achieve the target, 135 mg O₃/L was required. Once the target was reached, the COD in the feed was reduced to 183 mg/L by dilution. To achieve the new target only 80 mg O₃/L was required.

![Fig. 4 Pilot study with changing feed concentrations.](image-url)
Result
The manually controlled ozone system did not respond to the reduction in influent COD concentration. The system continued to produce 13.50 kg O₃/h for an assumed flow rate of 100 m³/h. The energy costs in this case were $11.97/h or $0.12/m³ of water. The automatically controlled ozone system produces only 8.00 kg O₃/h for the reduced wastewater concentration. The energy costs were reduced to $7.09/h or $0.07/m³ of water.

Cost Savings
Extrapolated over a year, costs of $105,000 would be incurred for the ozone treatment with the manual system. If the feed concentration is different for 50% of the operating time, $21,070 in operating costs can be saved by using automatic control. This amount corresponds to a savings of approximately 20% per year. If the investment costs for an ozone system of $525,000 with depreciation of 6% over 10 years are taken into account, 8.5% is saved per year.

The investment costs for the SAC measurement with annual maintenance and the programming work are approx. $14,210 which would be paid back in 8 months. Regulation by TOC, for which the investment with maintenance and running costs is $25,900, is paid back in approximately 1.5 years.

Conclusion
The use of an automated ozone system offers significant potential for savings and is therefore valuable to small/medium-sized companies. The possible savings in the running costs represent an additional attraction for managers at companies operating wastewater treatment plants to use this highly innovative treatment technology.

For the paper wastewater investigated here, the SAC value is excellently suited to use as a regulation parameter for an ozone system. The correlation with the BOD₅/COD ratio (coefficient of 0.82) is very good. The pilot studies performed clearly show the rapid and precise reaction to changing quality wastewater, an aspect which is the prerequisite for stable operation of the subsequent biological stage. In this way the statutory outlet figures can be reliably met. Additionally, cost-effective ozone dosing is achieved as only the ozone necessary to meet the related limits is used.

Based on the preliminary studies on the pilot studies, TOC also offers a good correlation to the BOD₅/COD ratio. Regulation using the SAC was preferred over the TOC as it is significantly faster.

NOTE: The correlation between SAC and BOD₅/COD ratio must be determined individually for each system.

The measuring technology

sc100™ Digital Controller
Universal controller for wall, pipe or switch panel installation. Connections for 2 digital sensors using splash-proof connectors. 2 analog current outputs, 3 floating changeover contacts (5A 115/230 Vac, 5 A 30 Vdc), digital interface for bus integration (ModBus, ProfiBus, LonBus).

UVAS sc Sensor
Precise, self-cleaning process probe for the instant measurement of the dissolved organic substances (SAC) in the wastewater. Technique without reagents or the need to take samples for measurement directly in the medium or in the bypass.

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