Modelling carbon oxidation in pulp mill activated sludge systems: calibration of Activated Sludge Model No 3

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Abstract Activated Sludge Model No 3 (ASM3) was chosen to model an activated sludge system treating effluents from a mechanical pulp and paper mill. The high COD concentration and the high content of readily biodegradable substrates of the wastewater make this model appropriate for this system. ASM3 was calibrated based on batch respirometric tests using fresh wastewater and sludge from the treatment plant, and on analytical measurements of COD, TSS and VSS. The model, developed for municipal wastewater, was found suitable for fitting a variety of respirometric batch tests, performed at different temperatures and food to microorganism ratios (F/M). Therefore, a set of calibrated parameters, as well as the wastewater COD fractions, was estimated for this industrial wastewater. The majority of the calibrated parameters were in the range of those found in the literature.

Keywords Activated sludge; ASM3; CTMP; modelling; pulp and paper; wastewater characterization

Introduction Although simulation of the activated sludge process is an important part of the design and operation of wastewater treatment plants, the modelling process is far from being perfected. Many conceptual models are developed each year to describe the processes involved in treating the organic material in different types of wastewaters and to predict treated effluent characteristics. New models have replaced early models that were originally labeled as “general models” by their authors.

Compared with the many models that have been developed for application to municipal wastewater, the simulation of pulp and paper wastewater treatment is at an early stage. The particular characteristics of pulp and paper wastewaters, such as high organic content, low nutrient content, high proportion of readily biodegradable substrate, and high temperature and toxicity, may require the use of an activated sludge model that is different from the models used for municipal wastewater, or should require at least a specific calibration of an existing model.

Previous works carried out at the University of British Columbia have made some advances in this task, calibrating Activated Sludge Model No 1 (ASM1) to bleached kraft pulp mill effluents (BKME) (Stanyer, 1997), and building a new model based on Activated Sludge Model No 2 (ASM2) for chemi-thermo mechanical pulping (CTMP) effluents (Sreckovic, 2001). However, the parameter values obtained by both researchers were significantly different from each other, as well as from municipal wastewater typical values, especially those found by Sreckovic (2001). Therefore, further work was required in order to check the similarity or dissimilarity of the pulp and paper model parameters in relation to the widely available information about domestic sewage.

The objective of this research was modelling of an activated sludge system treating CTMP wastewaters at a pulp and paper mill located in Port Alberni, British Columbia, and calibrating the model for these particular effluents. For this purpose, the Activated Sludge
Model No 3 (ASM3) (Gujer et al., 1999) was selected for a variety of reasons. First, there is significant evidence that supports the basic assumptions of the model, mainly about the accumulation of storage products inside the cell (Carucci et al., 2001; Dircks et al., 2001; Goel et al., 1998, 1999; Van Loosdrecht and Heijnen, 2002; Van Loosdrecht et al., 1997). Second, ASM3 has been recommended for wastewater treatment plants (WWTPs) treating industrial wastewater with a high concentration of chemical oxygen demand (COD), where the storage of readily biodegradable substrate is dominant (Koch et al., 2000), which is the case for the WWTP of interest. Finally, it has been proposed that metabolic reactions inside the microbial cells appear to continue for a prolonged period of time in sludge from a paper mill (Franta et al., 1994b), which suggests the relevance of stored products in the treatment of wastewaters of this type.

Three measurement campaigns were undertaken in order to calibrate the model properly. The most sensitive parameters, as well as the wastewater influent characteristics, were evaluated in batch tests using fresh wastewater and sludge. The analyses were completed using both respirometric and analytical laboratory techniques. The least sensitive parameters were not calibrated, so the use of ASM3 would require assuming those parameters from the literature.

Materials and methods

Port Alberni wastewater treatment plant
The activated sludge system located in Port Alberni treats the paper mill effluents generated in the following processes of the NorskeCanada Port Alberni Division pulp mill: groundwood, paper mill, CTMP, power boiler and woodroom. The wood used in the pulping process is 100% softwood. The bleaching process uses a sequence of hydrogen peroxide, sodium hydrosulfite, oxygen, and caustic soda. The WWTP consists of a pH adjuster, primary clarifier (not modeled), five complete mix bioreactors in series (“1A” and “1B” of 2,125 m³ each, and “2”, “3” and “4” of 5,250 m³ each), and a secondary clarifier. A more detailed description of the plant can be found in Koning et al. (1994).

The plant treats an average of 74,000 m³ d⁻¹, with the following average influent characteristics (primary effluent): COD of 594 g m⁻³, BOD of 250 g m⁻³, TSS of 27 g m⁻³, ammonia equal to zero, pH of 7.2, and temperature of 32°C. Nitrogen in the form of ammonia and urea is added to the recycle sludge in order to supply the nutrient requirements of the bacteria. Phosphorus is not added in the plant but it is added upstream, so its concentration is not limiting for the microorganisms.

Analytical methods
Total suspended solids (TSS), volatile suspended solids (VSS) and COD concentrations were determined according to Standard Methods (APHA et al., 1995). The soluble COD (COD₅) fraction was filtered using 0.45 µm pore size filters. TSS and VSS concentrations were measured using 1.5 µm pore size filters, equivalent to the filters used by the mill personnel. The respirometric batch tests were performed in a typical respirometer (i.e. as in Kappeler and Gujer, 1992), continually stirred. The dissolved oxygen (DO) probe (model YSI 5739, submergible) was connected through the DO meter (YSI model 52) to a computer, where the DO concentrations were recorded. The oxygen uptake rate (OUR) was calculated as the slope of a linear regression (least square method) of the DO concentrations. All the tests were performed with the addition of 10 g m⁻³ of nitrification inhibitor (Hach, formula 2533).

Batch test procedures
Two different types of batch tests were performed: for measuring the endogenous
respiration rate, a sample of sludge was aerated for several days, while measuring the OUR twice a day; and for measuring most of the remaining parameters, a sample of sludge was mixed with a sample of wastewater, and the OUR was monitored approximately every 7 minutes over a period of a few hours (2–6 hours). Different relative volumes of wastewater and sludge controlled the food to microorganism ratios (F/M) of the batch tests. Before starting each test, the sludge sample was aerated for several hours in order to achieve an endogenous state. The wastewater itself was aerated for several minutes, and the OUR, COD and CODS were measured for both wastewater and sludge. During the test, the OUR was monitored by periodically raising the DO to 6 g O2 m⁻³, switching the air off and recording the decrease in DO until it reached 4 g O2 m⁻³, at which point the air was switched on again and the cycle repeated (similar to the method proposed by Randall et al. (1991)). COD and CODS were measured again at the end of the test. The wastewater samples were collected at the primary clarifier outlet, and the sludge samples used for respirometric measurements were collected from the aeration basins “1A” and “4” of the plant.

Results and discussion

Yield coefficients estimation

The coefficient $Y_{STO}$ was estimated using the method proposed by Karahan-Gul et al. (2002), using Eq. (1). The term $\int OUR_{STO}$ refers to the oxygen used during the storage process, which can be graphically represented by the area under the curve shown in Figure 1.

$$Y_{STO} = 1 - \int OUR_{STO}/COD \text{ degraded}$$  \hspace{1cm} (1)

The COD degraded was calculated as the difference between the COD$_S$ at the beginning and at the end of the batch test. Since the duration of the test was relatively short, it was assumed that all the COD degraded was used for storage and therefore, was only $S_S$. The tests were performed with a relatively high F/M ratio (between 0.5 and 0.8) in order to obtain a sufficient number of OUR measurements during the storage stage to minimize the error in the calculation of $Y_{STO}$, as was suggested by Karahan-Gul et al. (2002), but lower than 2 to prevent mixed culture microorganisms from undergoing substantial multiplication (Chudoba et al., 1992). Five measurements gave an average $Y_{STO} = 0.90$, with a range between 0.85 and 0.95. The results are presented in Table 1.

The coefficient $Y_H$ was estimated based on the observed yield coefficient ($Y_{OBS}$), using Eq. (2). $Y_{OBS}$ is equivalent to $Y_H$ in ASM1, and represents the final amount of $X_H$ produced per unit of $S_S$ after all $X_{STO}$ is consumed. The value of $Y_{OBS}$ can be determined also by respirometry using Eq. (3). The tests to determine $Y_{OBS}$ were performed at very low F/M ratios (0.01–0.02) in order to ensure that all $X_{STO}$ was transformed into $X_H$ during the test.

**Figure 1** The shaded area represents the oxygen consumed by the “observed” growth process during a low F/M batch test.
The amount of oxygen utilized for growth and storage (OUR OBS) is shown graphically in Figure 1.

The amount of $S_S$ consumed during the low F/M tests was calculated using Eq. (1) rearranged as Eq. (4), and using the value of $Y_{STO}$ calculated previously. Two replicate respirographs were used for estimating the value of $Y_{OBS}$, with identical results ($Y_{OBS} = 0.68$; see Table 2). Therefore, the calibrated value for $Y_H$ was calculated as 0.76 g $X_H$ g$^{-1} X_{STO}$.

\[
Y_H = Y_{OBS} / Y_{STO}
\]

(2)

\[
Y_{OBS} = 1 - \int_0^{OUR_{STO}} / S_S \text{ consumed}
\]

(3)

\[
S_S \text{ consumed} = \int_0^{OUR_{STO}} / (1 - Y_{STO})
\]

(4)

Wastewater characterization

Inert soluble organic material ($S_I$). It is important to note that the so-called inert fraction of wastewater may not be totally inert, but depends on the degree of treatment reached by the specific WWTP analyzed. Therefore, for the purpose of modeling a particular WWTP, the effluent COD$_S$ (COD$_{S,eff}$) is an approximation of the influent $S_I$ ($S_{I,in}$) for a low loaded activated sludge plant (Metcalf and Eddy, 2003; Sollfrank et al., 1992). Further, since no generation of soluble inerts was considered ($f_{S_I} = 0$), the COD$_{in}$ was the only source of $S_I$ considered in this model calibration.

Since only the biodegradable components can be estimated by respirometry (Vanrolleghem et al., 1999), COD tests were performed for quantifying $S_I$. The COD$_{S,eff}$ was assumed to be equal to $S_{I,in}$ so COD$_{S,eff}$ was divided by COD$_{in}$ of a sample taken 16 hours before (corresponding to the hydraulic retention time of the complete WWTP) in order to obtain the $S_{I,in}$ fraction. $S_I$ was estimated to be between 0.11 and 0.17 times COD$_{in}$, with an average of 0.14. Table 3 presents the results of the wastewater characterization of the soluble COD fractions.

Readily biodegradable organic substrates ($S_S$). The $S_S$ fraction was estimated by two different methods. A first estimation of $S_S$ was required in order to calculate the yield coefficients ($Y_{STO}$ and $Y_H$), so the reduction in COD$_S$ within a batch test was assumed to be equal to the $S_S$ initially present in the sample ($f_{S_S,in} = 0.49$, based on tests 7-1, 7-3, 8-1, 8-3, and 9-1 in Table 3). Once the yields were calculated, a second set of $S_S$ estimations was

<table>
<thead>
<tr>
<th>Test</th>
<th>F/M (g COD/g VSS)</th>
<th>OUR$_{STO}$ (g O$_2$ m$^{-3}$)</th>
<th>$S_S$ consumed (g $S_S$ m$^{-3}$)</th>
<th>$Y_{STO}$ (g $X_{STO}$ g$^{-1} S_S$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-1</td>
<td>0.54</td>
<td>35.4</td>
<td>328</td>
<td>0.89</td>
</tr>
<tr>
<td>7-3</td>
<td>0.85</td>
<td>20.8</td>
<td>285</td>
<td>0.93</td>
</tr>
<tr>
<td>8-1</td>
<td>0.75</td>
<td>27.9</td>
<td>263</td>
<td>0.89</td>
</tr>
<tr>
<td>8-3</td>
<td>0.74</td>
<td>11.7</td>
<td>226</td>
<td>0.95</td>
</tr>
<tr>
<td>9-1</td>
<td>0.90</td>
<td>43.6</td>
<td>297</td>
<td>0.85</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test</th>
<th>F/M (g COD/g VSS)</th>
<th>OUR$_{OBS}$ (g O$_2$ m$^{-3}$)</th>
<th>$S_S$ consumed (g $S_S$ m$^{-3}$)</th>
<th>$Y_{OBS}$ (g $X_H$ g$^{-1} S_S$)</th>
<th>$Y_H$ (g $X_H$ g$^{-1} X_{STO}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>0.013</td>
<td>17.0</td>
<td>50.8</td>
<td>0.68</td>
<td>0.76</td>
</tr>
<tr>
<td>5-2</td>
<td>0.023</td>
<td>26.7</td>
<td>79.8</td>
<td>0.68</td>
<td>0.76</td>
</tr>
</tbody>
</table>
made by respirometry, using Eq. (4) (tests 4-1, 4-2, 5-1, and 5-2 in Table 3). Finally, the estimation obtained using respirometry \( f_{SS,in} = 0.49 \) was selected as the calibrated value for \( f_{SS,in} \), since this is the method proposed by ASM3 for estimating this parameter. High concentrations of readily biodegradable COD, in comparison with municipal wastewaters, have been observed in pulp mill effluents before (Babuna et al., 1998; Franta et al., 1994a,b).

Slowly biodegradable substrates \( (X_S) \) and particulate inert organic material \( (X_I) \). The particulate material only accounted for 16% of the COD_{in} in this system (see Table 3), so its relative importance is low compared with activated sludge systems treating municipal wastewater, for which the particulate fraction is around 44% of the COD_{in} (ASM3 default value).

\( X_S \), as defined in ASM3, is high molecular weight, colloidal and particulate organic substrate which must undergo hydrolysis before it is available for degradation. It is generally assumed that all \( X_S \) is retained on a 0.45 \( \mu \)m membrane filter (Gujer et al., 1999). However, based on the previous results, there was a significant portion of COD_{S} that was not \( S_I \) nor \( S_S \), so it was assumed to be the colloidal portion of \( X_S \). This colloidal fraction, sometimes called rapidly hydrolysable COD (Henze, 1992; Sollfrank and Gujer, 1991), may not be neglected in this wastewater characterization as it accounts for approximately 21% of the COD_{in}.

In the same way that the influent soluble inerts are not totally inert, the determination of the \( X_I/X_S \) ratio can present some problems, and it is very sensitive to the solids retention time (SRT) of the system (Brdjanovic et al., 2000; Van Veldhuizen et al., 1999). Therefore, the \( X_I/X_S \) ratio was calculated based on a TSS mass balance, as proposed by Hulsbeek et al. (2002) and Meijer et al. (2001). Using this method, \( f_{XI,in} \) was estimated by comparing the predicted sludge production rates with the measured rates as a function of the SRT. This full-scale sludge production mass balance was performed using a five day data period, corresponding to the week of the first measuring campaign. The estimated sludge production rate, and the measured sludge production rate were calculated using Eqs (5) and (6) respectively.

### Table 3  Wastewater characterization of soluble COD fractions

<table>
<thead>
<tr>
<th>Test</th>
<th>( T(\degree C) )</th>
<th>COD_{in} (g COD m(^{-3}))</th>
<th>COD_{S,in} (g COD m(^{-3}))</th>
<th>Wastewater tested</th>
<th>( S_S^a ) (g COD m(^{-3}))</th>
<th>( S_I/CoD_{in} )</th>
<th>COD_{S,in}/COD_{in}</th>
<th>S_{IX}/COD_{in}</th>
<th>( S_{IX}/S_{S,in} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 4-1</td>
<td>24.5</td>
<td>635</td>
<td>512</td>
<td>Filtered</td>
<td>340</td>
<td>0.54</td>
<td>0.81</td>
<td>0.14</td>
<td>0.68</td>
</tr>
<tr>
<td>Test 4-2</td>
<td>24.5</td>
<td>647</td>
<td>564</td>
<td>Unfiltered</td>
<td>388</td>
<td>0.60</td>
<td>0.87</td>
<td>0.16</td>
<td>0.76</td>
</tr>
<tr>
<td>Test 5-1</td>
<td>41.5</td>
<td>709</td>
<td>611</td>
<td>Filtered</td>
<td>559</td>
<td>0.79</td>
<td>0.86</td>
<td>0.14</td>
<td>0.93</td>
</tr>
<tr>
<td>Test 5-2</td>
<td>40.5</td>
<td>709</td>
<td>611</td>
<td>Filtered</td>
<td>337</td>
<td>0.48</td>
<td>0.86</td>
<td>0.14</td>
<td>0.62</td>
</tr>
<tr>
<td>Test 7-1</td>
<td>24.5</td>
<td>775</td>
<td>673</td>
<td>Filtered</td>
<td>335</td>
<td>0.43</td>
<td>0.87</td>
<td>0.14</td>
<td>0.57(b)</td>
</tr>
<tr>
<td>Test 7-2</td>
<td>22.5</td>
<td>775</td>
<td>673</td>
<td>Unfiltered</td>
<td>249</td>
<td>0.32</td>
<td>0.87</td>
<td>0.14</td>
<td>0.46(b)</td>
</tr>
<tr>
<td>Test 8-1</td>
<td>29.5</td>
<td>664</td>
<td>604</td>
<td>Filtered</td>
<td>233</td>
<td>0.35</td>
<td>0.91</td>
<td>0.14</td>
<td>0.49(b)</td>
</tr>
<tr>
<td>Test 8-3</td>
<td>31.5</td>
<td>664</td>
<td>604</td>
<td>Unfiltered</td>
<td>187</td>
<td>0.28</td>
<td>0.91</td>
<td>0.14</td>
<td>0.42(b)</td>
</tr>
<tr>
<td>Test 9-1</td>
<td>21.6</td>
<td>845</td>
<td>705</td>
<td>Unfiltered</td>
<td>523</td>
<td>0.62</td>
<td>0.83</td>
<td>0.15</td>
<td>0.77</td>
</tr>
</tbody>
</table>

\( ^a \) \( S_S \) presented in this table corresponds to estimations made by respirometry

\( ^b \) \( f_{SI,in} \) was assumed to be equal to 0.14

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\[ P_{X,\text{estimated}} = Q_{\text{in}} \cdot [X_{I,\text{in}} + (1 + f_{X,I,\text{in}} \cdot b_H) \cdot Y_{\text{OBS}} \cdot (\text{COD}_{\text{in}} - S_{I,\text{in}} - X_{I,\text{in}})/(1 + b_H \cdot \text{SRT})] \quad (5) \]

\[ P_{X,\text{measured}} = Q_{\text{waste}} \cdot X_{\text{waste}} \quad (6) \]

\[ X_{S,\text{in}} = \text{COD}_{\text{in}} - S_{S,\text{in}} - S_{I,\text{in}} - X_{I,\text{in}} \quad (7) \]

The result, which minimized the error sum of the squares between the sludge production estimated and measured, was an estimation of \( f_{X,I,\text{in}} \) equal to 0.07 of \( \text{COD}_{\text{in}} \). Subsequently, the total slowly biodegradable fraction was estimated using a \( \text{COD}_{\text{in}} \) balance (Eq. (7)), resulting in an estimation of \( f_{X,S,\text{in}} \) equal to 0.30.

Table 4 summarizes the wastewater characterization results and presents other pulp and paper wastewater characterizations for comparison purposes.

**Kinetic parameters estimation**

*Endogenous respiration rate (\( b_H \)).* The endogenous respiration rate was estimated from two long-term batch tests, without wastewater addition, at temperatures of 24°C and 30°C (Figure 2). The coefficient \( b_H \) was estimated as the slope of the curve from a plot of the logarithm of OUR versus time (Sollfrank and Gujer, 1991). The values of the endogenous respiration coefficients (0.11 d⁻¹ and 0.13 d⁻¹ respectively) were lower than those proposed by ASM3, but in the range of other values estimated for pulp and paper wastewaters: 0.05 d⁻¹ and 0.10 d⁻¹, (Stanyer, 1997); 0.16 d⁻¹ (Slade et al., 1991) (all reference values were transformed to ASM3 endogenous respiration equivalent and corrected to 30°C).

Since two measurements were not sufficient to estimate accurately the dependence of this parameter on temperature (\( \theta_{T,bH} \)), a different and simple approach was followed. The test consisted of a rapid increase in temperature of sludge in an endogenous state, so the resulting increase in the OUR was proportional to the increase of \( b_H \). Figure 3 presents the outcome of this test, which resulted in a \( \theta_{T,bH} = 0.04 \). This result was very similar to another and more complicated approach which resulted in an additional estimation of \( \theta_{T,bH} \) (based on ten batch tests measurements, described in more detail in Barañao (2003)).

**Table 4** Summary of COD influent fractions

<table>
<thead>
<tr>
<th>COD fraction</th>
<th>This study</th>
<th>Other pulp and paper references</th>
<th>Municipal wastewater (ASM3 default)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_S )</td>
<td>0.49</td>
<td>0.24 – 0.44</td>
<td>0.42</td>
</tr>
<tr>
<td>( S_I )</td>
<td>0.14</td>
<td>0.36 – 0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>( X_S )</td>
<td>0.30</td>
<td>0.42 – 0.23</td>
<td>0.11</td>
</tr>
<tr>
<td>( X_I )</td>
<td>0.07</td>
<td>0.07 – 0.03</td>
<td>0.14</td>
</tr>
<tr>
<td>Mill type</td>
<td>CTMP</td>
<td>BKME</td>
<td>BKME/TMP*</td>
</tr>
</tbody>
</table>

*TMP: Thermomechanical pulping

**Figure 2** Endogenous respiration decay of OUR in two batch reactors, at 24°C and 30°C respectively
Oxygen saturation constant ($K_{O2}$). The oxygen saturation constant was estimated using the method proposed by Kappeler and Gujer (1992), starting with an oxygen concentration of 4.0 g O$_2$ m$^{-3}$ and finishing with a concentration of 0.2 g O$_2$ m$^{-3}$. Figure 4 presents a plot of the oxygen switching function (as OUR measured over OUR$_{MAX}$) versus oxygen concentration. The results presented a good fit with $K_{O2} = 0.3$ for oxygen concentrations above 1 g O$_2$ m$^{-3}$, but a better fit with $K_{O2} = 0.6$ g O$_2$ m$^{-3}$ for oxygen concentrations lower than 1 g O$_2$ m$^{-3}$. Since the oxygen concentration is consistently above 1 g O$_2$ m$^{-3}$ in all the cells of the WWTP, 0.3 g O$_2$ m$^{-3}$ was selected as the calibrated value for $K_{O2}$.

Curve fitting for estimation of $k_{STO}$, $\mu_H$, $K_{STO}$, and $k_H$. The values of $k_{STO}$, $\mu_H$, $K_{STO}$, and $k_H$ were estimated based on the analysis of ten respirographs (respirometric curves) from batch tests, at different temperatures (22°C–42°C) and at different F/M ratios (from 0.01 to 0.90). The curve fitting procedure was performed with the least squares method, numerically minimized using the secant algorithm (Ralston and Jennrich, 1978). The results showed that a single set of parameters, with minor variations, was able to fit the data from different batch tests. This set of parameters includes those estimated above ($b_H$, $Y_{STO}$, and $Y_H$), as well as the wastewater characterization. The values of $\theta_T$ and $\mu_H$ were obtained from the variation of those parameters at different temperatures. The parameter $\mu_H$, however, adopted two different values depending on the F/M ratio ($\mu_H = 3.1$ d$^{-1}$ for tests at high F/M, and $\mu_H = 17.5$ d$^{-1}$ for test at low F/M). Then, the maximum observed growth rate ($\mu_{OBS}$) was estimated in order to have a reference value for choosing between these two different estimations of $\mu_H$.

The parameter combination ($\mu_{OBS} - b_H$) was obtained as the slope of the curve plotting the logarithm of the OUR in a test with high F/M, where $\mu_{OBS}$ is equivalent to ASM1 $\mu_H$. Two estimations of $\mu_{OBS}$ were performed in this way, with the results equal to 5.3 and 8.0 d$^{-1}$ (at 27.0 and 25.9°C respectively), with an average of 8.6 d$^{-1}$ (converted to 30°C). This estimation of $\mu_{OBS}$ was considered to represent a minimum value for $\mu_H$ (Eq. 7, from Barañao (2003)). Therefore, the tests performed at very low F/M gave a more reliable estimation of $\mu_H$ (17.5 d$^{-1}$ > 8.6 d$^{-1}$).

Figure 4 Plot of oxygen switching function, estimated as OUR/OUR$_{MAX}$, versus oxygen concentration (g O$_2$ m$^{-3}$)
Figure 5 presents two respirographs performed at low F/M (~0.015) and at different temperatures (25°C and 41°C respectively). Figure 6 presents two respirographs performed at relatively high F/M (~0.6) and at different temperatures (25°C and 32°C respectively). The line in all the graphs shows the best-fit model simulation. A summary of all the estimated parameter values is presented in Table 5.

Parameters not calibrated. The values of the parameters related to the production of $X_I$ during endogenous respiration and $S_I$ in hydrolysis ($f_{Xi}$ and $f_{Si}$ respectively) are widely used

![Figure 5](https://iwaponline.com/wst/article-pdf/50/3/1/421569/1.pdf)

Figure 5 Two respirographs at low F/M ratio. The best fit at 25°C (left) was obtained for $k_{STO} = 15$, $\mu_H = 15$, $K_{STO} = 0.05$, and $k_H = 42$. The best fit at 41°C (right) was obtained for $k_{STO} = 20$, $\mu_H = 31$, $K_{STO} = 0.2$, and $k_H = 2.1$

![Figure 6](https://iwaponline.com/wst/article-pdf/50/3/1/421569/1.pdf)

Figure 6 Two respirographs at high F/M ratio. The best fit at 25°C (left) was obtained for $k_{STO} = 13$, $\mu_H = 1.8$, $K_{STO} = 0.4$, and $k_H = 11.4$. The best fit at 32°C (right) was obtained for $k_{STO} = 19$, $\mu_H = 2.9$, $K_{STO} = 0.1$, and $k_H = 12$

Table 5 Summary of calibrated kinetic and stoichiometric parameters (kinetics parameters at 30°C with $\theta_T$ in parentheses)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>ASM3*</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_H$</td>
<td>d$^{-1}$</td>
<td>6.0 (0.04)</td>
<td>8.1</td>
</tr>
<tr>
<td>$k_{STO}$</td>
<td>d$^{-1}$</td>
<td>10 (0.07)</td>
<td>15.3 (0.02)</td>
</tr>
<tr>
<td>$K_{O2}$</td>
<td>g O$2$ m$^{-3}$</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>$K_{STO}$</td>
<td>g $X_{STO}$ g$^{-1}$ $X_H$</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>$\mu_H$</td>
<td>d$^{-1}$</td>
<td>4.0 (0.07)</td>
<td>17.5 (0.05)</td>
</tr>
<tr>
<td>$b_H$</td>
<td>d$^{-1}$</td>
<td>0.4 (0.07)</td>
<td>0.13 (0.04)</td>
</tr>
</tbody>
</table>

Stoichiometric parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{STO}$</td>
<td>g $X_{STO}$ g$^{-1}$ $S_S$</td>
<td>0.85</td>
</tr>
<tr>
<td>$Y_H$</td>
<td>g $X_H$ g$^{-1}$ $X_{STO}$</td>
<td>0.63</td>
</tr>
</tbody>
</table>

* In order to make the kinetic parameters comparable, it was assumed that ASM3 $\theta_T$ values were constant up to 30°C
and difficult to determine experimentally, so they were not calibrated for this particular WWTP. In addition, a sensitivity analysis determined that the model was relatively non-sensitive to these parameter values.

Since the major objective of this research was to model COD removal and because nitrification in this WWTP is not significant, the parameters related to the nitrification process were also not calibrated. Denitrification was not included either because the whole WWTP operates under aerobic conditions.

The saturation constant for substrate $S$ ($K_S$) was also assumed because of its low sensitivity with respect to the oxygen concentration and because of identifiability problems. The value of 10 g COD$_{SS}$ m$^{-3}$ (from Koch et al., 2000) was adopted because better fittings were achieved using this value instead of 2 g COD$_{SS}$ m$^{-3}$ proposed by ASM3.

Alkalinity as well as its related parameter ($K_{HCO}$), were not included in the calibration procedure because the WWTP pH controller adjusts any influent pH to 7.1 ± 0.4. Moreover, the wastewater alkalinity concentration (constant around 2 mole HCO$_3^-$ m$^{-3}$) would make the value of this switching function consistently in the range 0.95–0.96.

As proposed by Koch et al. (2000), since the respiration rate for $X_{STO}$ ($b_{STO}$) is difficult to estimate from batch respirometric tests, $b_{STO}$ was set equal to the endogenous respiration rate of $X_H$ ($b_{STO} = b_H$), as well as its dependence on temperature ($\theta_{T,bsto} = \theta_{T,bh}$).

**Conclusions**

ASM3 was calibrated for an activated sludge plant treating CTMP pulp and paper wastewaters. A single set of parameters, with minor variations, was able to fit a variety of batch test respirographs, with values similar to those found in the literature. The use of models developed originally for municipal wastewater in these effluents would simplify considerably the task of modelling and designing WWTP for treating pulp and paper effluents.

Monod kinetics can be used for predicting the substrate degradation kinetics of these effluents, and no toxic response was detected in the batch tests.

It was found that the high content of readily biodegradable substrates was an important factor in making ASM3 suitable for modelling the effluents of this WWTP.

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**References**


