Monitoring of a paper mill wastewater treatment plant using UV/VIS spectroscopy

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Abstract A submersible UV/VIS spectrometer was used to monitor a paper mill wastewater treatment plant. It utilises the UV/VIS range (200–750 nm) for simultaneous measurement of COD, filtered COD, TSS and nitrate with just a single instrument. The instrument measures in-situ, directly in the process. Paper mill wastewater shows typical and reproducible spectra at various process measuring points. There is a relative maximum at 280 mm due to the absorbance by dissolved organic substances, mainly ligninic acids. Comparison of absorbance spectra distinctly shows the decrease of this peak, indicating biological degradation throughout the treatment process. Summarising, one can say that paper mill wastewater cannot be monitored by a simple UV probe measuring only the absorbance at a single wavelength. The required information can only be gained from the whole spectra. Regarding plant control it is suggested that only the overall spectral information is used. Calibrations to conventional parameters are now merely carried out for purposes of reference-checking.

Keywords In-situ; on-line; paper mill wastewater; real-time; UV/VIS spectrometry; wastewater treatment

Introduction

A submersible UV/VIS spectrometer for in-situ real-time measurements is presented. The UV/VIS spectrometer proved to be a promising instrument to quantify wastewater pollutant loads for integrated management and control of municipal sewer networks and monitoring of the treatment plant itself. The submersible spectrometer utilises the UV/VIS range (200–750 nm) for simultaneous measurement of organic matter, suspended solids and nitrate with just a single instrument. The miniaturised UV/VIS spectrometer is a probe installed directly in the process. Therefore it requires no sampling, no sample preparation, and no reagents. The spectrometer is equipped with an auto-cleaning system that prevents film growth on the optical devices.

A global calibration for paper mill wastewater is provided as default configuration of the instrument. Usually high precision can be achieved using this standard parameter set. Calibrations to conventional parameters are now merely carried out for purposes of reference-checking. Only the spectral information can also be used for plant control.

UV/VIS spectrometer

The submersible UV/VIS spectrometer (Figure 1) is a spectrometric probe of about 0.6 m length and 44 mm diameter. It records light attenuation in the wavelength region between 200 nm and 750 nm and displays and/or communicates the result in real time. The instrument is a 2-beam 256 pixel UV/VIS spectrometer, with a Xenon lamp as a light source. The measurement takes place directly in-situ without sampling or sample treatment. Thus, measurement errors due to sampling, transport, storage, dilution etc. are not relevant. A single measurement typically takes about 15 seconds. The instrument is equipped with an auto-cleaning system using pressurised air. Due to the compact size the sensor can be easily
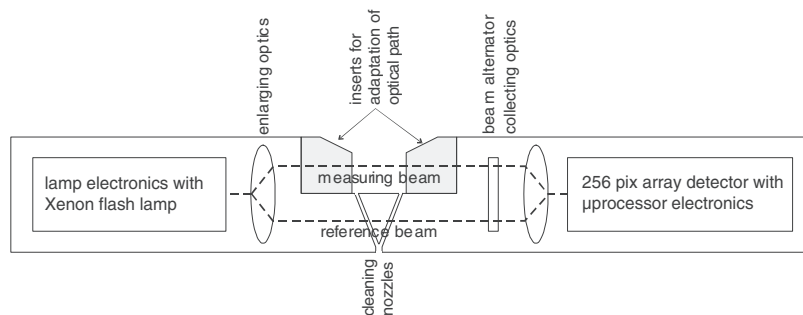
Figure 1 UV-VIS submersible spectrometer

applied in 2" bore holes, e.g. for groundwater monitoring (Langergraber *et al.*, 2002). An ex-proofed version is available for sewer applications.

The entire measurement procedure is controlled by on-board electronics which are included in the 44 mm tubular anodised aluminium housing. The communication is via RS232 or RS485 interface. The power supply can be by means of AC 220 V/50 Hz or DC 12–24 V, respectively. The low power consumption eases field application by means of battery or solar power supply. The probe has a water level meter and a data logger on board. The data logger is capable of storing complete absorption spectra of 1 month at a measuring interval of 30 minutes.

The path length can be adjusted from 2–100 mm opening a wide range of applications from ultra-pure waters (DOC > 10 µg/l) up to concentrated wastewaters with a COD of several 1,000 mg/l. A path length of 5 mm is usually used for wastewater applications. Spectrometric measurement methods are defined for single substances (e.g. nitrate, nitrite, benzene, phenol) as well as for surrogate parameters (SAC, turbidity/suspended solids, CODeq, TOCeq, DOCeq).

Turbidity compensation

Turbidity due to suspended substances causes light scattering, shading and thus influences absorption over the entire spectrum and is therefore an influencing factor on in-situ absorption measurements. Turbidity compensation has two tasks: the measurement of turbidity/suspended solid and baseline compensation for the measurement of dissolved substances. A mathematical equation has been developed which describes the relationship between scattering intensity and wavelength as a function of the particle diameter based on the basic relationships given by Huber and Frost (1998) and the well known spectral shape caused by suspended solids, which depends upon the wavelength with a factor λ^x, where x depends on the particle diameter. The turbidity compensation feature uses the original spectrum and estimates two parameters of the turbidity function. The results of the turbidity compensation have been shown to be very sensitive to the initial values of these parameters.

Sensor calibration

Chemometric models are used for correlating the concentrations of the required determinants to spectra. Direct chemometric models cannot be used for wastewater because there is no linear relation of the absorbance of a single determinant as required by the Lambert–Beer law. This is due to the parameters used for wastewater analysis (surrogate parameters, e.g. COD and TSS, are commonly used) and due to the special characteristics of wastewater (strong correlations between the various parameters, e.g. COD is strongly correlated with filtered COD and TSS). Therefore indirect chemometric models which are

based on estimating the calibration parameters from calibration mixtures have to be used. Using indirect chemometric models the validity of the Lambert–Beer law is no longer a prerequisite, the modelling of the background in a principal component becomes feasible, and systems of even highly correlated spectra can also be used for multi-component calibration (Otto, 1999). Additionally, the basic assumption for standard correlation problems, that reference measurements have to be error-free, is not required. (Danzer *et al.*, 2001). The applied model – partial-least-square regression (PLS) – especially accounts for concentration-spectra relationships and results in the most robust calibrations at present (Otto, 1999).

For the multivariate calibration procedure the entire evaluation of the spectra is used. The calibration model is built by means of PLS, various validation procedures and outlier tests to reach both high correlation quality and robustness. To perform PLS the spectra and the reference measurements have to be normalized. A recursive procedure includes the multivariate calibration with PLS, a multiple cross-validation, and the detection and elimination of outliers and is repeated until a good calibration result is obtained. The result of the calibration procedure is a recovery function. The recovery function is obtained by plotting the reference measurements (actual targets) vs. the predicted values (estimated targets). A more detailed description of the calibration procedure is given by Langergraber *et al.* (2003).

The broad range of available wavelengths allows high flexibility for the choice of the best correlating wavelengths for the calibration function and also for the avoidance of cross-sensitivities. This is an advantage compared to systems, which provide absorption measurements of a single or two wavelengths only.

The UV/VIS spectrometer provides a global calibration for the parameters of concern, but recalibration with local reference samples will significantly improve the performance (trueness and precision) for quantitative measurements. The local calibration is based on reference grab samples analysed for the parameters of interest. The local calibration can be performed without demounting of the probe. The experience showed that most of the time the reference data are the critical part of the whole calibration procedure. Therefore it is essential to guarantee the quality of the reference measurements (regarding reference analysis method, measurement range, sampling errors, identity of samples and randomisation of sampling) to obtain good calibration results.

Results and discussion

Typical UV/VIS spectra for paper mill wastewater

Figure 2 depicts typical and reproducible spectra at various measuring points of a paper mill wastewater treatment plant (influent and effluent of the activated sludge tank, and effluent of the secondary clarifier). The spectra increase steadily with decreasing wavelength, which is characteristic of the influence of particles. Only the relative maximum at 280 mm is distinct from the influence of the turbid substances, due to the absorbance by dissolved organic substances, mainly ligninic acids. A shoulder at this wavelength is usually caused by biodegradable carbon compounds. A comparison of the absorbance spectra of the influent and the effluents of the activated sludge tank and secondary clarifier respectively distinctly shows the decrease of this peak, indicating the biological degradation of the organic substances in the course of the treatment.

Calibration results

During the calibration period all different plant specific wastewater compositions have been observed. This could be reached by covering all operating conditions of the paper mill's production cycle. Table 1 summarises the obtained calibration results.
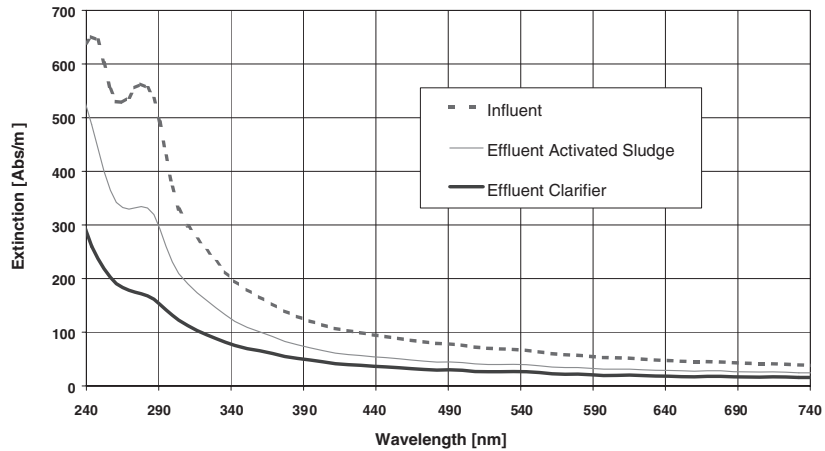
Figure 2 Typical spectra at various locations of a paper mill WWTP

Single wavelength calibration. The correlation coefficients obtained using a single wavelength calibration were poor. The highest correlation coefficient reached was $R^2 = 0.60$ (using the absorbance at 242 nm) for COD in the effluent of the clarifier. The measurement of nitrate nitrogen was not possible with a single wavelength. The results clearly show that single wavelength measurements cannot be used for paper mill wastewater.

Multivariate calibration procedure. For the global calibration that used data from three different paper mill wastewater treatment plants the obtained coefficients of determination were high except for effluent COD. However, the local calibration improved the correlation coefficient significantly and a correlation coefficient of $R^2 > 90\%$ could be reached. Only by using the multivariate calibration procedure was the measurement of NO_3-N possible. A calibration for TSS was not possible due to a systematic error in the laboratory method for TSS analysis during the calibration period.

Figure 3 shows the correlation between COD measured in the laboratory and the equivalent COD (CODeq) measured by the UV/VIS spectrometer. The squares show the data from this plant used for the global calibration, the circles are data obtained during the validation period. A change in the slope of the correlation function could be observed. The determined reason was not provable, a change in the operator performing the lab analysis and/or in the method of laboratory analysis for COD is suspected to have caused this change of the slope. This shows that a local calibration could be necessary for improving the trueness of the spectral data, if the locally used lab methods are said to be true. The local calibration for COD in this case was easily performed by the operator changing the slope of the correlation function.

Table 1 Correlation coefficients (R^2) for different calibration procedures

Location	Influent		Effluent		
Parameter	COD	Filtered COD	COD	Filtered COD	NO_3-N
Correlation with SAC254	0.25	0.22	0.58	0.53	[2]
Best single wavelength calibration[1]	0.27 (272)	0.27 (272)	0.60 (242)	0.59 (282)	[2]
Multivariate calibration – global[3]	0.63	0.58	0.48	0.76	0.87
Multivariate calibration – local	0.95	0.95	0.90	0.91	[4]

[1] Values in brackets give the wavelength showing the best correlation
[2] A single wavelength calibration was not possible for NO_3-N
[3] For the global calibration data from three paper mills were used
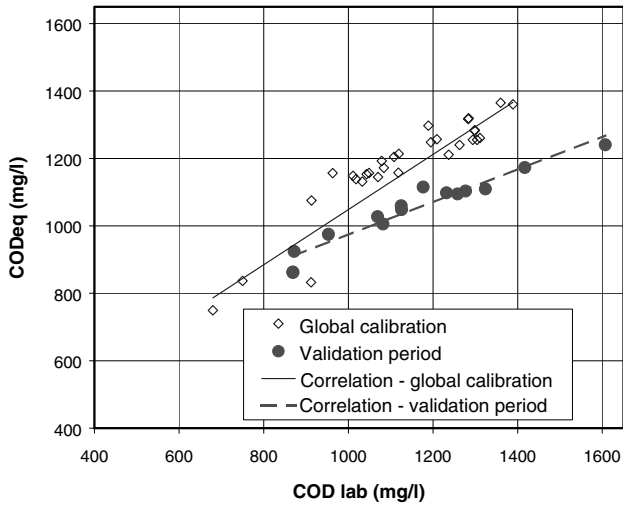[4] Not performed

Figure 3 Correlation between laboratory COD and CODeq for calibration and validation

Time series

Figure 4 and Figure 5 show time series for the validation period using the obtained local calibration for COD in the influent, and for COD and NO_3-N in the effluent respectively. The characteristics in the time series of COD and filtered COD are very similar for both influent and effluent. Due to the auto-cleaning function of the sensor no drift of the measurement data could be observed.

Conclusions

The presented results clearly show that in particular single wavelength measurements cannot be applied for paper mill wastewater. In general this is also true for wastewater. High coefficients of determination could be achieved for the global calibration for the UV/VIS spectrometer that uses the whole spectrum from 200 to 750 nm for the evaluation.
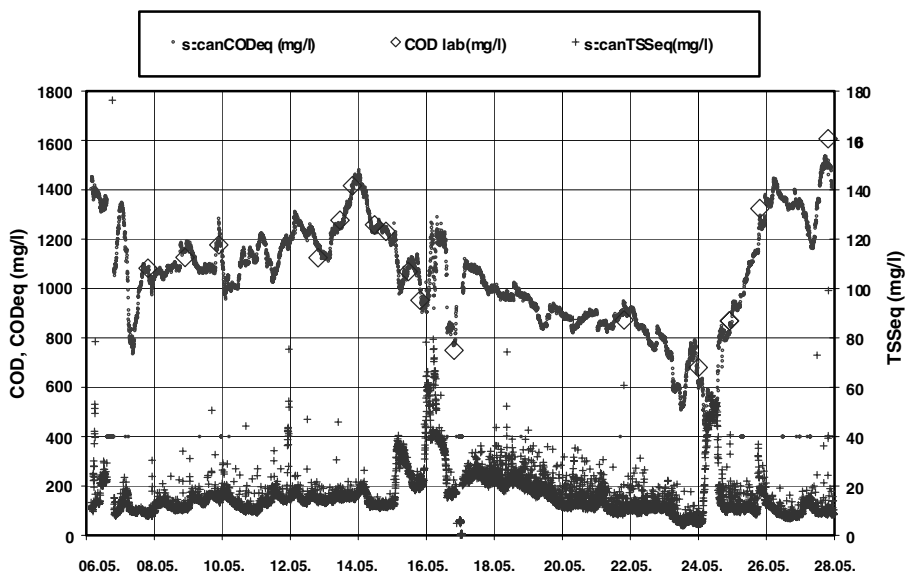

Figure 4 COD and TSS in the influent of the paper mill wastewater treatment plant
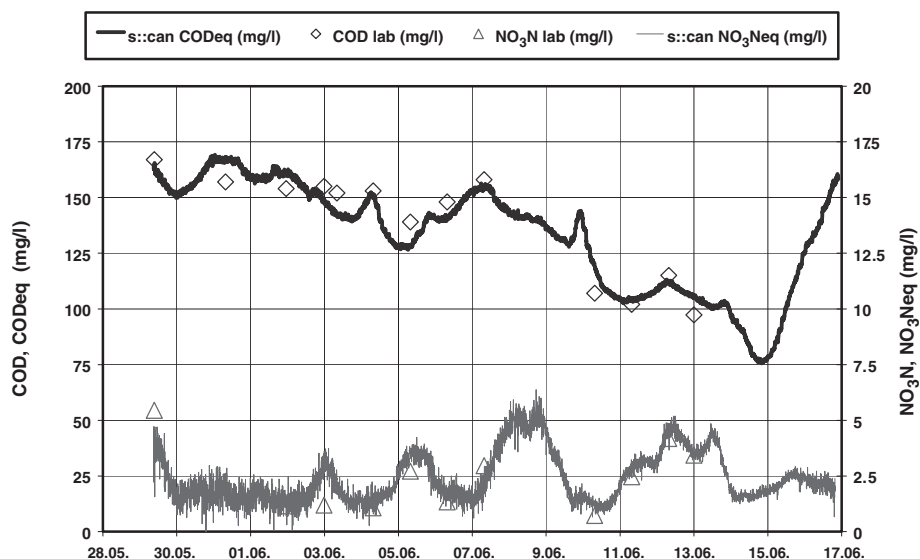
Figure 5 COD and NO₃-N in the effluent of the paper mill wastewater treatment plant

A local calibration, performed by the operator, increases the match for the validation lab results.

The instrument measures in-situ, directly in the process. Therefore no sampling, no sample preparation, and no reagents are required. The auto-cleaning system of the UV/VIS spectrometer which is operated with pressured air prevents trends in the time series due to film growth on the optical devices.

The experience has shown that a parameter describing the dissolved organic matter is particularly suitable for operation and/or control of the performance of a paper mill treatment plant. Regarding plant control it is suggested that only the overall spectral information is used for controlling the dosing of nutrients and for early warning of high loads. Calibrations to conventional parameters are now merely needed to fulfil effluent standards and additionally are carried out for purposes of reference checking.

Acknowledgements

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