I. Troch, F. Breitenecker, eds. ISBN 978-3-901608-35-3

OXYGEN UPTAKE RATE MEASUREMENTS AS A TOOL FOR DETERMINISTIC MODELLING OF PULP AND PAPER WASTEWATER TREATMENT PLANTS

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Abstract. Oxygen uptake rate measurements in laboratory experiments have been utilised for deterministic modelling of a biological wastewater treatment plant treating pulp and paper mill wastewater. The measurements have been used to estimate the maximum oxygen uptake rate of the sludge of the plant that is the single most important process parameter at most pulp and paper wastewater treatment plants where only COD is removed. Together with routine measurement from the influent and effluent uptake rate measurements have also been used to estimate the fractions of the incoming COD to the plant. The model calibration procedure is also presented.

1 Introduction

Deterministic modelling of wastewater treatment plants took a great leap forward in 1987 when the first IAWPRC model, Activated Sludge Model no 1 (ASM1) was released [3]. Several commercial models have utilised the modelling concepts. During the next decades new models have been introduced, bench marking of the different models made and especially universities have started to utilise the tools in research. In contrast, the practical use of modelling was and is still limited. The main reason is assumed to be that the basic requirements in terms of measurements of wastewater and sludge characterisation is too time and economy demanding. Further, the number of good examples of real economical savings or improvement of treatment based on modelling is still limited. The present paper is an attempt to present a modelling strategy for wastewater treatment plants within the pulp and paper industry based on simple measurements of oxygen uptake rate (OUR) combined with existing standard measurements programs from the treatment plants. The strategy is implemented at the treatment plant of Stora Enso Fine Paper at Oulu pulp mill.

1.1 Strategy for model calibration

Activated sludge plants for treatment of wastewater from the pulp and paper industry are normally made for COD removal only since the content of nitrogen and phosphorus is so low that additional nutrients have to be added in order to get biological treatment without severe nutrient limitation problems. This enables a rather simple strategy for calibration of deterministic models as only one biological process – degradation of organic matter is dominating. Further when only COD degradation needs to be taken into account the amount and degradability of the organic matter in the influent is the only real important substrate information needed to characterise the wastewater. Oxygen uptake rate measurements are a valuable tool for estimation of the central parameter in COD degradation and in combination with routine measurements from the influent and effluent from the plants a reasonable estimate of the COD degradability can be made. The model of the treatment plant can easily be calibrated to have the same maximum oxygen respiration rate as found in the experiment and with the proper calibration of the incoming COD in fractions of degradability the model parameters domination the function of the plant has been modelled. In the present paper details of the procedures are presented together with measurements from one full scale plant.

1.2 The wastewater treatment plant of Stora Enso Fine Paper at Oulu pulp mill

The pulp mill of Stora Enso Fine Paper at Oulu produces about 340 000 tons of pulp annually and the activated sludge plant treats an average of 32 000 m^3 wastewater per day. Also small amounts of wastewater from chemical plants are treated. The treatment plant consists of a primary clarifier, an equalization basin, an aeration basin and a secondary clarifier. The primary clarifier is used to remove easily settling solids. Soluble COD is consumed in the aeration by microorganisms. The plant lay-out is shown in Figure 1 and the basic information about the plant is found in Tables 1 and 2.

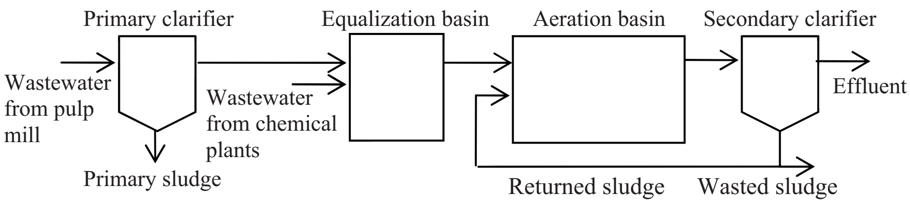

Figure 1. Process layout of the wastewater treatment plant at Stora Enso Fine Paper, Oulu

	Number	Area (m^2)	Volume (m^3)
Primary clarifiers	1	1963	9100
Equalization basins	1		11 000
Activated sludge basins	1	3400	25 000
Secondary clarifiers	1	2827	12 150

Table 1. Technical information of the wastewater treatment plant at Stora Enso Fine Paper, Oulu

	Influent	After primary sedimentation	Effluent	Discharge limits (kg/d)
Flow (m^3/d)	32 000		32 000	
COD (mg/l)	1600	1200	500	45 000
BOD_7 (mg/l)	440	270	17	
Tot-N (mg/l)	7		3.3	500
Tot-P (mg/l)	1.7		0.7	55
Temperature (ºC)	42	40		

Table 2. Characteristics of the influent, after primary sedimentation, effluent and discharge limits at the wastewater treatment plant at Stora Enso Fine Paper, Oulu. Values are yearly averages

2 Materials and methods

2.1 Oxygen Uptake Rate measurements

Oxygen Uptake Rate measurements were made as described in [2]. Two different types of measurements were made. The maximum OUR of the sludge has been made with addition of acetate as carbon source. OUR measurement with addition of the wastewater from the plant has been made in order to contribute to the wastewater characterisation. The oxygen respiration by heterotrophic bacteria is easy to measure. By determination of the oxygen consumption during a limited period of time, OUR can be found. The measurements can be performed in various ways and many types of equipment are available on the market, but the fundamental idea behind the measurement is illustrated in Figure 2.

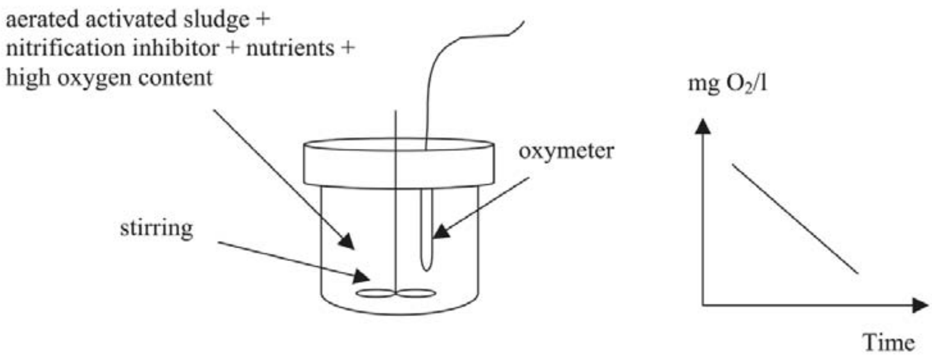

Figure 2. Illustration of the principle of the OUR measurements

For OUR measurements, aerated activated sludge containing necessary nutrients and nitrification inhibitor (in order to eliminate oxygen consumption due to nitrification) is used. During some minutes the decrease of oxygen concentration in the sludge solution is registered. The relationship between the decreases in oxygen concentration and time is normally found to be linear as shown in Figure 2 and the oxygen uptake rate is determined by calculations of the slope of the curve. If the oxygen uptake rate is related to suspended solids or the volatile suspended solids, the specific oxygen uptake rate is obtained. By alternating the aeration of the sludge in intervals it is possible to follow OUR during a longer period and the development in OUR as COD degradation takes place can be followed as shown in Figure 3. The figure shows the specific OUR for activated sludge from Källby WWTP in Lund with addition of acetate in order to find the maximum OUR for that specific sludge.

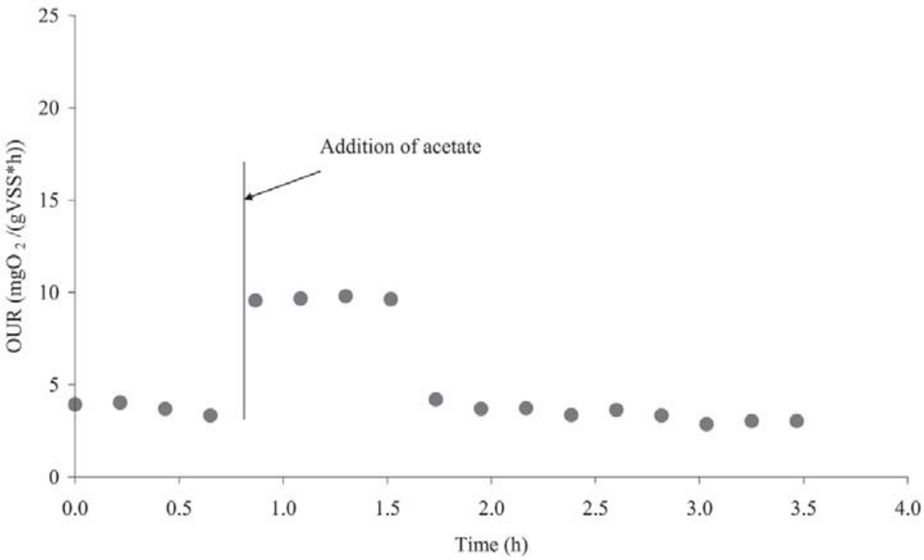

Figure 3. Oxygen uptake rate graph/respirogram for activated sludge from Källby WWTP in Lund, [2]

Besides the maximum respiration rate of the sludge OUR can be used for characterization of the degradability of the incoming wastewater simply by making OUR measurements with the relevant sludge and wastewater. The oxygen respiration will reflect the degradability as shown in the illustration in Figure 4. Combined with measurements of COD in the influent and effluent a reasonable estimate of the different fractions of COD can be made.

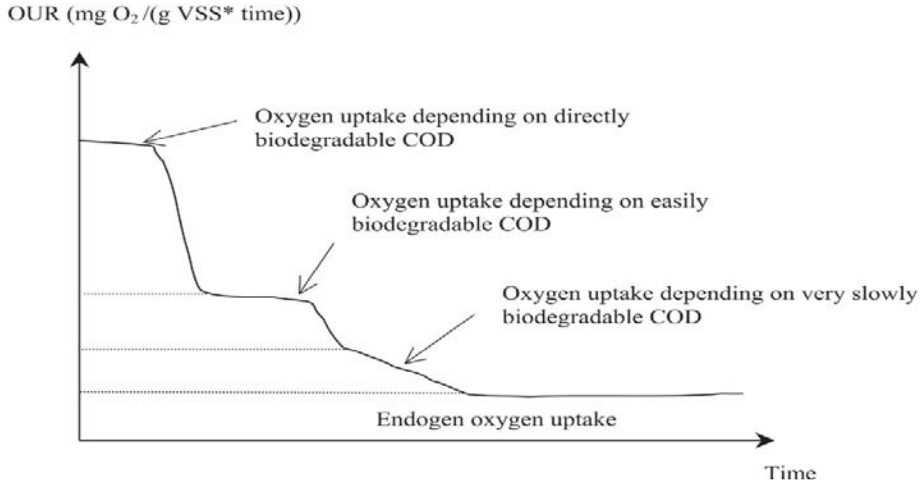

Figure 4. Typical development of the respiration rate as a function of time for wastewater according to [4]

COD fractionation is described many times, and it can be found for example in [7]. The readily biodegradable COD can be directly taken up by the biomass without further hydrolysis in the ASM1 model. The readily biodegradable substrate concentration can be calculated utilizing the area beneath the OUR curve and the heterotrophic yield coefficient by

$$S_S(0) = \frac{1}{1-Y_H}\left(\int_0^{t_{fin}} r_{ex}\,dt\right) \tag{1}$$

where $S_S(0)$ is the directly biodegradable substrate initially present in the biomass and wastewater, Y_H is the heterotrophic yield coefficient, t_{fin} is the end point of integration where the readily biodegradable substrate is completely oxidized and r_{ex} is the exogenous respiration rate.

Slowly biodegradable substrate (X_S) is another source of carbon for the biomass in the ASM1 model. Unlike the readily biodegradable substrate, it cannot pass the cell membrane directly and must first be hydrolyzed to S_S. Slowly biodegradable substrate can also be calculated using (1) by choosing the start point of integration where the S_S is completely oxidized and the end point where the X_S is completely oxidized.

Heterotrophic yield coefficient (Y_H) is required for calculating the biodegradable fractions of COD. Y_H can also be evaluated using respirometry and COD measurements using the following equation:

$$Y_H = \frac{COD^{Degraded} - \int r_{ex}(t)dt}{COD^{Degraded}} \tag{2}$$

where $COD^{Degraded}$ is the difference initial and final COD concentration of the mixture of wastewater and biomass.

The most straightforward way for evaluating influent wastewater soluble inert COD is to estimate the amount of COD that is constant in the secondary clarifier effluent. In a well functioning activated sludge treatment plant the effluent contains very little solids, and therefore the inert COD is assumed to be soluble. [5]

2.2 Methods of analysis

Measurements of COD filtrated and VFA have been carried out for filtered samples. Cellulose filters No. 1002 with a filtering rate of 250 ml/min were used for all filtration of samples. COD was analysed using Dr Lange tests LCK 114. All readings of Dr Lange analyses were performed using a Dr Lange LP2W. SS and VSS were analysed according to Standard Methods [1]. VFA was analysed by means of gas chromatography, Agilent 6850 Series GC System.

3 Results and discussion

3.1 OUR measurements and wastewater characterisation

Results from the OUR measurements with the sludge and wastewater from the activated sludge treatment plant of Stora Enso Fine Paper at Oulu pulp mill are not yet available for the deadline of this paper, and therefore results from OUR experiments with the sludge and wastewater from similar treatment plant of Stora Enso Fine Paper at Nymölla pulp and paper mill are presented. Similar experiments with the sludge and wastewater from the Oulu mill are underway, and the results will be available for the presentation of this paper.

Sludge was sampled from the effluent of the aeration basin, and wastewater from the influent of the aeration basin. The oxygen uptake rate of the sludge was measured as a function of time as described in Section 2. Temperature of the aeration basin was measured to be 30 ºC at the time of the sampling, and this temperature was maintained during the OUR measurements. Two reactors were filled with 450 ml of sludge and 450 ml of water, and 72 ml COD from acetate was used as a carbon source in one reactor and 192 ml COD from wastewater in the other. Suspended solids concentration, total COD and soluble COD were also measured from both the sludge and the wastewater. Results of the suspended solids and COD measurements are displayed in Table 3. Results of the oxygen uptake rate measurements with acetate as the carbon source are presented in Figure 5 and with wastewater as the carbon source are presented in Figure 6.

Measurement	Sludge	Wastewater
Total COD (mg/l)	7290	1920
Filtered COD (mg/l)	420	1830
Suspended solids (g/l)	6.3	0.08

Table 3. COD and suspended solids measurements of the sludge and wastewater from Nymölla pulp and paper mill

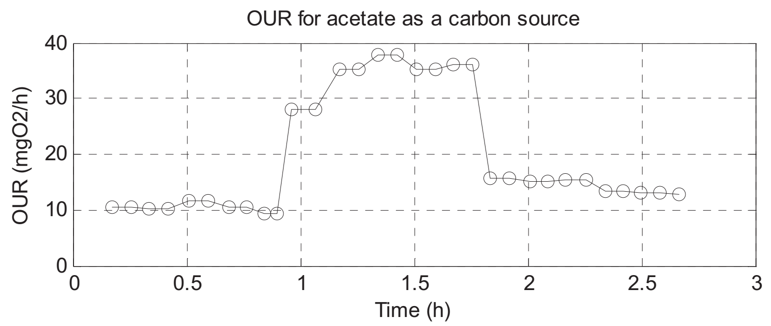

Figure 5. OUR measurements for estimation of the maximum specific respiration rate of the sludge

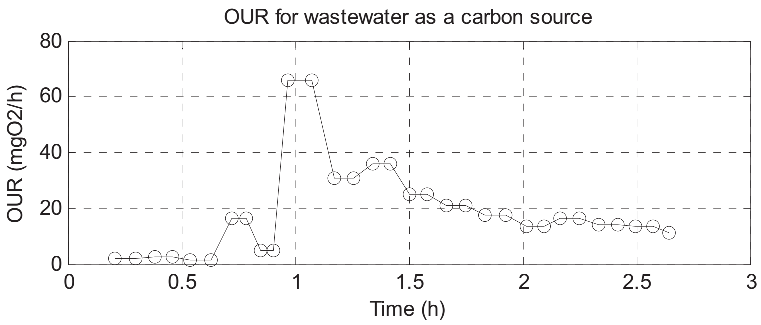

Figure 6. OUR measurements for estimation of the COD fractions

Acetate should be very easily degradable substrate, and is commonly used for determining the maximum respiration rate of the sludge. In this case, however, the sludge has adapted to utilizing different carbon compounds present in the pulp mill wastewater, and respiration rate for acetate is lower than maximum rate for wastewater. Therefore the maximum specific respiration rate can be found from the OUR measurements with wastewater. The maximum respiration rate was found to be 27.8 mg O_2 / gVSS · h.

Heterotrophic yield coefficient is required to calculate the biodegradable COD fractions with (1). A typical value for heterotrophic yield coefficient according to [6] is Y_H = 0.60 (g biomass)/(g COD used). This typical value results in very low fractions of biodegradable COD, and therefore the yield coefficient was calibrated utilising OUR measurements with acetate as the carbon source. In this calibration procedure all COD from acetate was assumed to be readily biodegradable. The heterotrophic yield coefficient value was then adjusted until biodegradable fraction calculated with (1) was 100%. The calibrated value of heterotrophic yield coefficient was estimated to be $Y_H = 0.75$.

Fractions of readily and slowly biodegradable COD were estimated from the OUR measurements with wastewater as the carbon source presented in Figure 6. The areas below the OUR curve corresponding to readily degradable and slowly degradable substrate excluding the endogenous respiration were calculated using numerical integration. Biodegradable COD fractions of the wastewater were calculated according to (1), and results are presented in Table 4.

As can be seen from Table 3, almost all COD (95%) is soluble. Therefore estimating particulate inert COD is not of great significance in this case. Soluble inert COD was estimated from the secondary clarifier effluent during normal operation, when very little solids were escaping from the clarifier. The estimated soluble inert COD is presented in Table 4.

	Start point of integration (h)	End point of integration (h)	Fraction of COD
Readily biodegradable	0.965	1.34	30.6%
Slowly biodegradable	1.34	2.02	11.8%
Soluble inert			45%
Other fractions and uncertainty			12.6%

Table 4. Results of the COD fractionation

Estimated biodegradable fractions seem reasonable as they make most of the COD that is not soluble inert. Rest of the total COD that doesn't belong to the fractions presented in Table 4 is very slowly biodegradable COD and particulate inert COD that were not measured in this study. Also the soluble inert COD may have varied from the average value presented in Table 4, narrowing the difference between total COD and the sum of estimated fractions even further.

3.2 Modelling

Building the plant and adding all physical properties is straightforward in commercial simulation programs. The wastewater characterisation can be added based on the principles above. Model constants can be changed in order to reach the same maximum specific oxygen respiration found in the experiments. Typically the maximum growth rate of heterotrophic bacteria is the only model constant that is needed to adjust in order to get a reasonable calibration. Further a fine tuning of the model can be based on comparison of modelled results with measured data, and making final changes to influent characteristics and parameters based on this comparison. The calibrated model may next be used for a number of purposes such as trouble shooting or for evaluation of different control strategies and optimised process operation. For plants treating wastewater from pulp and paper mills different nutrient control strategies could be a good choice for utilisation of the calibrated deterministic model.

4 Conclusions

Practical use of deterministic models of the activated sludge process needs to be based on calibration of the important model parameters specific for the actual type of the plant and the intended use. Also the incoming wastewater has to be characterised with respect to the significant fractions of substances. A model of a biological wastewater treatment plant treating wastewater from a pulp and paper mill only needs information about the oxygen uptake rate of the sludge and the fractions of the COD in the wastewater with respect to degradability. A simple Activated Sludge Model calibration procedure based on oxygen uptake rate measurements is presented. Both model parameter optimisation and COD fractionation is made utilizing only OUR, soluble and total COD, and suspended solids measurements. The described calibration procedure has been tested and found to be feasible with samples from Stora Enso Fine Paper Nymölla pulp and paper mill, and will be used in a more comprehensive measurement campaign with Stora Enso Fine Paper Oulu pulp mill.

5 Acknowledgements

This research was supported by the Finnish Funding Agency for Technology and Innovation (Tekes), Kemira Oyj, Stora-Enso Oyj and UPM-Kymmene Oyj.

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