Evaluation of a new model for the reduction of excess sludge production by ozonation of return activated sludge: what solids COD fraction is affected?
Dominic Frigon and Siavash Isazadeh

ABSTRACT
This paper aims at clarifying the effect of ozone on the RAS solids to model activated sludge systems equipped with RAS-ozonation processes for the reduction of sludge production. A common hypothesis is that ozone only affects active biomass by promoting cryptic growth. Data from a pilot-scale study were used to test this and two other model extensions to IWA-ASM3. All model extensions were able to simulate the observed linear reduction in sludge production with increasing ozone dose when the MLVSS are kept constant. However, model simulations showed the inconsistency of the cryptic growth hypothesis with the extent of sludge reduction. The second tested model extensions assumes that ozone affects all the solids fractions (active biomass, endogenous residue, and influent inert particulate COD) equally. This extension could properly simulate the observed sludge reduction, but it failed to predict the trends in effluent BOD₅, ATP/VSS, and nitrification rates. A third tested model extension, which performed better, assumes that biomass is inactivated at a specific rate higher than the specific rate of transformation by ozone of the other solids fractions. Finally, the predictions from this model extension were most accurate if either (i) the nitrifiers were inactivated at a lower rate then heterotrophs, (ii) the nitrifiers model parameters (e.g., maximum growth rate) were changed under ozone (i.e., metabolic adaptation, (iii) or both.

Key words | nitrification, ozone, process modeling, sludge production, activated sludge model

INTRODUCTION
The cost of excess sludge disposal around the world has increased considerably, forcing activated sludge treatment plants to reduce sludge production by adopting new technologies. Among them, the ozonation of return activated sludge (RAS) has had some success in a number of installations in Europe and Asia, where a typical installation would guarantee a reduction in sludge production of 40%. However, the explanation of the effect that ozone has on sludge remains a matter of debate among practitioners, limiting the predictability of the performance of new installations. A first hypothesis on the effect of ozone commonly described in the literature is that it promotes biomass cryptic growth by attacking cellular integrity (Chu et al. 2009). Although probably valid, this interpretation seems to be incomplete in light of modeling results using current IWA activated sludge models (e.g., IWA-ASM3; Gujer et al. 1999). Using these models, the proportion of microbial biomass in the mixed liquor volatile suspended solids (MLVSS) is predicted to be around 40–50% for a typical municipal activated sludge treatment plant. Considering a 40% reduction in sludge production, it appears that the ozone process would dramatically limit the growth of bacteria suggesting that process failures are likely, which is not observed in the field. A second hypothesis on the effect of ozone is that it transforms (not oxidizes) RAS solids COD into soluble and particulate biodegradable COD. COD solubilisation upon exposure to ozone is well known (Dytczak et al. 2007; Chu et al. 2009). In this hypothesis, the sludge production is reduced because, as the transformed COD is consumed by bacteria, a proportion “1−Yield” is lost. Furthermore, cryptic growth could be
accounted for by the transformation of biomass COD into
substrate COD and its subsequent re-consumption by the
biomass. A third hypothesis on the effect of ozone on the
RAS solids is that it could inactivate (kill) bacterial biomass
as it does for disinfection processes (Kobayashi et al. 2001;
Lee et al. 2005). Note that this hypothesis is not independent
from the second hypothesis.

The current work aims at investigating which one or
which combination of hypotheses has the highest expla-
natory power. It also aims at clarifying if all COD fractions
of the solids are affected similarly by the ozone. To this
end, the analysis of results from a pilot-plant study is
presented. In addition to the common measurements of
the reduction of excess sludge production and of the
concentrations of soluble COD and BOD$_5$ in the effluent,
three other sludge properties were measured: maximum
nitrification rate, ATP content (related to the level of active
biomass) and anaerobic digestibility of the excess sludge.
As the various modeling hypotheses have specific predic-
tions on the biomass content of the sludge, the latter three
measurements provided important information for their
accurate differentiation.

### MODEL PRESENTATION

The three model configurations that were tested are simple
extensions of the IWA-ASM3 model (Gujer et al. 1999). They
are presented in Gujer Matrix format in Table 1; note that
natural decay is the same as in IWA-ASM3 and is presented
only for reference purposes. The notation follows the same
one used in the initial presentation of ASM3 (Gujer et al.
1999). The model extensions can be referred to as (1) Trans-
formation of Biomass Only (i.e., cryptic growth), (2) Equal
Transformation of All Solids COD Pools (this extension is a
simplified version of the model of Manteroia et al. 2001) (3)
Inactivation of Biomass and Transformation of Non-Biomass
Pools ($X_S + X_I$). The transformation processes describe the
conversion of the solids COD into fractions of substrate COD
(both soluble [$f_{SS}$] and particulate [$1-(f_{SI}+f_{SS}+f_{OX})$])
and

<table>
<thead>
<tr>
<th>Process</th>
<th>COD Pools</th>
<th>Rates</th>
<th>Tested Models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural decay*</td>
<td>$X_H$, $X_{STO}$, $X_A$, $X_I$, $X_S$</td>
<td>$b$, $b$</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>1) Heterotrophs</td>
<td>$f_d$</td>
<td>$-(1-f_d)$</td>
<td>$b X_H$</td>
</tr>
<tr>
<td>2) Storage</td>
<td>$-1$</td>
<td>$-1$</td>
<td>$b X_{STO}$</td>
</tr>
<tr>
<td>3) Nitrifiers</td>
<td>$-1$</td>
<td>$-(1-f_d)$</td>
<td>$b X_A$</td>
</tr>
</tbody>
</table>

Transformation due to ozone

<table>
<thead>
<tr>
<th>Process</th>
<th>COD Pools</th>
<th>Rates</th>
<th>Tested Models</th>
</tr>
</thead>
<tbody>
<tr>
<td>4) Heterotrophs</td>
<td>$1-(f_{SI}+f_{SS}+f_{OX})$</td>
<td>$f_{SI}$, $f_{SS}$</td>
<td>$-f_{OX}$, $k_{ox} X_H$</td>
</tr>
<tr>
<td>5) Storage</td>
<td>$1-(f_{SI}+f_{OX})$</td>
<td>$f_{SS}$</td>
<td>$-f_{OX}$, $k_{ox} X_{STO}$</td>
</tr>
<tr>
<td>6) Nitrifiers</td>
<td>$1-(f_{SI}+f_{SS}+f_{OX})$</td>
<td>$f_{SI}$, $f_{SS}$</td>
<td>$-f_{OX}$, $k_{ox} X_A$</td>
</tr>
<tr>
<td>7) Inert Solids</td>
<td>$1-(f_{SI}+f_{SS}+f_{OX})$</td>
<td>$f_{SI}$, $f_{SS}$</td>
<td>$-f_{OX}$, $k_{ox} X_{I}$</td>
</tr>
<tr>
<td>8) Substrate Solids</td>
<td>$-(f_{SI}+f_{SS}+f_{OX})$</td>
<td>$f_{SI}$, $f_{SS}$</td>
<td>$-f_{OX}$, $k_{ox} X_{S}$</td>
</tr>
</tbody>
</table>

Inactivation due to ozone

<table>
<thead>
<tr>
<th>Process</th>
<th>COD Pools</th>
<th>Rates</th>
<th>Tested Models</th>
</tr>
</thead>
<tbody>
<tr>
<td>9) Heterotrophs</td>
<td>$f_d-f_{SI}$</td>
<td>$1-(f_d+f_{SS}+f_{OX})$</td>
<td>$f_{SI}$, $f_{SS}$</td>
</tr>
<tr>
<td>10) Storage</td>
<td>$-1$</td>
<td>$1-(f_{SS}+f_{OX})$</td>
<td>$f_{SS}$</td>
</tr>
<tr>
<td>11) Nitrifiers</td>
<td>$-1$</td>
<td>$1-(f_{SS}+f_{OX})$</td>
<td>$f_{SS}$</td>
</tr>
</tbody>
</table>

---

*Decay is presented simply as reference

1: $b$: Means that the process was included in the model extension.

2: Definition of rate constants in Model Extensions 1 and 2: $k_{ox} - k_{ox}$ substrate/$f_{OX} + f_{SS}$; $k_{ox}$ substrate $= $ measured.

3: Definition of rate constants in Model Extensions 3: $k_{ox} - k_{ox}$ substrate $= f_{SI} + f_{OX} + f_{SS}$ substrate $= $ measured; $b_{ox} - b_{ox}$ substrate $= D_{ox} + X_{S} + X_{STO}$

---

Table 1 | Gujer matrix of the tested model extensions to the IWA-ASM3 model to describe the effect of ozone contactors
non-biodegradable soluble COD ($f_{SI}$) with a small fraction ($f_{OX}$) of the COD being oxidized. For simplicity and because it is not possible to really differentiate them at this time, the fractions ($f_{SI}$, $f_{SS}$, and $f_{OX}$) considered in every transformation processes are the same (Table 1). The transformation of slowly biodegradable substrates ($X_S$) was described differently than the transformation of the other fractions since it was assumed that a fraction “$1-(f_{SI} + f_{SS} + f_{OX})$” would be generated for each unit ($-1$) of $X_S$ transformed (Table 1). For the inactivation of the biomass of both the heterotrophs ($X_H$) and nitrifiers ($X_A$), it was assumed that the same non-biodegradable particulate fraction of biomass formed during decay ($f_{biomass}$) was also generated. It was further assumed that the non-biodegradable soluble fraction ($f_{SI}$) was generated from the non-biodegradable fraction of biomass. Note that for transformation and inactivation, the storage pool ($X_{STO}$) was assumed not to generate non-biodegradable fractions.

Two new rate constants are introduced with the proposed modeling framework: the transformation rate constant ($k_{O3}$) and the inactivation rate constant ($b_{O3}$). The two rate constants could not be measured directly in our experiments, but they are related to two specific rates readily available from the pilot-reactor operation data: the fraction of the aerated COD solids solubilised per day ($k_{O3, solubilisation}$) and the fraction of aerated COD solids inventory treated by ozone per day ($k_{treated}$). Assuming (1) that the rate of solubilisation is a good measure of the extent of the ozone reaction, and (2) that it is proportional to the fraction of biomass inactivated ($f_{inactivation}$) upon exposure to ozone, we get the following relationships:

\[
\text{Extensions 1 & 2: } k_{O3} = k_{O3, solubilisation}/(f_{SI} + f_{SS})
\]
\[
\text{Extension 3: } k_{O3} = [k_{O3, solubilisation}/(f_{SI} + f_{SS}) - b_{O3} \times f_{biomass}] / [1 - f_{biomass}]; \quad b_{O3} = k_{treated} \times f_{inactivation}
\]
\[
\text{where } f_{biomass} = (X_H + X_A + X_{STO}) / (X_H + X_A + X_{STO} + X_S + X_I)
\]

**EXPERIMENTAL APPROACH**

**Pilot-scale study**

The accuracy of the model extensions at describing the experimental data was tested by analysing the results of a pilot-scale study conducted at the Régie d’Assainissement des Eaux du Bassin LaPrairie (RAEBL) wastewater treatment plant near Montréal (Canada) during Fall 2009. This municipal activated sludge plant has the particularity of receiving approximately 50% of its COD load from two industrial sources: a paper products plant and a food processing plant with a roughing biological treatment. The RAEBL plant produces 1.25 g-sludge/g-BOD$_5$ at a volatile fraction (%VSS) of 79%, which is much higher than the typical 0.3–0.5 g-sludge/g-BOD$_5$ often observed at municipal treatment plants (Tchobanoglous et al. 2003). This is due to the high influent fraction of non-biodegradable particulate COD which was found during this study using the IWA-ASM3 model to be 46% (typical $f_{SI} \approx 10–20\%$) (Gujer et al. 1999; Koch et al. 2001). Finally, the high inert particulate COD fraction could be due in part to the lack of primary clarifier.

Two parallel pilot-scale reactors (ozonated test and control) were built outfitted with a 1 m$^3$ aeration tank (split in two by a baffle with a 1/5 area opening) and a 0.7 m$^3$ settling tank. The influent wastewater was pumped from after the full-scale aerated grit chamber to an overflowing distribution tank with a few minutes hydraulic residence time (HRT), and then it passed through a 5-mm screen in line to the reactors. The average aerated HRTs of the units were 13.7 h and the average aerated solids residence time (SRT) of the control reactor was 5.9 days (including effluent solids). The ozonated test system was equipped with an ozone contactor from Air Liquide Canada, comprised of an ozone dissolution loop with a venturi and a vertical gas separator tube. A constant portion of the RAS flow was treated in the ozone contactor, but the ozone dosage in the contactor was varied to change the COD solubilisation rate. The dosage was measured using ozone gas analyzers located on the O$_3$-generator exit gas stream and O$_3$-reactor exit gas stream. Finally, the test reactor was operated such that the MLVSS was kept the same in both reactors.

**Analyses**

The analysis of (volatile) suspended solids ([VSS]), COD, nitrogen species and BOD$_5$ were performed on 24-hour composite samples of the influent stream and effluent streams by using the methodology described in standard methods (APHA 1995). Ammonia (NH$_4^+$), nitrite (NO$_2^-$), and nitrate (NO$_3^-$) were measured in microplate-scale version of colorimetric methods by the 2-phenylphenol-nitroprusside, N-(1-naphthyl)-ethylenediamin dihydrochloride and salicylic acid methods, respectively (Vendrell & Zupancic 1990; Rhine et al. 1998). The low food-to-microorganism (F/M) bioassay described by Water Environment Research Foundation (WERF) was used to measure the nitrifier’s activity (Melcer et al. 2003). In this procedure approximately 2000 mg/L of MLSS was incubated with NH$_4^+$ at constant pH, and the NO$_2^-$ and NO$_3^-$ production was monitored for a few days.
hours. Adenosine triphosphate (ATP) was quantified by QuenchGone 21 Wastewater ATP bioluminescence kit from LuminUltra (Fredericton, New Brunswick, Canada) according to the manufacturer’s protocol. Anaerobic digestion was performed by mixing a portion of mixed liquor with anaerobic biomass and monitoring for three weeks the production of CH₄ by pressure difference and gas chromatography.

**Model simulations and calibration**

Model simulations were performed using the solver Aquasim ver 2.0 (Reichert et al. 1998). The influent COD fractionation was determined by considering the measured total COD and ammonia in the influent and fitting the influent soluble COD, influent VSS, effluent soluble COD, effluent soluble BOD, effluent nitrate and sludge production of the control reactor. The kinetics parameters used were the same as the ones published with the IWA-ASM3 except for the half-saturation constants for the heterotrophic organic substrate (KS) and for the nitrifiers’ ammonia substrate (Kₐ, NH₄), which were respectively calibrated to approximate the observed effluent soluble BOD₅ and ammonia concentrations in the control reactor.

Once the basic model was calibrated (COD fractionation, KS and Kₐ, NH₄), the parameters related to the model extensions were adjusted to fit as closely as possible the observations from the ozonated test reactor. The COD solubilisation rate (kΟ₃, solubilisation) and the solids ozonation rate (ktreated) were measured during the experiment and the fraction of COD oxidation (fΟ₃) was determined from the amount of ozone utilized and the theoretical stoichiometry. Once these parameters were set, it was observed that the remaining parameters could be adjusted sequentially as follows: (I) fₛΙ/fₛ3 was adjusted to fit the effluent inert soluble COD, (IIa-only for Model Extension 3) f deactivate was adjusted to the maximum level that could maintain good nitrification, and (IIb-for all extensions) fSS was adjusted to match the level of sludge reduction observed.

**RESULTS AND DISCUSSION**

**Initial model simulations**

An extensive simulations study found that, for operations at constant MLVSS, the reduction in sludge production is linear with respect to the solids inventory solubilisation rate constant (kΟ₃, solubilisation) for Model Extensions 1 and 2 (data not presented). The same applies to Model Extension 3 if it is assumed that the inactivation rate constant (bΟ₃) is proportional to the solubilisation rate constant. Previous studies by others have reported a decrease in sludge production linearly related to the ozone utilized when the MLVSS was kept constant (Dytczak et al. 2007; Paul & Debellefontaine 2007; Manterola et al. 2008). In these studies, it was observed that the amount of COD solubilised was linearly related to the dose of ozone contacted with the solids, even if a non-productive (no solubilisation) low dose is sometimes observed (i.e., it is linear after the non-productive dose is met) (Paul & Debellefontaine 2007; Manterola et al. 2008). In our pilot-scale experiment, we also observed a linear solubilisation of COD with respect to the ozone dose (data not shown). Consequently, this modeling exercise shows that the linear reduction of sludge production in function of the ozone dose is an intrinsic property of the system. Furthermore, it suggests that the efficiency of sludge reduction (mass of sludge production reduced per mass of ozone utilized) is as much a function of the efficiency of the ozone reactions as it is a function of the activated sludge and biomass characteristics. For example, conventional and nitrification/denitrification activated sludge systems have different sludge yields, which leads to a higher efficiency for the system with the lower yield (e.g., Dytczak et al. 2007). A complete discussion of this point is beyond the scope of this paper.

**Pilot-scale study**

The pilot-study was conducted in Fall 2009. Four levels of ozone treatment (including no ozone treatment) were tested during the study, each with a test period of 3–4 weeks (Phase I to IV in increasing ozone dosage). The average SRT for the control reactor remained around 5.9 days while it reached approximately 12 days for the ozonated reactor during the last test phase with the highest ozone treatment level (Figure 1a). The aerated MLSS concentrations in both reactors were kept at similar concentrations throughout the study (Figure 1b). The %VSS remained similar in both reactors throughout the study at 82% with a slight decrease to 78% in the ozonated reactor towards the end of the last test period (Figure 1b). Finally, the temperature of the process went from 18°C to 15°C during the study period, which probably had minimal effects on the activated sludge operation and performance.

The sludge production was evaluated by monitoring the amount of solids wasted through either the WAS or effluent flows and by calculating differences in total solids inventory (aeration tank and clarifier). The reduction in sludge production was evaluated by averaging the sludge production per COD loaded in each phase and calculating the ratio between the two reactors (production in ozonated reactor/production...
in control reactor; hereafter the sludge production ratio, SPR. SPR reduction with respect to the sludge solubilisation rate was observed to fall close to the linear relationship suggested by the initial modeling exercise with a slope for the SPR_{VSS} and SPR_{SS} of \(-7.35\) days and \(-6.48\) days, respectively (Figure 2). In the last test period, when the highest level of ozone treatment was applied, the SPR reached 0.54 as evaluated for VSS production and 0.56 for total solids production, which was slightly higher than what was evaluated by linear regression. Finally, during the experiment, approximately 0.17 g-O\(_3\) per day was necessary to reduce excess sludge production per day by 1 g-TS. This is slightly higher than previously observed ratios (Chu et al. 2009) probably due to the difficulty of thickening the solids at the bottom of the clarifier (RAS suspended solids remained on average around 3300 mg/L, 1.66 times the average MLSS concentration).

The effluents of both reactors were also monitored during the study period. We report here only the average soluble COD, soluble BOD\(_5\) and nitrate concentrations observed during the last experimental phase (Phase IV; Table 2). Ammonia nitrogen was never detected for both reactors, suggesting a complete nitrification. However, the nitrate concentration in the effluent of the ozonated reactor was higher than in the control reactor by 58% (Table 2), suggesting that more ammonia was available for nitrification. The effluent soluble COD and soluble BOD\(_5\) were higher in the ozonated reactor by 106% and 161%, respectively (Table 2). A higher soluble COD was probably due to the formation of non-biodegradable soluble COD during sludge solubilisation by ozone. However, a higher soluble BOD\(_5\) is indicative of an increased effective decay rate of the heterotrophic biomass in the ozonated reactor or the formation of slowly degradable soluble microbial product (Grady et al. 1999).

In addition to typical operation parameters, a number of sludge characteristics were determined for this study...
Table 2 | Comparison between observed experimental data from pilot-scale reactors during the last experimental phase and the best simulations from the calibrated model extensions to the IWA-ASM3

<table>
<thead>
<tr>
<th>Experimental Observations</th>
<th>Control</th>
<th>Ozonated</th>
<th>Change</th>
<th>Control Reactor ASM3</th>
<th>Model Extension 1</th>
<th>Model Extension 2</th>
<th>Model Extension 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Value</td>
<td>Change</td>
<td>Value</td>
</tr>
<tr>
<td>$f_{SW}/f_{SS}$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.45</td>
<td>0.45</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>$f_{SS}$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>$I_{inactivation}$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{O3}$ (day$^{-1}$)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.388</td>
<td>0.112</td>
<td>0.100</td>
<td>0.248</td>
</tr>
<tr>
<td>$b_{O3}$ (day$^{-1}$)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.388</td>
<td>0.112</td>
<td>0.100</td>
<td>0.248</td>
</tr>
<tr>
<td>Sludge Reduction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPR$<em>{VSS}$ vs $k</em>{O3, solubilization}$ (day)</td>
<td>$-7.35 \pm 1.19^*$</td>
<td>NA</td>
<td>$-1.72$</td>
<td>$-7.35$</td>
<td>$-7.35$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent Qualities</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soluble COD (mg/L)</td>
<td>30 $\pm$ 3</td>
<td>63 $\pm$ 3</td>
<td>+111%</td>
<td>32</td>
<td>118 $+$ 269%</td>
<td>60 $+$ 88%</td>
<td>66 $+$ 106%</td>
</tr>
<tr>
<td>Soluble BOD$_5$ (mg/L)</td>
<td>2.7 $\pm$ 0.8</td>
<td>7.0 $\pm$ 1.8</td>
<td>+165%</td>
<td>3.0$^+$</td>
<td>54.8 $+$ 1716%</td>
<td>3.5 $+$ 16%</td>
<td>7.0 $+$ 132%</td>
</tr>
<tr>
<td>Effluent NO$_3^-$ (mg-N/L)</td>
<td>7.6 $\pm$ 1.1</td>
<td>12.0 $\pm$ 0.8</td>
<td>+58%</td>
<td>8.0</td>
<td>0.0 $-$ 100%</td>
<td>9.1 $+$ 14%</td>
<td>6.6 $-$ 18%</td>
</tr>
<tr>
<td>Sludge Qualities</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATP Level (mg ATP/g VSS)</td>
<td>Heterotroph/VSS</td>
<td>Heterotroph/VSS</td>
<td>(10$^{-2}$ g X$_H$/VSS/g VSS)</td>
<td>1062 $\pm$ 105</td>
<td>766 $\pm$ 189</td>
<td>-28%</td>
<td>12.8</td>
</tr>
<tr>
<td>Max. NO$_3^-$ Prod. (g N/kg VSS/day)</td>
<td>Nitrifiers/VSS</td>
<td>(10$^{-2}$ g X$_A$/VSS/g VSS)</td>
<td>46.2 $\pm$ 2.8</td>
<td>37.0 $\pm$ 2.8</td>
<td>-20%</td>
<td>0.806</td>
<td>0.000</td>
</tr>
<tr>
<td>Nitrifiers/VSS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anaerobic Digestion (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anaerobic Digestion</td>
<td>43.2$^+$</td>
<td>45.8$^+$</td>
<td>+6%</td>
<td>43.2$^+$</td>
<td>36.5</td>
<td>-15%</td>
<td>49.7</td>
</tr>
<tr>
<td>Model: $1-X_r$/VSS</td>
<td>NA</td>
<td>17.2</td>
<td>-56%</td>
<td>26.7 $+$ 55%</td>
<td>21.3 $+$ 24%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$Default model parameters were used except for $K_{NH}$ $A_1 = 0.05$ and $K_{NH} = 10.31$; influent total COD: 405 mg/L, and influent NH$_4^+$-N: 14.2 mg/L.

$^+$: Model simulations were performed in COD units and 0.6 g BOD$_5$/g COD was assumed (Grady et al. 1999).

$^+$: To fit the observed mineralization rate, 31.4% of $X_r$ was assumed to be anaerobically biodegradable.
The maximum nitrification rate as defined by the maximum nitrate production rate following an ammonia spike in a lab-scale assay was determined five times in a period spanning the second half of Phase III and the first half of Phase IV. The average nitrification rate was reduced by 20% in the ozonated test reactor compared to the control reactor (Table 2), which indicates that the level of nitrifiers in the MLVSS was lower in the test reactor. During Phase IV, the average level of ATP per VSS was 28% lower in the test reactor, suggesting that also the overall biomass level in the ozonated test reactor was lower. Finally, the anaerobic biodegradability of the sludge was maximally 6% higher in the test reactor (Table 2).

**Evaluation of model extensions**

The influent COD fractionations and two half-saturation constants \( K_S \) and \( K_{A,NH} \) was determined by considering the measured total COD and \( NH_4^+ \) in the influent and fitting the influent soluble COD, influent VSS, effluent soluble COD, effluent soluble \( BOD_5 \), effluent \( NH_4^+ \), effluent \( NO_3^- \) and sludge production of the control reactor. The influent COD fractions were found to be: soluble readily substrate \( (S_r) \) 44%, particulate slowly degradable substrate \( (X_s) \) 6%, inert soluble COD \( (S_i) \) 3%, and inert particulate COD \( (X_i) \) 46%. The high level of inert particulate COD \( (X_i) \) in the influent of the RAEBL wastewater treatment plant is helpful in evaluating the model extensions because the level of active biomass in the sludge as calculated by the model is pretty low, which amplifies the biomass dynamics. Consequently, the three model extensions can produce clearly different simulation predictions for the effluent and biomass levels in the MLVSS between the ozonated test and the control reactors. These differences provide crucial evidence for the evaluation of the model extensions’ accuracy.

Simulations of Model Extension 1 Transformation of Biomass Only found the steepest possible slope of \( SPR_{VSS} \) vs specific ozone solubilisation rate to be \(-1.72 \text{ days}^{-1}\), a much lower efficiency than the slope of \(-7.35 \text{ days} \) observed in the pilot-scale experiment (Table 2). Other trends in effluent and sludge characteristics were also not met (Table 2). These results suggest that the cryptic growth hypothesis alone is insufficient to predict the performance of RAS-ozonation processes for sludge reduction.

Simulations of Model Extension 2 Equal Transformation of All Solids COD Pools reproduced the performance of reduction in \( SPR_{VSS} \) vs specific ozone solubilisation rate (slope \(-7.35 \text{ days} \)) observed experimentally (Table 2). However, this model extension predicts an increase in heterotrophic and nitrifying biomass levels. Since the level of \( ATP/MLVSS \) and the specific nitrification rate \( (NO_3^- \) formation rate/MLVSS) decreased, this model extension is less likely. Furthermore, this model extension failed to predict the increase in soluble \( BOD_5 \) in the effluent. Therefore, it seems that Model Extension 2 has deficiencies that would be difficult to fix within this modeling framework.

Model Extension 3 Inactivation of Biomass and Transformation of Non-Biomass Pools was able to produce model simulations that reproduced the increase in effluent soluble \( BOD_5 \) and the reduction in specific maximum nitrification rate (observed in the model as a reduction in the nitrifying biomass; Table 2). The simulation result reported in Table 2 was the one with the highest biomass inactivation factor \( U_{inactivation} = 0.41 \) that would maintain a reasonable nitrification activity. The level of heterotrophic biomass from this simulation is the same as in the control, which is an improvement over Model Extension 2 (i.e., lower biomass level than for Model 2 simulation). The accuracy of the simulation would be improved by lowering the heterotrophic biomass level without lowering further the nitrifying biomass. This simulation result could be achieved either (i) by assuming lower inactivation rates for nitrifiers than for ordinary heterotrophs as suggested before (Boehler & Siegrist 2004), (ii) by assuming that the nitrifying biomass metabolically adapts to the ozone treatment which changes model parameters such as maximum specific growth rate, or (iii) by assuming both. At this point, the data are insufficient to make any recommendations on how to increase the accuracy of the predictions.

In the simulation of Model Extension 3, the concentration of nitrate in the effluent is slightly reduced due to a reduction in the extent of nitrification. This deficiency would be solved (i) by including the improvements suggested above, and (ii) by considering that the inert particulate COD from the influent contains a certain quantity of ammonia nitrogen released upon the action of ozone. At the time of writing this paper, the level of nitrogen in the influent solids remained to be determined. Yet, it appears that the inaccuracies of Model Extension 3 could be solved while the ones of the other model extensions could not. In conclusion, it seems that Model Extension 3 is the most promising to predict the performance of the activated sludge treatment system and the changes in sludge characteristics.

**CONCLUSION**

- We tested the accuracy of three model extensions to IWA-ASM3 to predict the performance of an activated sludge
system submitted to RAS-ozonation for the reduction of sludge production.

- A pilot-scale study was used as the case study for model evaluation.
- The model extension which assumed that the biomass was inactivated at a higher rate than the rest of the solids fraction were transformed by ozone showed the best performance at fitting the data from a pilot-scale study.
- Although the trends were more correctly predicted by this model extension, some inaccuracies in model predictions of the nitrification rates were observed, suggesting that further model improvement are necessary to describe the nitrifiers.

ACKNOWLEDGMENTS

Vivianne Villegas made this report possible by operating the pilot-scale reactors. We also thanked the technical assistance of various technical staff at the Régie de l’Assainissement des Eaux du Bassin LaPrairie throughout this project. Michel Epiney of Air Liquide Canada is thanked for his practical comments and his thought provoking discussions. This work was supported in part by the Régie de l’Assainissement des Eaux du Bassin LaPrairie.

REFERENCES


