PROJECT REPORT

MODIFICATION OF AN IWA-ASM3 OZONATION EXTENSION MODEL, STUDY CASE, AND GLOBAL SENSITIVITY ANALYSIS (GSA).

by

LUIS ENRIQUE URBINA RIVAS

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Department of Civil Engineering
And Applied Mechanics

McGill University
Montreal

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Nomenclature

Paper Notation	Description	Unit
$ATP\text{-}VSS\ ratio$	ratio between amount of ATP and amount of VSS	mg-ATP/g-VSS
$bo_{3\,factor}$	ratio between bo_3 and ko_3 (bo_3/ko_3)	fraction
bo_3	ozone inactivation rate constant, fraction of total biomass inventory inactivated by ozone per day	1/day
$b_{H,O2,20°C}$	decay coefficient for heterotrophic biomass at 20 degrees	g-COD_{Xb} /g-COD_{XH}/day
COD_{TOT}	total COD influent concentration	g-COD_{TOTAL}/m^3
f_a'	fraction of active biomass and storage of the aerated solids	g-COD_{Xa} /g-COD_{XTOTAL}
f_a	fraction of active biomass of the aerated solids	g-COD_{Xa} /g-COD_{XTOTAL}
$f_{biomass}{}^*$	fraction of active biomass and storage of the aerated solids	g-COD_{Xa} /g-COD_{XTOTAL}
f_d	fraction of biomass leading to inert particulate products	g-COD_{Xb} /g-COD_{Xa}
$f_{inactivation}$	fraction of biomass treated that is inactivated by ozone	fraction
f_{OX}^t	fraction of oxidized COD generated by ozone transformation of non-biomass	g-COD_{OX}/g-$COD_{x(I+S)}$
$f_{OX}{}^*$	fraction of oxidized COD generated by ozone treatment of particulate COD	g-COD_{OX}/g-COD_{XTOTAL}
$f_{SI}^{t'}$	fraction of soluble inert COD of the solubilized fraction generated by the transformation of particulate non-biomass by ozone ($f_{SI}^t/(1-f_{XS}^t)$)	g-COD_{SI}/g-$COD_{S(S+I+OX)}$
$f_{SI}'{}^*$	fraction of inert soluble COD generated by ozone solubilization of particulate COD	g-COD_{XS}/g-COD_{XTOTAL}
f_{SI}^i	fraction of soluble inert COD generated by ozone inactivation of biomass	g-COD_{SI}/g-COD_{Xa}
f_{SI}^t	fraction of soluble inert COD generated by ozone transformation of non-biomass	g-COD_{SI}/g-$COD_{X(I+S)}$
$f_{SI,inf}$	fraction of soluble inert COD of total influent COD	g-COD_{SI}/g-COD_{TOTAL}
f_{SS}^i	fraction of soluble biodegradable COD generated by ozone inactivation of biomass	g-COD_{SS}/g-COD_{Xa}
f_{SS}^t	fraction of soluble biodegradable COD generated by ozone transformation of non-biomass	g-COD_{SS}/g-$COD_{X(I+S)}$
$f_{SS,inf}$	fraction of soluble biodegradable COD of total influent COD	g-COD_{SS}/g-COD_{TOTAL}

f_{SS}*	fraction of soluble biodegradable COD generated by ozone treatment of particulate COD	g-COD_{XS}/g-COD_{XTOTAL}
$f_{transformation}$	fraction of non-biomass treated that is transformed by ozone	fraction
$f_{XaA,inf}$	fraction of autotrophic biomass of total influent COD	g-COD_{XA}/g-COD_{TOTAL}
$f_{XaH,inf}$	fraction of heterotrophic biomass of total influent COD	g-COD_{XH}/g-COD_{TOTAL}
$f_{XI,inf}$	fraction of particulate inert COD of total influent COD	g-COD_{XI}/g-COD_{TOTAL}
f_{XS}^{i}	fraction of particulate biodegradable COD generated by ozone inactivation of biomass	g-COD_{XS} /g-COD_{Xa}
f_{XS}^{t}	fraction of particulate biodegradable COD generated by ozone transformation of non-biomass	g-COD_{XS} /g-$COD_{X(I+S)}$
$f_{XS,inf}$	fraction of particulate biodegradable COD of total influent COD	g-COD_{XS}/g-COD_{TOTAL}
f_{XS}*	fraction of particulate biodegradable COD generated by ozone treatment of particulate COD	g-COD_{XS} /g-COD_{XTOTAL}
HRT	hydraulic retention time	day
$ko_{3,reacted\ factor}$	ratio between $ko_{3,reacted}$ and $ko_{3,solubilization}$	fraction
$ko_{3,reacted}$	ozone reaction rate, fraction of total COD solids inventory reacted with ozone per day	1/day
$ko_{3,solubilization}$	ozone solubilization rate, fraction of total COD solids inventory solubilized by ozone per day	1/day
$ko_{3,treated}$	treatment rate, fraction of total COD solids inventory exposed to ozone per day	1/day
ko_3	ozone transformation rate constant, fraction of non-biomass COD solids inventory transformed by ozone per day	1/day
$K_{A,NH}$	ammonium half-saturation coefficient for autotrophic biomass	g-N/m^3
$k_{H,20°C}$	maximum specific hydrolysis rate at 20 degrees	g-COD_{SS}/g-COD_{XH}/day
K_{NH}	ammonium half-saturation coefficient for heterotrophic biomass	g-N/m^3
K_{NO}	nitrite+nitrate half-saturation coefficient for denitrifying heterotrophic biomass	g-N/m^3
K_S	half-saturation coefficient of soluble biodegradable COD for heterotrophic biomass	g-COD_{SS}/m^3
$k_{STO,20°C}$	storage rate constant for heterotrophic biomass at 20 degrees	g-COD_{XSTO}/g-COD_{XH}/day

K_X	half-saturation coefficient for hydrolysis of slowly degradable substrate for heterotrophic biomass	g-COD$_{XS}$/g-COD$_{XH}$
$MLVSS$	mixed liquor volatile suspended solids	g-COD$_{XTOTAL}$/m^3
$ro_{3,reacted}$	non-normalized reaction rate, total concentration of particulate COD reacted per day	g-COD/m^3/day
$ro_{3,solubilization}$	non-normalized solubilization rate, total concentration of particulate COD solubilized per day	g-COD/m^3/day
S_I	soluble inert COD concentration	g-COD$_{SI}$/m^3
S_{NH}	soluble ammonium and ammonium (NH4 + NH3) nitrogen concentration	g-N/m^3
S_{NO}	soluble nitrate and nitrite nitrogen concentration	g-N/m^3
$S_{O\ factor}$	ratio between the oxygen concentration in the clarifier and in the aerated reactor	fraction
S_O	dissolved oxygen concentration	g-O/m^3
S_S	soluble readily biodegradable substrate concentration	g-COD$_{SS}$/m^3
sol_{factor}	ratio between the solubilization fractions of the inactivation process and the solubilization fractions of the transformation process $((f_{SI}^i + f_{SS}^i)/(f_{SI}^t + f_{SS}^t))$	fraction
SRT_C	solids retention time of control reactor	day
SRT_{O3}/SRT_C	ratio between SRT_{O3} and SRT_C ($\mathrm{SRT}_{\mathrm{O3,factor}}$)	factor
SRT_{O3}	solids retention time of ozonated reactor	day
SPR	ratio between the biosolids production of an ozonated reactor and of a regular biological reactor	fraction
SRC	standard regression coefficient	fraction
T	temperature	°C
TKN	total Kjeldahl nitrogen inflow concentration	g-N/m^3
$\mu_{H,20°C}$	maximum specific growth rate for heterotrophic biomass at 20 degrees	1/day
X_a	biomass concentration $(X_A + X_H)$	g-COD$_{Xa}$/m^3
X_A	active autotrophic biomass concentration	g-COD$_{XA}$/m^3
X_b	particulate products concentration arising from biomass decay	g-COD$_{Xb}$/m^3
X_H	active heterotrophic biomass concentration	g-COD$_{XH}$/m^3
X_I	particulate inert organic matter concentration	g-COD$_{XI}$/m^3
X_S	slowly biodegradable substrate concentration	g-COD$_{XS}$/m^3
X_{STO}	cell internal storage product of heterotrophic organisms concentration	g-COD$_{XSTO}$/m^3
X_{TOTAL}	total solids concentration	g-COD$_{XTOTAL}$/m^3

$Y_{H,O2}$	yield for heterotrophic biomass	g-COD_{XH}/g-COD_{STO}
Y_O	overall heterotrophic biomass yield ($Y_{H,O2} \times Y_{STO,O2}$)	g-COD_{XH}/g-COD_{SS}
$Y_{STO,O2}$	yield for the cell internal storage product of heterotrophic biomass	g-COD_{XSTO}/g-COD_{SS}

*: notation corresponding to the one used by Frigon and Isazadeh (2011) but redefined here.

Abstract

The production and disposal of sludge by the wastewater treatment facilities is an increasing concern both financially and logistically. One way to address this problem is by implementing ozonation of the returned activated sludge to reduce the amount of biosolids produced. The current drawback of this technology is that, due to the lack of reliable biological models, main process changes and costs in capital and operation can be accurately assessed only by pilot-scale studies. The current work aimed at developing a reliable model for RAS ozonation activated sludge systems. The work was divided into three steps.

(1) An extension to the International Water Association-Activated Sludge Model 3 (IWA-ASM3) describing the transformation of biosolids by ozone developed by Prof. Frigon's group was reviewed and detected inconsistencies were corrected. The mathematical description of biomass ozone inactivation was changed to make the ozone inactivation fractions independent from the biological decay fraction, and to make a distinction between the inactivation fractions and transformation fractions. In addition another distinction was made between the rate of treatment ($ko_{3,treatment}$) and the rate of reaction ($ko_{3,reacted}$).

(2) Data obtained in a pilot-scale study conducted in 2009 were finally used to validate the reviewed IWA-ASM3 model. Key wastewater treatment metrics such as biosolids inventory, excess biosolids production, effluent soluble inert and biodegradable COD, and effluent nitrate and ammonium were successfully fitted. The data fitting results also confirmed the assumption that the biomass is more sensitive to the presence of ozone, a higher inactivation rate constant (bo_3), than the non-biomass fraction, a lower transformation rate constant (ko_3).

(3) A global sensitivity analysis of the model extension was then conducted. The analysis found the reduction of biosolids production to be highly sensitive to operational parameters (solids retention time, biodegradable influent solids COD fraction, temperature, and overall system yield) and then to be medium sensitive to ozone transformation parameters (ozone particulate substrate fraction, ozone inactivation rate constant, and ozone soluble inert fraction) and finally to be mainly insensitive to biological parameters (biomass natural decay rate, hydrolysis half saturation coefficient, and substrate half saturation coefficient among others).

1) Introduction

One of the main operational costs incurred by wastewater treatment plants (WWTP) is the disposal of excess biosolids. Although the cost of waste disposal in Quebec is lower than in near Canadian provinces and U.S. states (Fig. 1), it has been rapidly increasing over the last decade in Quebec as it can be seen in the example of the WWTP RAEBL (Fig. 2). As biosolids disposal can range from 40% to 60% of the total operation cost of a WWTP (Foladori et al. 2010), the increases in both disposal cost and biosolids quantity to dispose of result in financial and operational problems for treatment facilities.

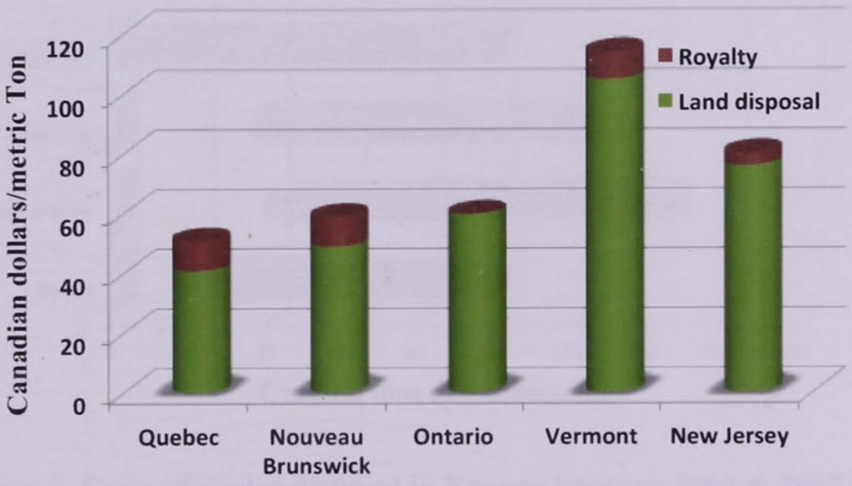

Figure 1. Comparison of waste disposal costs in different Canadian provinces and U.S. states near the province of Quebec (Houngue 2004)

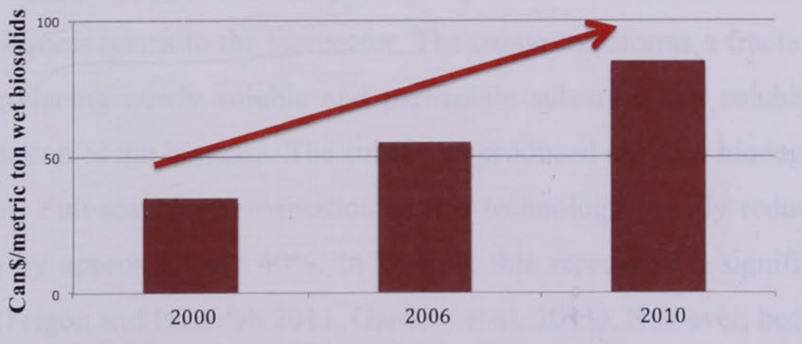

Figure 2. Increase in biosolids disposal cost at the Regie d'Assinissement des Eaux du Bassin LaPrairie (RAEBL), Quebec over the last decade (Gilbert Samson, pers. comm., 2011)

Biosolids treatment, transport and disposal costs in various countries have been found to range from €250 to more than €1000 (CAN $ 321 to 1284, 28 November 2012) per ton of total dry solids and a range of cost for biosolids disposal in Europe can be seen in Fig. 3 (Foladori et al. 2010). The different factors that play an important role in the final biosolids disposal costs are among others: land resource, transport cost, distance to disposal location, need for fertilizers, and regulations (Foladori et al. 2010).

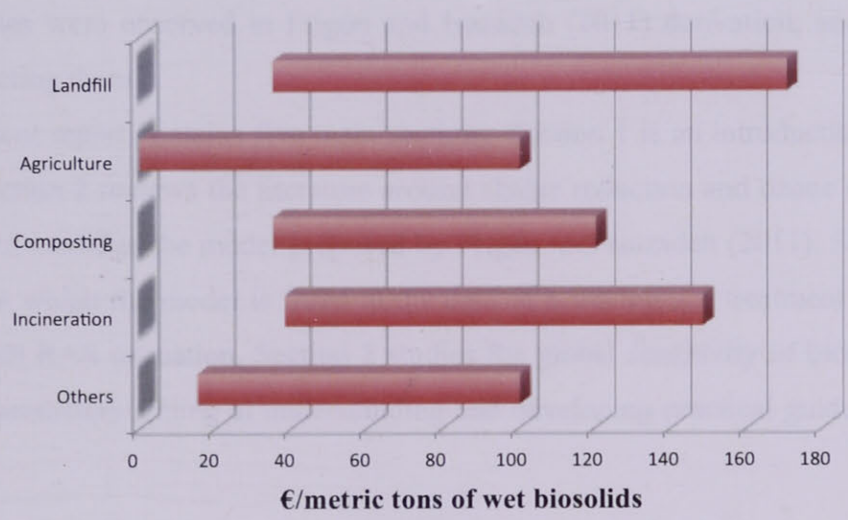

Figure 3. Costs of sludge disposal in Europe between 2003 & 2007 (Foladori et al. 2010).

A solution to this problem is the ozonation of a portion of the return activated sludge (RAS) flow with a subsequent return to the bioreactor. The ozone transforms a fraction of the biosolids in the sludge producing newly soluble and particulate substrate and soluble inert COD, and inactivating a fraction of the biomass. The substrates produced are then biodegraded again in the biological reactor. Full-scale implementation of this technology usually reduces the amount of excess biosolids by approximately 40%. In Europe, this represents a significant economy for sludge disposal (Frigon and Isazadeh 2011, Gardoni et al. 2011). However, because of the cost of disposal in Quebec is still much lower than in Europe, the economic viability of this technology is very sensitive to the ozone dose necessary to achieve the desired reduction. Currently, a precise determination of the dose can only be done by pilot-scale analysis because of the lack of reliable models and prediction approaches. Hence, the goal of this work is to develop a model describing the transformation of biosolids by ozone leading to reduction of excess solids production.

Frigon and Isazadeh (2011) evaluated three extensions to the International Water Association-Activated Sludge Model 3 (IWA-ASM3) to describe the transformation of biosolids by ozone. They concluded that the extension with the best performance at fitting the data from a pilot-scale study was the one in which ozone biomass inactivation rate constant and non-biomass volatile solids transformation rate constant were assumed different. However, some inconsistencies were observed in Frigon and Isazadeh (2011) derivation; and this work aimed first at correcting them.

The present report contains five main sections. Section 1 is an introduction to the subject to be study. Section 2 reviews the literature around sludge reduction and ozone modelling. Section 3 reviews and modifies the model proposed by Frigon and Isazadeh (2011). Section 4 presents a case study in which the model is fitted to the data of a wastewater treatment pilot-plant system equipped with RAS ozonation. Section 5 studies the global sensitivity of biosolids reduction to the model parameters aiming at understanding and developing practical guidelines for ozonated system.

2) Literature Review

2.1) Wastewater Treatment Process

Biological wastewater treatment plants vary in configuration. Units that can be found in this treatment process (Fig. 4) are grit chamber, primary settler, aerated reactor, secondary settler, return activated sludge (RAS) line, and sludge dewatering units, among others (Metcalf & Eddy. et al. 2003). In this process the organic compounds present in the wastewater is subject to biological degradation producing biomass. The biomass in the biological reactor is mainly composed by heterotrophs, a type of bacteria that uses organic compounds as the energy and carbon source for growth. The solids that exit the biological reactor are separated in the secondary settler; which according to the International Water Association Activated Sludge Model 3 (IWA-ASM3) formulation only leaves the soluble inert COD fraction in the water (Henze 2000). The settled biomass and settled non-biomass solids become the excess biosolids that requires disposal. Typical wastewater treatment plants operation parameters ranges can be seen in Table 1.

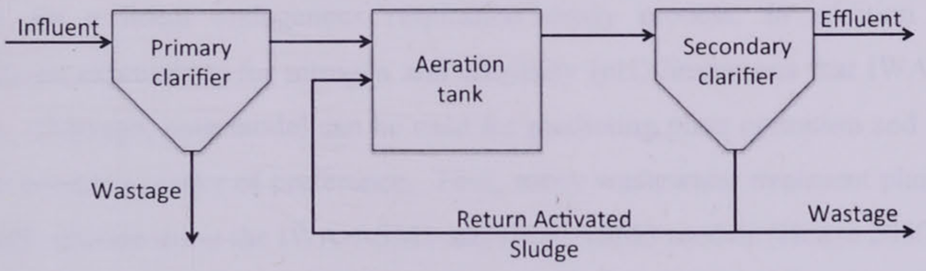

Figure 4. Configuration of a biological wastewater treatment process

Table 1. Standard operational parameters

Operational parameter	Value	Unit
Solid retention time (SRT)	4-14	Day
Hydraulic retention time (HRT)	3-5	Hour
Recycling ratio (R)	25-100	%
Temperature (T)	3-30	°C

Rittmann and McCarty 2001, Metcalf & Eddy. et al. 2003

2.2) Wastewater Treatment Activated Sludge Models

Typical wastewater treatment processes are modelled and designed following one of the International Water Association-Activated Sludge Model 1, 2 or 3 (IWA-ASM 1, 2, or 3). The IWA-ASMs describe the conversion of the influent chemical oxygen demand (COD) through the biological treatment system (Henze 2000). The IWA-ASMs includes kinetic, stoichiometric, operational and environmental parameters that describes and quantifies the biological activity in the treatment system, allowing the monitoring and prediction of key wastewater treatment variables such as effluent characteristics, wastage and biological reactors behavior. The main differences between IWA-ASM1 and IWA-ASM3 are the assumptions to describe heterotrophic COD conversions, while IWA-ASM2 has essentially the same structure as IWA-ASM1 with the addition of a microbial population to model the enhanced biological phosphorus removal process (Henze 2000). The IWA-ASM3 contains a storage process (production of poly-β-hydroxyalkanoates is assumed) that the IWA-ASM1 does not includes, and it replaces the lysis-regeneration decay process that gives many difficulties to measure the kinetic parameter used in IWA-ASM1 for a linear endogenous respiration decay process. In addition IWA-ASM3 considers kinetic expressions for nitrogen and alkalinity (pH) limitations that IWA-ASM1 does not includes. Although, both model can be used for predicting plant operation and the choice of either model remain a matter of preference. Thus, many wastewater treatment plants have been design and still operate using the IWA-ASM1 and IWA-ASM2 models (Henze 2000).

The IWA-ASM3 model keeps track of many variables that help to maintain mass balance of the biodegradation process (Fig. 5). Some of these variables are: soluble biodegradable solids (S_S), soluble inert solids (S_I), particulate biodegradable solids (X_S), particulate inert solids (X_I), heterotrophic biomass (X_H), autotrophic biomass (X_A), and biomass storage (X_{STO}) among others. The biodegradable components ($S_S \; and \; X_S$) are subject to biodegradation in the wastewater treatment process. The soluble inert solids (S_I) leave the wastewater treatment system with out being treated. The particulate inert solids (X_I) are accumulated and leave the system in the excess biosolids. The active biomass ($X_H \; and \; X_A$) is subject to growth and decay consuming biodegradable solids ($S_S \; and \; X_S$) and producing inert solids (X_I). The biomass storage (X_{STO}) is the energy stored by the biomass to be used for cell synthesis, an intermediate step between the biodegradable solids (S_S and X_S) and the active biomass (X_H and X_A). The particulate inert solids (X_I) can also be referred as non-degradable solids (Henze 2000).

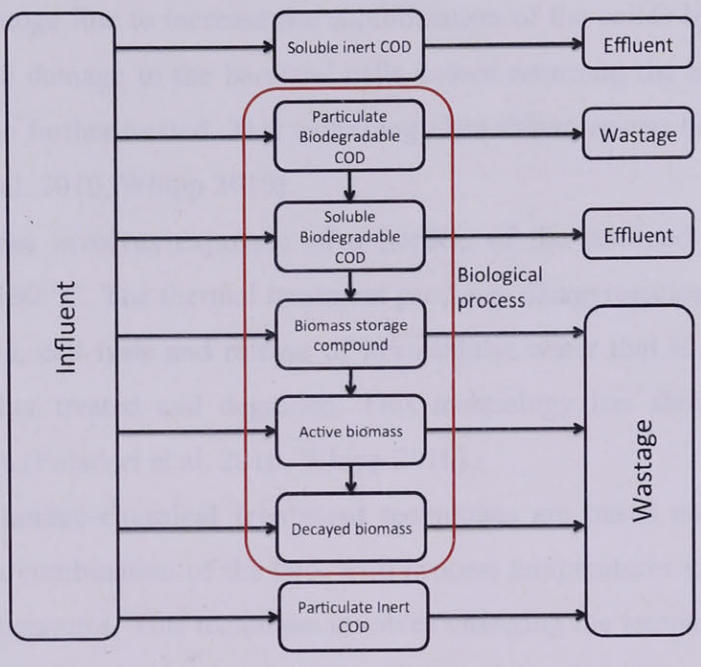

Figure 5. ASM3 schematic

2.3) Sludge Reduction Technologies

A wide variety of sludge reduction technologies have been developed with the purpose of reducing the amount of excess biosolids that the wastewater treatment plants produce. These technologies are available on the international market. A summary of some of these technologies is given here.

Oxic Settling Anaerobic process (OSA) adds an anaerobic reactor to treat a fraction of the returned activated sludge (RAS) flow. The objective is to make the active biomass consume its adenosine triphosphate (ATP) storage, reduce the biomass production yield, induce cryptic growth and increase biomass decay. This system has shown 20% to 50% reduction in the excess biosolids production (Foladori et al. 2010).

Cannibal^{TM} System, a technology designed by Siemens Water Technology Corp, uses anaerobic digestion to reduce the biosolids production. The difference between the cannibal system and the OSA system is that cannibal system is more efficient due to additional units and equipment (side-stream interchange bioreactor and solids separation module) added to the process. This technology has shown excess biosolids reduction of 40% to 70% (Foladori et al. 2010).

Mechanical Disintegration involves the application of a mechanical force on a portion of the return activated sludge line to increase the solubilization of the solids by the disaggregation of biological flocs and damage to the bacterial cells before returning the biosolids back to the biological reactor to be further treated. This technology has shown excess biosolids reduction of 5 to 24% (Foladori et al. 2010, Whipp 2010).

Thermal treatment involves exposure of a portion of the returned activated sludge to temperatures around 100 °C. The thermal treatment produces disaggregation of flocs, high level of solids solubilization, cell lysis and release of intracellular water that is then returned to the biological to be further treated and degraded. This technology has shown excess biosolids reduction of 20 to 55% (Foladori et al. 2010, Whipp 2010).

Chemical and Thermo-chemical treatment techniques are based on the use of acid or alkaline reagents, or a combination of the two, with process temperatures ranging from 50 – 90 °C or at ambient temperatures. This technique involves changing the temperature and pH of the wastewater away from their optimal values, causing cell breakage in microorganisms that promotes high degrees of cell lysis-cryptic growth. This technique has shown excess biosolids reduction by 50-60%. (Foladori et al. 2010)

Ultrasonic Disintegration utilizes ultrasonic waves with frequencies between 20 kHz and 10 MHz to reduce the flocs size increasing availability of organic substrates for bacterial cells; thus enhancing sludge biodegradability in the process. Disintegration of the flocs occurs due to cavitation. Liquid exposed to the ultrasound forms small gas bubbles in the bulk liquid that grow till they reach their resonant radius and collapse violently, causing intense local heat of up to 5000K, higher pressures of up to 1000 bar at the gas-liquid interface, and powerful shearing forces and turbulence. This technology has shown sludge reduction of 25–60% (Foladori et al. 2010, Tiehm et al. 2001, Nickel and Neis 2007).

Ozonation uses ozone (O_3) to degrade particulate solids into more easily biodegradable components. Ozone is usually generated onsite with pure oxygen (O_2) or dried air and electrical discharges, and it is applied to the solids through an ozone reactor. This ozone reactor can be fed with mixed liqueur or return activated sludge (RAS), but grater sludge reductions have been achieved with RAS. The treated solids can be returned to the wastewater or sludge treatment units for further degradation (Fig. 6). This technology has shown sludge reduction of 30-100%. (Foladori et al. 2010).

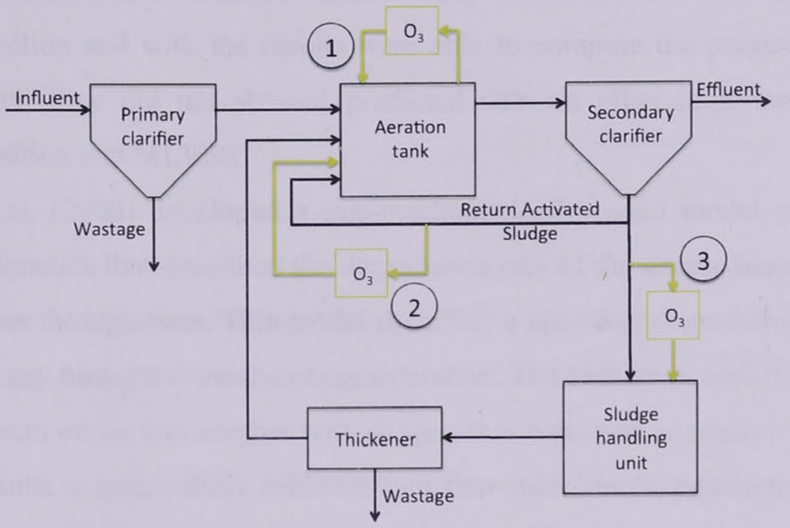

Figure 6. Three possible ozone reactor configurations (1,2 and 3)

2.4) Ozone modelling

Many journal articles have been published with research related to the effects of ozone over a wastewater treatment system but very few made an attempt at developing models that can explain and predict its effects in a system.

Saktaywin et al. (2005) developed a steady-state model for an ozonated sequencing batch reactor process with a phosphorus crystallization removal unit. The steady-state model describes the MLVSS concentration in the biological reactor, the phosphorus concentration after the ozone unit and the phosphorus removal after the crystallization unit. The authors operated an ozonated sequencing batch laboratory-scale reactor. With the results of the experiment the authors were able to compute the parameters needed to run her model, that are the solubilization of biosolids, the biodegradability of the solubilized COD and the inactivation ratio due to ozone. With this information the authors run some scenarios to predict the system behavior. The authors did not make a comparison between key measured data such as MLVSS and phosphorus removal with the model prediction of these variables. The model also did not take into consideration any change of their key parameter due to operational conditions or to biomass characteristic.

Wang et al. (2008) developed a steady-state model for an ozonated membrane bioreactor process. The steady model indicates which is the flow of return sludge that must go through the ozone contactor for a given ozone dose to produce zero excess biosolids. The authors operated a laboratory-scale ozonated membrane reactor. They were successful at achieving zero excess biosolids production and with the results were able to compute the parameters needed for the model. However, they did not showed predicted data on other important variables such as effluent composition and MLVSS.

Richard et al. (2008) developed a non-mechanistically based model using a pseudo-first-order reaction kinetics that described the degradation rate of the excess biosolids in an ozonated digestion process through time. This model describes a chemical degradation of the biosolids, it did not include any biological treatment consideration. The authors operated two laboratory-scale digesters, one with ozone and another with oxygen that was used as control. The author used the experiments results to successfully calibrate their first order kinetic parameter. However, the use of this calibration is limited to the system studied and does not provide any rational for system optimization.

The three mathematical models described above have been developed taking into account specific treatment systems (sequencing batch reactor, membrane reactor, and digestion unit). Furthermore, they considered only a partial description of biochemical reactions, and they were tested on a limited number of laboratory-scale experiments. Consequently, there overall usefulness is very limited. Finally, these models did not follow the well-known IWA-ASM model structures making it difficult to implement them in a wastewater treatment system. Other models have been developed using the IWA-ASM model structures that are presented as follows.

Manterola et al. (2007) developed an extensive mathematical model based on the IWA-ASM1. The mathematical model can be used in several wastewater treatment processes configuration and describes a complete mass transformation and complete contaminants charge, including excess sludge reduction. The model structure allows for an easy connection of the ozonated unit with other processes units to simulate a more complex wastewater treatment system. The model takes into consideration a change of the chemical composition of the biomass and of the inert solids by ozone. The authors operated two wastewater treatment pilot plants for which only the solubilized solids and the solubilized nitrogen data is compared with model prediction. The author did not compare key variables such as MLVSS, excess sludge reduction or effluent characteristics with the model prediction.

Frigon and Isazadeh (2011) developed and tested three mathematical model based on the IWA-ASM3. The first mathematical model assumed that the ozone only affects the biomass in the treated sludge. The second mathematical model assumed that the ozone affect the biomass and inert solids of the treated sludge with the same reaction rate. This second model was a simplification of the model developed by Manterola et al. 2007. The third mathematical model assumed that the ozone affects the biomass and inert solids of the treated sludge at different reaction rates, and that the biomass was more affected than inert solids. To test the three models the author operated a wastewater treatment pilot plant for 100 days. The pilot plant had two biological reactors, one ozonated and the second as control. The ozonated reactor was operated at three ozone doses. The third mathematical model was the best performance to match the measured results of the pilot plant, excess sludge reduction, effluent characteristics and biomass activity. This model describes the mass transformation of the treated sludge and the effect on the different wastewater treatment process variables such as mixed liquor volatile suspended solids, excess biosolids production, and effluent composition. This model also allows an easy connection of the ozonated unit with other processes units to simulate a more complex wastewater treatment system.

Even though the model of Manterola et al. (2007) was developed following the IWA-ASM1 structure, the big amount of variables and lumped variables used makes it a complex process to analyse and implement. It does not gives an indication of which are the key parameters for the successful implementation of the model. This model also carries the problems intrinsic to the IWA-ASM1 structure mentined in section 2.2. By the contrary, the model of Frigon and Isazadeh (2011) that is developed following the IWA-ASM3 structure is presented in a simple and clear format that is more simple to analyse and implement. It also carries the benefits of the IWA-ASM3 structure over the IWA-ASM1 structure, that are a storage process, a linear endogenous respiration decay process, and kinetic expressions for nitrogen and alkalinity (pH) limitations.

3) Modification of a New Model for the Reduction of Excess Sludge Production by Ozonation of Return Activated Sludge

3.1) Objective

This section aimed at reviewing the third IWA-ASM3 ozonation model extension presented by Frigon and Isazadeh (2011), and correcting a number of inconsistencies in definitions and mass balances. To reach the goal, the work focused on: clarifying the different assumptions, adjusting the model structure, and verifying consistencies of definitions.

3.2) Modelling Methods

3.2.1) IWA-ASM3 Model Extension

The theoretical framework under which the IWA-AM3 model extension was developed is presented in the paper of Frigon and Isazadeh (2011). The main assumption is that the biomass is more sensitive to be inactivated by ozone than non-biomass solids is to be transformed by ozone. Consequently, different rates for the ozone inactivation process and the ozone transformation process are considered. As a result of biomass inactivation and non-biomass solids COD transformation processes, COD is generated in three different pools: soluble inert COD, soluble substrate, and particulate substrate (Fig. 7).

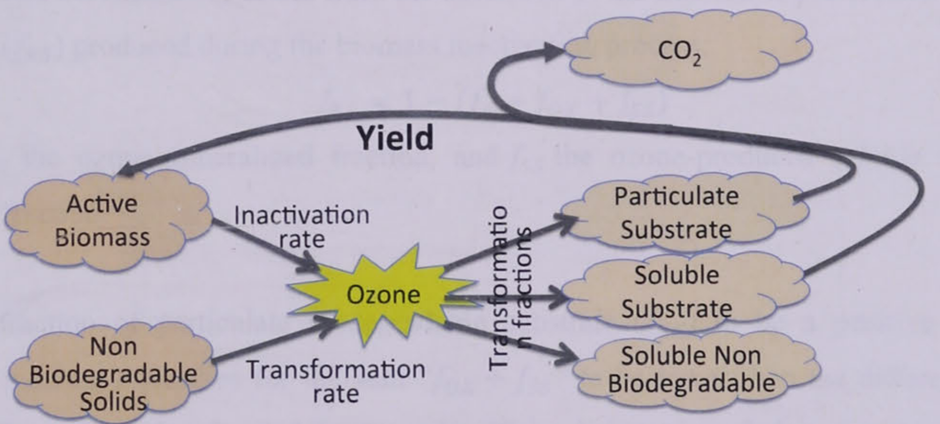

Figure 7. IWA-ASM3 model extension

3.3.2) Analysis Method

The main analysis method used in the review of the IWA-ASM3 model was the mass balance of all the COD fractions and a portion of the COD fractions around all the ozonated-biological wastewater treatment units: the biological reactor, the clarifier, the ozone contactor and the whole system. In order to test the congruency of the model under different scenarios, possible values for kinetic and stoichiometric parameters were used from a compiled database published by Hauduc et al. (2011). By the end of the review process the definitions of several model parameters were adjusted.

3.4) Results and Discussion

A close inspection of the IWA-ASM3 model extension in Frigon and Isazadeh (2011) led to the observation of the following inconsistencies.

3.4.1) Inconsistencies Due to f_d in Inactivation and Transformation Processes

Frigon and Isazadeh (2011) assumed that the fraction of soluble inert COD (f'_{SI}) produced by biomass inactivation is formed from the decayed biomass fraction (f_d). This assumption had several ramifications through the model, which created a number of inconsistencies. The ***first inconsistency*** is that this assumption requires f'_{SI} to be lower than f_d. They further assumed that the values of f'_{SI} for biomass inactivation and non-biomass solids COD transformation were the same. Because of this second assumption, the restriction of the soluble inert fraction value ($f'_{SI}<f_d$) in the inactivation process also becomes a restriction for the non-biomass solids transformation process.

A ***second inconsistency*** arises from the definition of the fraction of particulate biodegradable substrate (f_{XS}) produced during the biomass inactivation process:

$$f_{XS} = 1 - (f_d + f_{OX} + f_{SS}) \quad (1)$$

where f_{OX} the ozone-mineralized fraction, and f_{SS} the ozone-produced soluble biodegradable substrate fraction.

For the fraction of particulate biodegradable substrate (f_{XS}) to be a positive real number, equation number 1 requires for the sum "$f_{OX} + f_{SS}$" to be lower than the difference "$1 - f_d$", limiting the values that f_{OX} and f_{SS} can take. Since it is assumed that the ozone-mineralized fraction (f_{OX}) and the ozone-produced soluble biodegradable substrate fraction (f_{SS}) have the same values for the inactivation and transformation processes, these values also become restricted for the transformation process ($f_{OX} + f_{SS} < 1 - f_d$).

The solution to these problems was to redefine the inactivation process as follows. The biomass at the contact with ozone is inactivated producing the following fractions: from the heterotrophic and autotrophic nitrifying active biomass (X_H and X_A) a decayed fraction (f_d) is formed; from the difference ($1-f_d$) three fractions are formed, a soluble inert fraction (f_{SI}^{i}), a soluble biodegradable substrate fraction (f_{SS}^{i}), and a particulate biodegradable substrate fraction ($f_{XS}^{i} = 1-f_{SI}^{i} - f_{SS}^{i}$). To make a difference between the fractions generated in the inactivation process and the transformation process, each fraction has been added a superscript with the initial letter of the process to which they belong, "i" for inactivation process and "t" for transformation process (i.e. f_{SI}^{i}, f_{SI}^{t}). From the biomass storage ($\mathrm{X_{STO}}$), only particulate biodegradable substrate ($\mathrm{X_S}$) is produced.

The transformation process of the non-biomass component ($\mathrm{X_I} + \mathrm{X_S}$) remained the same producing the following fractions: a soluble inert fraction (f_{SI}^{t}), a soluble biodegradable substrate fraction (f_{SS}^{t}), a mineralized fraction (f_{OX}^{t}), and a particulate biodegradable substrate fraction ($f_{XS}^{t} = 1 - f_{SI}^{t} - f_{SS}^{t} - f_{OX}^{t}$).

These changes make the values of the soluble inert fraction, soluble biodegradable substrate fraction, mineralized fraction and particulate biodegradable substrate independent from the decay fraction and make a differentiation between the fractions from the inactivation process and the transformation process. A new Gujer matrix is presented in Table 2 that summarizes all the changes described above.

3.4.2) Ozonation Rates

In the paper from Frigon and Isazadeh (2011), the non-biomass solids COD transformation rate constant (ko_3) and the biomass inactivation rate constant (bo_3) of the third model extension are described as follow:

$$ko_3 = \frac{\left(\frac{ko_{3,solubilisation}}{f_{SI}' + f_{SS}} - bo_3 \times f_{biomass}\right)}{1 - f_{biomass}} \tag{2}$$

$$bo_3 = ko_{3,treated} \times f_{inactivation} \tag{3}$$

where $ko_{3,solubilisation}$ (rate at which the solids are transformed from particulate COD to soluble COD) and $ko_{3,treated}$ (rate at which the solids are exposed to ozone, COD charge into the ozone contactor per day/COD inventory present in the treatment system) were measured values; f'_{SI}, f_{SS} and $f_{inactivation}$ were fitted parameters; ko_3, bo_3 and $f_{biomass}$ were calculated, and the biomass fraction was defined as:

$$f_{biomass} = \frac{X_H + X_A + X_{STO}}{X_H + X_A + X_{STO} + X_S + X_I} \qquad (4)$$

where X_H (heterotrophic biomass concentration), X_A (nitrifiers biomass concentration), X_{STO} (biomass storage concentration), X_S (particulate substrate concentration), and X_I (particulate inert COD concentration) were calculated values.

Table 2: Gujer matrix reviewed ozonation extension (see nomenclature table for definitions)

Process	COD Pools								Rates
	X_H	X_{STO}	X_A	X_I	X_S	S_I	S_S	So_3	
Non-biomass transformation									
Inert solids (X_I)				-1	$1-f_{SI}^t-f_{SS}^t-f_{OX}^t$	f_{SI}^t	f_{SS}^t	f_{OX}^t	$ko_3 \times X_I$
Substrate solids (X_S)					$-1+(1-f_{SI}^t-f_{SS}^t-f_{OX}^t)$	f_{SI}^t	f_{SS}^t	f_{OX}^t	$ko_3 \times X_S$
Biomass inactivation									
Heterotrophs (X_H)	-1			f_d	$(1-f_{SI}^i-f_{SS}^i) \times (1-f_d)$	$f_{SI}^i \times (1-f_d)$	$f_{SS}^i \times (1-f_d)$		$bo_3 \times X_H$
Storage (X_{STO})		-1			$+1$				$bo_3 \times X_{STO}$
Nitrifiers (X_A)			-1	f_d	$(1-f_{SI}^i-f_{SS}^i) \times (1-f_d)$	$f_{SI}^i \times (1-f_d)$	$f_{SS}^i \times (1-f_d)$		$bo_3 \times X_A$

$$bo_3 = \frac{ko_{3,reacted} - \dfrac{ko_{3,solubilization}}{f_{SI}^t + f_{SS}^t}}{f_a' - f_a * (1-f_d) \times sol_{factor}}$$

$$ko_3 = \frac{\left(\dfrac{ko_{3,solubilization}}{f_{SI}^t + f_{SS}^t}\right) \times f_a' - ko_{3,reacted} \times (1-f_d) \times f_a \times sol_{factor}}{(1-f_a') \times \left(f_a' - f_a \times (1-f_d) \times sol_{factor}\right)}$$

$$f_a' = \frac{X_H + X_A + X_{STO}}{X_H + X_A + X_{STO} + X_S + X_I}$$

$$f_a = \frac{X_H + X_A}{X_H + X_A + X_{STO} + X_S + X_I}$$

$$\mathrm{sol}_{\mathrm{factor}} = \frac{f_{SS}^i + f_{SI}^i}{f_{SS}^t + f_{SI}^t}$$

The formulation of the non-biomass solids transformation rate constant (ko_3) and the biomass inactivation rate constant (bo_3), derive from the definitions on the biomass inactivation process and non-biomass transformation process. As the biomass inactivation process was modified (discussed in section 3.4.1), the inactivation transformation rate constants were redefined. The new definitions of both constants maintained the main concepts developed in Frigon and Isazadeh (2011), these are a differentiation of the ozone biomass inactivation and the ozone non-biomass transformation rates constants, and a direct relationship of these rates with the solubilization and the overall reaction of particulate COD with ozone. These definitions are described as follows:

$$ro_{3,solubiliztion} = ko_3 \times (X_I + X_S) \times (f_{SS}^t + f_{SI}^t) + bo_3 \times (X_H + X_A) \times (1 - f_d) \times (f_{SS}^i + f_{SI}^i) \qquad (5)$$

$$ro_{3,reacted} = ko_3 \times X_I + ko_3 \times X_S + bo_3 \times (X_H + X_A) + bo_3 \times X_{STO} \qquad (6)$$

where the superscripts "t" and "i" refers to the transformation process and the inactivation process respectively, and $ro_{3,solubilization}$ and $ro_{3,reacted}$ are the non normalized ozone-solubilization and ozone-reaction rates, respectively, expressed in g-COD/m^3/day .

The ozone inactivation rate constant (bo_3) and the ozone transformation rate constant (ko_3) are derived from these two previous equations and expressed as:

$$bo_3 = \frac{ko_{3,reacted} - \dfrac{ko_{3,solubilization}}{f_{SI}^t + f_{SS}^t}}{f_a' - f_a * (1 - f_d) \times sol_{factor}} \qquad (7)$$

$$ko_3 = \frac{\left(\dfrac{ko_{3,solubilization}}{f_{SI}^t + f_{SS}^t}\right) \times f_a' - ko_{3,reacted} \times (1 - f_d) \times f_a \times sol_{factor}}{(1 - f_a') \times \left(f_a' - f_a \times (1 - f_d) \times sol_{factor}\right)} \qquad (8)$$

where $ko_{3,solubilization}$ is a measured value and remains with the same definition, $ko_{3,reacted}$ is the rate at which the solids react with the ozone and is a fitted value, f_a' is the fraction of biomass in the biosolids inventory, f_a is the fraction of active biomass in the biosolids inventory, $\text{sol}_{\text{factor}}$

is the ratio between the soluble fractions due to the inactivation process and the soluble fractions due to the transformation process and they are defined as follows:

$$f_a' = \frac{X_H + X_A + X_{STO}}{X_H + X_A + X_{STO} + X_S + X_I} \tag{9}$$

$$f_a = \frac{X_H + X_A}{X_H + X_A + X_{STO} + X_S + X_I} \tag{10}$$

$$\mathrm{sol}_{\mathrm{factor}} = \frac{f_{SS}^i + f_{SI}^i}{f_{SS}^t + f_{SI}^t} \tag{11}$$

The ozone treatment rate ($ko_{3,treated}$) is the rate at which the biosolids are exposed to ozone. This includes a fraction of biosolids that has a chemical reaction with ozone and changes its composition, and a fraction of biosolids that does not react with ozone and remains unchanged. The ozone reaction rate ($ko_{3,reacted}$) is the rate at which the biosolids have a chemical reaction with ozone. This includes a fraction of biosolids that reacts with ozone and is transformed to soluble COD, and a fraction of biosolids that reacts with ozone and remains as particulate COD. The ozone solubilization rate ($ko_{3,solubilized}$) is the rate at which the biosolids have a chemical reaction with ozone that leads to a transformation from particulate COD to soluble COD. This includes a fraction of biosolids that reacts with ozone and is transformed to soluble substrate and a fraction that is transformed to soluble inert COD. Only the biosolids that react with ozone are reflected in the ozone transformation or inactivation fractions ($f_{SS}^i, f_{SI}^i, f_{XS}^i, f_{SS}^t, f_{SI}^t, f_{XS}^t, f_{OX}^t$).

From the inactivation rate constant (bo_3) and the transformation rate constant (ko_3) new definitions, the following relationship is found which has to be met in order for the model to give consistent results:

$$\frac{(1 - f_d) \times f_a \times Sol_{factor}}{f_a'} =< \frac{ko_{3,solubilization}}{ko_{3,reacted} \times (f_{SI}^t + f_{SS}^t)} =< 1 \tag{12}$$

3.4) Conclusion

- The design of the ozone inactivation process was changed to make the inactivation fractions independent from the decay fraction. The ozone transformation process remained the same.

- The transformation rate constant (ko_3) and inactivation rate constant (bo_3) were redefined according to the change in the ozone inactivation process design modifications.
- New parameters were introduced in the model: a distinction between the inactivation fractions and transformation fractions, and a rate of reaction ($ko_{3,reacted}$).
- Even though there have been some changes in the model, the main concept of differentiated ozone biomass inactivation rate constant and ozone non-biomass transformation rate constant is maintained.

4) Modelling the Reduction of Excess Biosolids Production by Ozonation: A Case Study

4.1) Objective

The objective of this section is to use a case study for the evaluation of the IWA-ASM3 extension model to predict the most important wastewater treatment variables: biosolids inventory, biosolids production, effluent soluble inert and biodegradable COD, and effluent nitrate and ammonium.

4.2) Materials and Methods

4.2.1) Data and Pilot Plant

The data used for this study was collected from the operation of a wastewater treatment pilot plant at the Regie d'Assainissement des Eaux du Bassin LaPrairie (RAEBL) in Quebec, Canada. The information collected belonged to the period of the 13th September 2009 to 21st December 2009. The data set consisted of influent and recycling rates; oxygen concentration and temperature in the reactors; total COD, centrifuged COD, total suspended solids and volatile suspended solids measurement of the influent, effluent, reactor, clarifier, wastage and returned line; filtered BOD_5 measurement from the effluent; ammonium, nitrite and nitrate measurement from the influent and effluent; and ATP test in the reactors. All the wastewater examination measurements were done following the methodology described in standard methods (Clesceri et al. 1996). A journal with the most relevant events of the pilot plant and a data set of the wastewater treatment influent performed by the full-scale plant were also available.

The wastewater treatment pilot plant (Fig. 8) consisted in two parallel reactors, two clarifiers with a return line and an ozone contactor. One of the reactors was a regular biological system, and the second reactor was an ozonated biological system connected to the ozone contactor. The influent of the two biological reactors was the same as for the full-scale plant. Both reactors were managed with similar operation condition except for the solid retention time with the objective to match their MLVSS. The samples collected from the influent, effluent, and ozone contactor were two days composite, and the samples collected from the reactors, clarifiers, wastage and return line were grab samples.

4.2.2) Simulation Software and Simulation Program File

The simulation software used was the solver AQUASIM (Reichert 1998). The simulation program file used was a modified version of the third IWA-ASM3 model extension program used in the paper of Frigon and Isazadeh (2011). The modifications of this program were explained in the second first section of this report.

Figure 8. Wastewater treatment pilot plant, control reactor (right) and ozonated reactor (left)

The simulation program file was set up to simulate the conditions of the pilot plant (Fig. 9). The main difference was that due to sludge accumulation in the clarifier, the bottom section of it behaved as an anoxic reactor. The simulation program file used in this study case includes this dynamic. As seen in Fig. 9, the compartment 1 represents the aerated reactor, compartment two represents the bottom section of the clarifier that behaves as an anoxic reactor and compartment

3 represents the top section of the clarifier that contains the suspended solids that leave through the effluent.

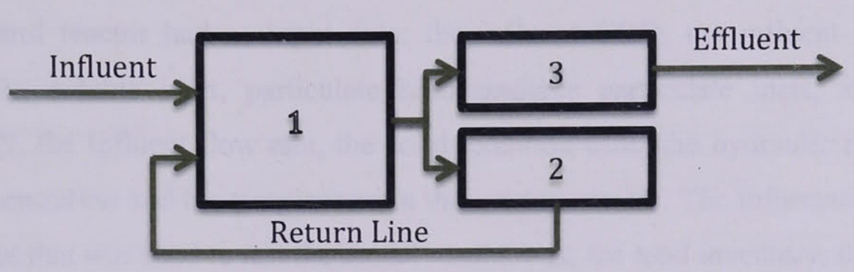

Figure 9. Simulation program scheme (1-aerated reactor, 2-clarifier bottom section, 3-clarifier top section)

4.2.3) Statistical Tests

Two statistical tests were used to evaluate the results of the simulations versus the data collected from the wastewater treatment pilot plant. The first statistical test was the t-student test for paired data points (Mac Berthouex and Brown 2002) and the second statistical test was the maximum axis (MA) method (Legendre and Legendre 1998). The first test was used to narrow down possible simulated solutions for the study case, and the second test was used to rank which of those solutions gave a better fit. The ordinary least square (OLS) test was also performed for references purposes as it is a commonly used test. As explained in Legendre and Legendre (1998) the OLS test, or R^2 test, is not the best method to evaluate the goodness of a simulation. The support programs for these test were Microsoft excel for the t-test and the Model II regression (Legendre 2001) from the university of Montreal for the MA method.

4.2.4) Fitting Procedure

First, four model parameters from the IWA-ASM3 model (soluble biodegradable half saturation constant [K_S], the autotrophs ammonium half saturation constant [$K_{A,NH}$], the clarifier oxygen concentration [S_O], and the influent particulate inert fraction [$f_{XI,inf}$]) and common between the two reactors were calibrated by fitting the data from the control reactor. From the excess biosolids data, effluent data, reactor data and clarifier data the solids retention time (SRT) was computed. From the effluent and influent measurements (filtered, centrifuged and total COD) the influent fractions were computed. It was assumed that the biomass load from the influent was negligible. The particulate inert fraction $(f_{XI,inf})$ was left as a fitting parameter of the regular biological reactor. The influent nitrogen was calculated using a study done in the full-scale plant.

The control reactor had as input data: the influent COD, the influent fractions (soluble biodegradable, soluble inert, particulate biodegradable particulate inert, and biomass), the influent TKN, the influent flow rate, the solid retention time, the hydraulic retention time, the oxygen concentration and the temperature in the aerated reactor. The information available from the pilot plant that was used to test the model results was: the total inventory, the effluent soluble biodegradable COD, the effluent soluble inert COD, effluent ammonium, effluent nitrate, and wasted COD. A range of values was simulated for each parameter (Table 3) following a grid format, and the results of the simulations were tested against the operational data using a paired t-student test with 95% confidence interval.

Once the four common parameters had been calibrated, the parameters describing the ozonation process were in turn calibrated. The solubilization rate $(ko_{3,solubilization})$ was calculated as the difference in the soluble COD after the ozone contactor and the soluble COD measured before the ozone contactor multiplied by the total COD flow to the ozone contactor divided by the total inventory, eq. 13. The procedure to calculate the effluent soluble biodegradable COD, the effluent soluble inert COD, the solid retention time (SRT), and hydraulic retention time (HRT) was the same used in the control reactor.

$$ko_{3,solubilization} = \frac{(soluble\ COD\ after\ O_3contactor - Soluble\ COD\ before\ O_3contactor)\times COD\ flow\ to\ the\ O_3contactor}{(COD\ concentration\ in\ the\ reactor)\times(volume\ of\ the\ reactor)} \qquad (13)$$

To match pilot plant data with the model predictions of the effluent soluble inert COD, the effluent soluble biodegradable COD, the inventory and the wastage of the ozonated reactor, three parameters were used for fitting, the ozonation soluble inert fraction, the ozonation soluble biodegradable fraction (f_{SS}^t, f_{SS}^i), and the reaction rate factor $(ko_{3,reacted\,factor} = ko_{3,reacted}/ko_{3,solubilization})$. The oxygen concentration of the ozonated clarifier was used to match the effluent nitrite and the effluent ammonium model prediction with the collected data. In a similar manner as in the control reactor, ranges of values were simulated for each parameter (Table 3), and the results of the simulations were tested against the collected data from the pilot plant with a t-student test for paired values with a confidence interval of 95%. Finally, the results of the possible combinations of fitting parameters that passed the t-student test were evaluated with the maximum axis (MA) test to detect possible biases. The scenario that gave the best simulation result and that satisfied the fitting parameters range from the control and ozonated reactors was selected as a final result.

The ATP concentration in the solids (an estimate of the active biomass fraction) was also tested for both reactors. The ATP data was used to compare the predicted active biomass in the in the control reactor and ozone reactor. The predicted inactivation rate constant (bo_3) and the transformation rate constant (ko_3) were also evaluated to discard scenarios in which any of the two rates became negative. Negative values for these rates are physically impossible and must be discarded. This leaves as possible results positive inactivation rate constants that can be higher or lower than positive transformation rate constants.

Table 3: Parameters ranges used in 3000 simulations

Parameter	Range
Influent particulate inert fraction	0.1 - 0.6
Clarifier oxygen ratio	0 - 0.1
Ozone soluble inert fraction	0 - 0.4
Ozone soluble biodegradable fraction	0 - 0.5
Ozone reaction rate factor	1 - 2.5
Soluble substrate half saturation constant	0 - 10
Ammonium autotrophs half saturation constant	0 - 1

4.3) Results and Discussion

In the fitting process over than 3000 scenarios were simulated for the control and ozonated systems. A detailed table with the maximum axis (MA) test, the t-student test (t-test) and the ordinary least square test (OSL) statistical results for 13 best combinations of parameter values can be seen in Appendix A. During the fitting process it was observed that the best-simulated scenarios were the ones that included the highest ozonated soluble biodegradable fraction (f_{SS}^{t},f_{SS}^{i}), or the ones that included the highest influent particulate inert fraction ($f_{XI,inf}$) and the highest reacted rate factor ($ko_{3,reacted\ factor}$). These last results also favored the scenarios where the inactivation rate constant (bo_3) was higher than the transformation rate constant (ko_3). The calibrated parameters for the best-simulated scenario can be seen in Table 4 and the graphical results of the measured results versus the model prediction of many variables can be seen in Fig. 10 to 19.

The best-fitted scenario shows an inactivation rate constant (bo_3) up to 2.8 times higher than the transformation rate constant (ko_3) and a treatment rate ($ko_{3,treated}$) is several times higher than the reacted rate ($ko_{3,reacted}$). The fitted parameter $ko_{3,reacted\ factor}$ indicates a reaction rate ($ko_{3,reacted}$) 2.034 times higher than the solubilization rate ($ko_{3,solubilization}$). The relationship established between the rates show congruence with the proposed assumptions in theoretical development of model, biomass more sensible to the ozone than the non-biomass, COD reacted with ozone higher than the COD solubilized by ozone, and COD treated by the ozone contactor higher than the COD reacted with ozone. The variability of these rates through the experiment was a result of the variation of operational conditions such as the inventory, the ozone dose and the RAS flow.

In Table 4 can be seen that the ozonated soluble biodegradable fraction (f_{SS}^{t}, f_{SS}^{i}) is 1.048 times higher than the ozonated soluble inert fraction (f_{SI}^{t}, f_{SI}^{i}). This ratio is positive in the sense that more COD will exit the system as CO_2 due to biological activity and negative in the sense that a higher wastage will be observed due to more biomass formation than if the ozonated inert soluble COD fraction had been higher. These fractions are a result of the specific characteristic of the treated sludge and the amount of ozone injected in the system.

In Fig. 10 and Fig. 11 it can be observed how the measured biosolids inventory increases in the control and ozonated reactors through the experiment. This increase of inventory is mainly due to accumulation of solids in the clarifiers. It is also observed that the inventory levels of both reactors have a similar value through the experiment. This is due to the effort to maintain the mixed liquor suspended solids and the operational conditions of both reactors as close as possible to make a better assessment of the sludge reduction. Finally it can be seen that the inventory of both reactors ranges from 2kg COD to 6 kg COD, and that the model prediction matches the measured values.

In Fig. 12 and Fig. 13 it can be observed that the soluble inert COD from the control reactor does not have any particular trend during the experiment but the soluble inert COD from the ozonated reactor has an increasing trend during the experiment and higher values than the control reactor. The difference in the soluble inert COD of both reactors is due to the ozonation process. As the amount of ozone on the ozonated reactor is increased through the experiment we can see also an increase of the soluble inert COD. It can be seen how the model prediction matched the measured data. The effluent inert COD represents the majority of the soluble COD that leaves the wastewater treatment process.

In Fig. 14 and Fig. 15 it can be observed that the effluent soluble substrate from the ozonated reactor is higher than the one from the control reactor through the experiment. This difference is due to the solubilization and the biomass inactivation effect of the ozonation process. The more ozone is injected in the system more solids will be solubilized as biodegradable substrate and more biomass will be inactivated reducing the systems capacity to consume the new soluble substrate. The increase of the effluent soluble substrate concentration could be important if the wastewater treatment plant effluent is already close to the BOD_5 discharge limit. It can also be seen that the model prediction matched the measured data.

In Fig.16 and Fig. 17 it can be observed that the nitrate concentration of the ozonated reactor is slightly higher than the nitrate concentration of the control reactor. The difference in the nitrate concentration is due to the release of ammonium inside the bacteria cell during its ozone inactivation process that will later become nitrate due to the autotroph nitrification process. It can be seen that the model prediction passes through the middle of the collected data.

As can be seen from Fig. 10 to 17, the model is successful in predicting the inventory of the system, the amount of COD in the effluent and the amount of nitrate. In the same manner the wasted COD and the effluent ammonium are also successfully predicted. The predicted values for all the mentioned parameters successfully passed the t-student test with a confidence interval of 95 % and the inventory and wastage successfully gave a very high correlation in the major axis (MA) test.

The biomass by the ATP measurements and the biomass model prediction of the ozone and the control reactor showed in Fig. 18 and Fig. 19 passed the t-student test with 95% confidence interval. Even though these test were successful they are not a source of validation of the model due to the small amount of samples, less than 7. This small amount of samples allowed for a broad range for positive results in the t-student test.

Table 4: Calibrated model parameters

Parameter	Unit	Limits/value
Operational parameters - influent		
Soluble inert fraction $(f_{SI,inf})$	g-COD$_{SI}$/g-COD$_{TOTAL}$	0.090
Soluble biodegradable fraction $(f_{SS,inf})$	g-COD$_{SS}$/g-COD$_{TOTAL}$	0.335
Particulate biodegradable fraction $(f_{XS,inf})$	g-COD$_{XS}$/g-COD$_{TOTAL}$	0.345
Biomass fraction $(f_{XaA,inf} + f_{XaH,inf})$	g-COD$_{Xa}$/g-COD$_{TOTAL}$	0.000[§]
Particulate inert fraction $(f_{XI,inf})$	g-COD$_{XI}$/g-COD$_{TOTAL}$	0.230
Ozone parameters – ozonation fractions		
Soluble inert fraction (f_{SI}^{t}, f_{SI}^{i})	g-COD$_{SI}$/g-COD$_{X}$	0.2883
Soluble biodegradable fraction (f_{SS}^{t}, f_{SS}^{i})	g-COD$_{SS}$/g-COD$_{X}$	0.302
Particulate biodegradable fraction (f_{XS}^{t}, f_{XS}^{i})	g-COD$_{XS}$/g-COD$_{X}$	0.3998
Oxidized fraction (f_{OX}^{t})	g-COD$_{OX}$/g-COD$_{X}$	0.0100[Ŧ]
Ozone parameters – ozonation rates		
Inactivation rate constant (bo_3)	1/day	0.0604±0.0604*
Transformation rate constant (ko_3)	1/day	0.0373±0.0373*
Biological parameters - constants		
Soluble substrate half saturation constant (K_S)	g-COD$_{SS}$/m^3	9.75
Ammonium autotrophs half saturation constant $(K_{A,NH})$	g-N/m^3	0.30

[§]: assumed value. Biomass composition in the influent is very low and the biological community in the biological process is different.

[Ŧ]: assumed value. The ozone dose is low enough to mineralize only a small fraction of the treated COD. No difference of COD concentration can be detected before and after ozonation.

*: average and range of fitted values. The fitted value for this parameter changes through the simulation.

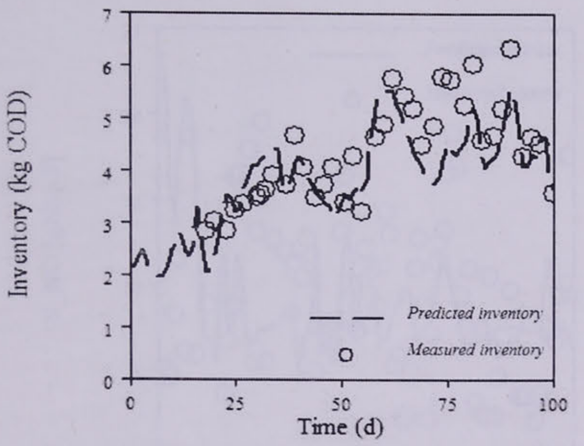

Figure 10. Control reactor inventory

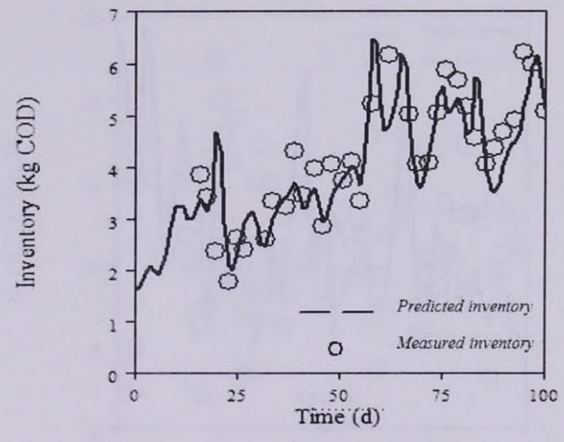

Figure 11. Ozonated reactor inventory

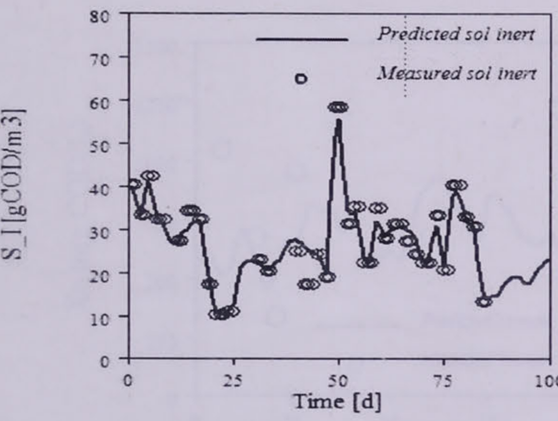

Figure 12. Control reactor effluent soluble inert COD

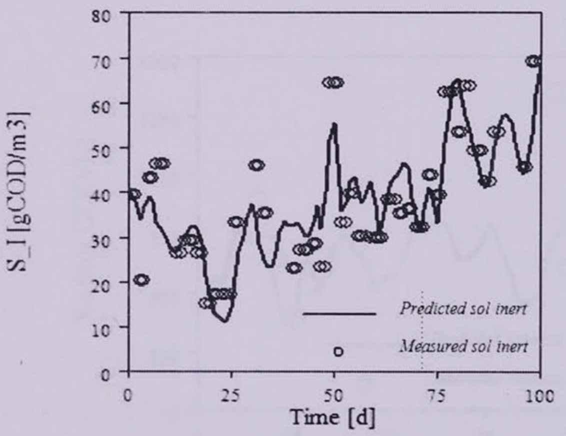

Figure 13. Ozonated reactor effluent soluble inert COD

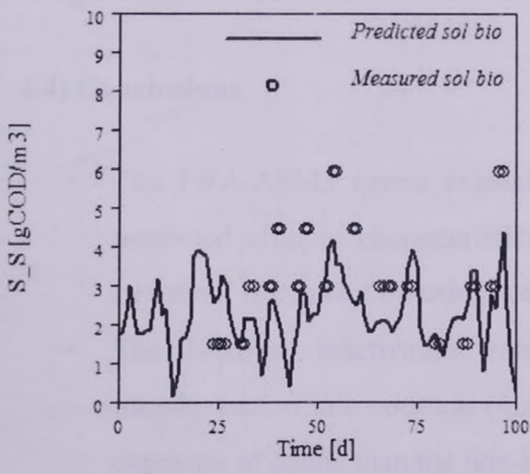

Figure 14. Control reactor effluent soluble biodegradable COD

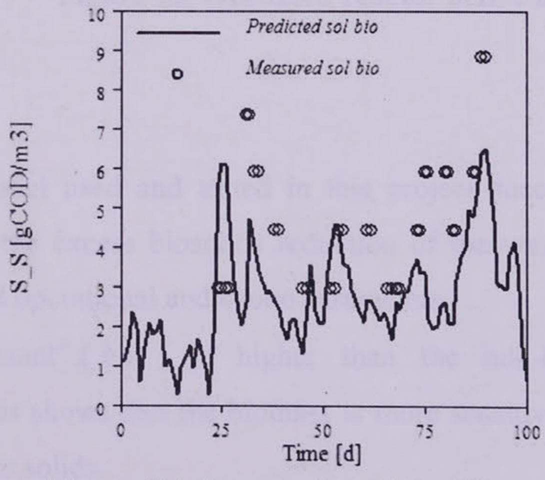

Figure 15. Ozonated reactor effluent soluble biodegradable COD

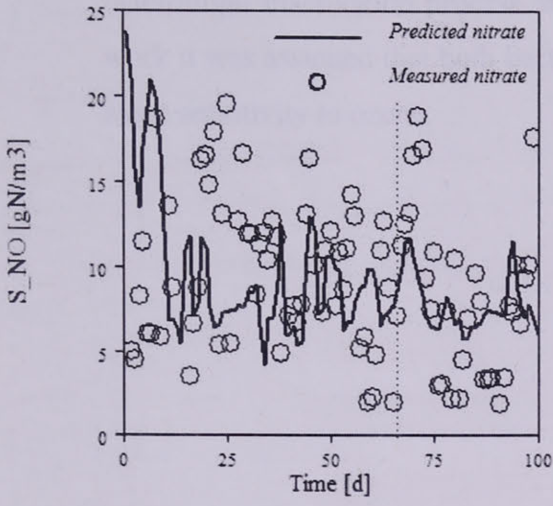

Figure 16. Control reactor effluent nitrate

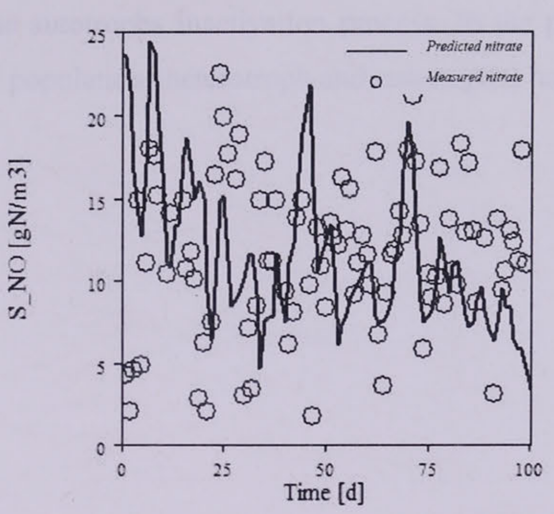

Figure 17. Ozonated reactor effluent nitrate

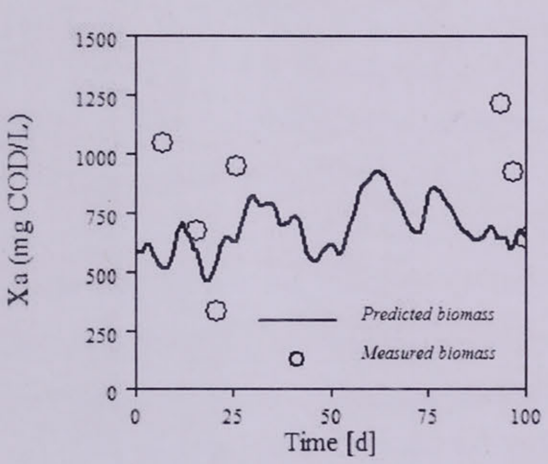

Figure 18. Control reactor active biomass

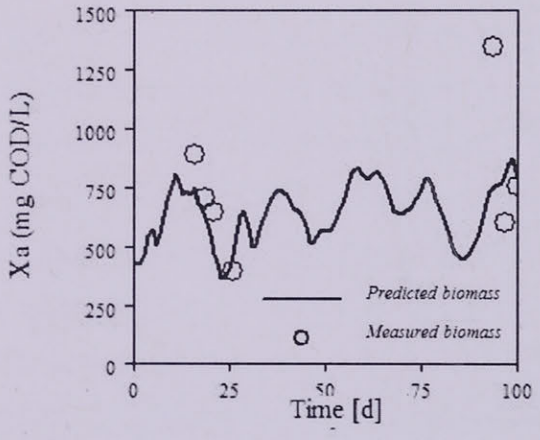

Figure 19. Ozonated reactor active biomass

4.4) Conclusions

- The IWA-ASM3 ozone extension model used and tested in this project successfully predicted effluent characteristics and the excess biosolids reduction of the wastewater treatment pilot plant by using measured operational and ozone parameters.
- The biomass inactivation rate constant (bo_3) is higher than the non-biomass transformation rate constant (ko_3). This shows that the biomass is more sensitive to the exposure of ozone than the non-biomass solids.

- Further studies need to be done to identify the difference in the ozonation fractions on the transformation process and the inactivation process, and the difference between the heterotroph inactivation process and the autotrophs inactivation process. In the present work it was assumed that both bacterial population (heterotroph and autotrophs) have the same sensitivity to ozone.

5) Modelling the Reduction of Excess Biosolids Production by Ozonation: Global Sensitivity Analysis

5.1) Objective

The objective of this section is the identification and analysis of the most important parameters that affect the performance of an ozone-biological model that predicts the reduction in sludge production to be obtained by the implementation of a RAS-ozonated technology. This will allow a better understanding of the behavior of the RAS-ozonated technology under different scenarios.

5.2) Simulation Methods

5.2.1) Global Sensitivity Analysis (GSA) Methodology

The global sensitivity analysis methodology as described by Saltelli (2004) was used. The first step was to define the parameters to be analyzed and their upper and lower boundaries. A total of sixteen parameters were selected and their boundaries were set using peer-reviewed articles and books, using expert opinion and using a combination of both as seen in table 5. The expert opinion was given over the parameters of the ozone model extension by its two authors.

The second step consisted in the sampling of these parameters. For this step the Latin Hypercube sampling procedure was chosen (McKay et al. 1979, Sin et al. 2009, Helton and Davis 2003). A total of 500 values were sampled for each parameter and a total of 500 vectors were generated for 500 different operational conditions. This step was supported by the use of Microsoft Excel.

The third step consisted in the simulation of each one of these vectors for a regular complete mixed reactor and for an ozonated complete mixed reactor with the same mixed liquor volatile suspended solids (MLVSS) equilibrium concentration of both reactors by manipulating the solid retention time (SRT) of the ozonated reactor. This step was supported by the use of the software AQUASIM (Reichert 1998) and three extensions of this program that were created for this purpose.

The fourth step consisted in the calculation of the output of interest, which is the sludge production ratio slope (SPRs) (Foladori et al. 2010, Frigon and Isazadeh 2011). The SPRs is the slope generated from the plot of the sludge production ratio (SPR) and the solubilization rate

($ko_{3,solubilization}$). The sludge production ratio (SPR) was calculated for each of the 500 simulation cases. The SPR is the ratio between the amounts of biosolids generated by the ozonated reactor divided by the amount of biosolids generated by the regular reactor. Each of the 500 simulations had a given solubilization rate. These two data results (SPR and $ko_{3,solubilization}$) from the simulation gives one data point to calculate the SPRs. The second chosen data point was a known point, this is when the solubilization rate ($ko_{3,solubilization}$) is equal to zero the sludge production ratio (SPR) is equal to one. With these two pair of points the sludge production ratio slope (SPRs) was computed for the 500 vectors.

Table 5: Global sensitivity analysis parameter and limits selection

Notation	Description	Unit	Minimum (Ref.)		Maximum (Ref.)	
$b_{H,O2,20°C}$	decay coefficient for heterotrophic biomass at 20 °C	g-COD_{Xb}/g-COD_{XH}/day	0.1	(anoxic) (Hauduc et al. 2011)	0.3	(oxic) (Hauduc et al. 2011)
bo_3/ko_3	ratio between bo_3 and ko_3 ($bo_{3\,factor}$)	N.U.	1	(Frigon and Isazadeh 2011)	4	expert opinion, (Frigon and Isazadeh 2011)
COD_{TOT}	total COD influent concentration	g-COD_{TOTAL}/m^3	250	(Metcalf & Eddy. et al. 2003)(T-3-15)	900	(Metcalf & Eddy. et al. 2003)(T-3-19)
f_{SI}^t	fraction of soluble inert COD generated by ozone transformation of non-biomass solids	g-COD_{SI}/g-$COD_{X(I+S)}$	0	expert opinion, (Frigon and Isazadeh 2011)	0.3	expert opinion, (Frigon and Isazadeh 2011)
$f_{SS,inf}$	fraction of readily degradable COD on total COD	g-COD_{SS}/g-COD_{TOTAL}	0.3	derived from (Metcalf & Eddy. et al. 2003)(T-3-15)	1	(Metcalf & Eddy. et al. 2003)(T-3-15)
f_{XS}^t	fraction of particulate biodegradable COD generated by ozone transformation of non-biomass solids	g-COD_{XS}/g-$COD_{X(I+S)}$	0	expert opinion, (Frigon and Isazadeh 2011)	0.65	expert opinion, (Frigon and Isazadeh 2011)
HRT	hydraulic retention time	Day	0.125	(Metcalf & Eddy. et al. 2003)(T-8-16)	1.25	(Metcalf & Eddy. et al. 2003)(T-8-22)
$k_{H,20°C}$	maximum specific hydrolysis rate at 20 °C	g-COD_{SS}/g-COD_{XH}/day	3	(Hauduc et al. 2011)	9	(Hauduc et al. 2011)
K_S	half-saturation coefficient of soluble biodegradable COD (Ss) for heterotrophic biomass	g-COD_{SS}/m^3	2	(Hauduc et al. 2011)	10	(Hauduc et al. 2011)

Table 5: Global sensitivity analysis parameter and limits selection (continued)

Notation	Description	Unit	Minimum (Ref.)		Maximum (Ref.)	
K_X	half-saturation coefficient for hydrolysis of slowly degradable substrate (Xs) for heterotrophic biomass	g-COD$_{XS}$/g-COD$_{XH}$	0.75	(Sin et al. 2010), (Gujer et al. 1999)	1.25	(Sin et al. 2010), (Gujer et al. 1999)
$k_{STO,20°C}$	storage rate constant for heterotrophic biomass at 20 °C	g-COD$_{XSTO}$/g-COD$_{XH}$/day	10	(Hauduc et al. 2011)	12	(Hauduc et al. 2011)
SRT_C	solids retention time of control reactor	Day	3	(Metcalf & Eddy. et al. 2003)(T-8-16)	30	(Foladori et al. 2010), (Metcalf & Eddy. et al. 2003)(T-8-22)
T	temperature	°C	3.5	(Metcalf & Eddy. et al. 2003)(F-2-11)	35	(Metcalf & Eddy. et al. 2003)(page 55)
$\mu_{H,20°C}$	maximum specific growth rate for heterotrophic biomass at 20 °C	1/day	2	(Hauduc et al. 2011)	3	(Hauduc et al. 2011)
$Y_{H,O2}$	yield for heterotrophic biomass	g-COD$_{XH}$/g-COD$_{STO}$	0.7	(anoxic) (Hauduc et al. 2011)	0.8	(oxic) (Hauduc et al. 2011)
$Y_{STO,O2}$	yield for the cell internal storage product of heterotrophic biomass	g-COD$_{XSTO}$/g-COD$_{SS}$	0.54	(anoxic) (Hauduc et al. 2011)	0.8	(oxic) (Hauduc et al. 2011)

The fifth step consisted in the estimation of the standardized regression coefficients (SRC) (Saltelli 2004). This value was obtained by making a linear regression of the results of the sludge production ratio slope (SPRs) versus the 16 parameters that were sampled. The regression was performed over the centered and standardized value of each sample (simulated parameter value minus the average value of the sampled parameter divided by the standard deviation of its group, with an intercept of zero).

$$\frac{Y^k - \mu_Y}{\sigma_Y} = \sum_{i=1}^{r} \left(\beta_{X_i} \times \frac{X_i^k - \mu_{X_i}}{\sigma_{X_i}} \right) + \varepsilon_k \qquad (14)$$

where X_i^k is the kth sampled value of the ith parameter, r is the number of parameters, Y^k is the SPRs for the kth samples values, β_{X_i} is the standardized regression coefficient (SRC) for the parameter X_i, and ε_k is the regression error.

5.3.2) Statistical Analysis Methodology

The reproducibility and the significance of the results are two important concerns when performing a Global Sensitivity Analysis. In order to show the reproducibility of the methodology and its results, the procedure was performed three times expecting to obtain similar standardized regression coefficients (SRC) and similar R^2 values. In order to assess the significance of the regressions and of the standardized regression coefficient, the magnitude of the R^2 values and of the student t test were used, respectively (Sin et al. 2009, Helton and Davis 2003).

5.3.3) IWA-ASM3 Model Extension File and Simulation Program

The simulation program used to perform the global sensitivity analysis is AQUASIM (Reichert 1998). The simulation program file used included all the modifications indicated in section 3.4 of this report as summarized in Table 2.

5.4) Results and Discussion

5.4.1) Parameters Standard Regression Coefficient

The computed values of the regression coefficients of the different parameters are shown in Table 4 in decreasing order of importance. The three simulations had similarly high R^2 values (average 0.89), indicating reproducibility and a good linear correlation between the samples and the results of the simulations. Saltelli (2004) suggests at a R^2 of 0.7 or above the SRC correctly represent the global sensitivities of parameters, which was the case here. Table 4 is divided in two sections. The upper section with the highest SRC shows the significant parameters, and the lower section that has lowest SRC shows the non-significant ($P<0.05$) parameters. The SRC have an absolute value and a sign. The absolute value indicates the importance of the model parameter. The higher the absolute SRC the more sensitive is the model output to changes in this model parameter. The sign indicates the direction of changes in the model outputs compared to the direction of changes in the parameter values. Here, an increase in the value of a parameter that has a negative sign in its SRC will generate a steeper sludge production ratio slope (SPRs), improving the reduction in the sludge production of the ozonated system, as explained in Fig. 20.

5.4.2) Parameter SRC Interpretation

The interpretations of the effect of the eight most significant parameters listed in the upper section of Table 6 are stated as follows:

Solid retention time (SRT_C): An increase in the SRT reduces the proportion in the biomass in the sludge and increases the proportion of non-degradable particulate COD (X_I). Thus, greater gains in sludge reduction occur at high SRT_C. Fruthermore, higher SRTs forces more of the biodegradable COD generated by ozonation to be mineralized in the biological process and leave the system as CO_2.

Ozone particulate biodegradable transformation fraction (f_{XS}^{t}): An increase in the particulate biodegradable transformation fraction due to ozonation represents a decrease of the solubilization fractions. Reducing the solubilization fractions and maintaining the solubilization rate ($ko_{3,solubilization}$) *de facto* increases the transformation (ko_3) and the inactivation (bo_3) rate constants (eq. 1,2 and 3). In turn, this produces an increase in the overall amount of particulate COD transformed by ozone.

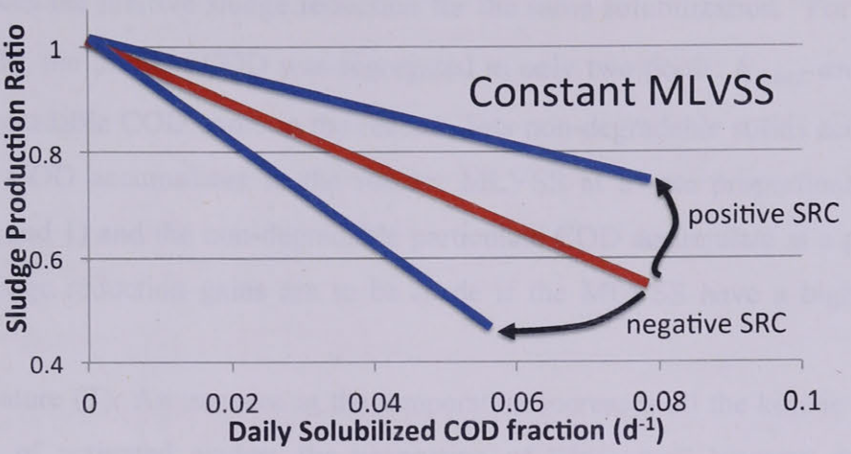

Figure 20. Sludge production ratio slope variation by increase of parameter values

Table 6: Standard regression coefficient (SRC) for the sludge reduction ratio slope

Parameter	Type	Average SRC	95% confidence interval
R^2		0.8902	
Statistically Significant Parameters			
SRT_C	Operational	-0.7823	±0.0299
f_{XS}^{t}	Ozone	-0.4315	±0.0332
$f_{SS,inf}$	Operational	0.1375	±0.0300
T	Operational	-0.1054	±0.0299
bo_3/ko_3	Ozone	0.0973	±0.0300
$f_{SI}^{t'}$[1]	Ozone	-0.0615	±0.0336
Y_O[2]	Operational	0.0583	±0.0300
$b_{H,O2,20°C}$	Biological	-0.0416	±0.0301
Statistically Non-Significant Parameters			
K_X	Biological	0.0213	±0.0300
K_S	Biological	-0.0180	±0.0299
HRT	Operational	0.0136	±0.0299
COD_{TOT}	Operational	-0.0075	±0.0301
$\mu_{H,20°C}$	Biological	0.0050	±0.0300
$k_{STO,20°C}$	Biological	-0.0038	±0.0300
$k_{H,20°C}$	Biological	0.0015	±0.0332

1: $f_{SI}^{t'} = f_{SI}^{t}/(1 - f_{XS}^{t})$
2: $Y_O = Y_{H,O2} \times Y_{STO,O2}$

Influent biodegradable fraction ($f_{SS,inf}$): As the SRC is positive; this means that a higher $f_{SS,inf}$ reduces the relative sludge reduction for the same solubilization. For the purpose of the current study, the influent COD was segregated in only two pools: $f_{SS,inf}$ and $f_{XI,inf}$. Thus, as more biodegradable COD come in the reactor, less non-degradable solids accumulate. Because degradable COD accumulates in the reactor MLVSS at a rate proportional to the net yield (between 0 and 1) and the non-degradable particulate COD accumulate at a proportional rate of 1, more sludge reduction gains are to be made if the MLVSS have a higher non-degradable fraction.

Temperature (T): An increase in the temperature increases all the kinetic parameters. At the high SRTs of activated sludge, the proportion of "decaying" biomass and non-degradable MLVSS is set by the decay rate constant. The increase in the decay rate increases the proportion of non-degradable MLVSS and enhances the decaying of biomass newly formed from the production of degradable COD by ozonation

Inactivation-transformation ratio (bo_3/ko_3): An increase in the bo_3/ko_3 ratio ($bo_{3\,factor}$) enhances the inactivation process. As above, ozone attack on the non-degradable solids enhances the sludge reduction.

Ozone soluble inert fraction prime ($f_{SI}^{t'}$): An increase in the soluble inert COD fraction generates more soluble inert COD due to ozonation and reduces the amount of biodegradable substrate generated. The amount of COD that exits the system as soluble inert COD is more than the quantity of COD that exits the system as CO_2 in the biodegradation process of the biodegradable substrate produced.

Overall yield (Y_O): An increase on the overall yield produces a reduction of the COD that leaves the system as CO_2 in the biological process after ozonation.

Biomass decay rate ($b_{H,O2,20°C}$): As stated before, at the high SRTs of activated sludge, the proportion of "decaying" biomass and non-degradable MLVSS is set by the decay rate constant. The increase in the decay rate increases the proportion of non-degradable MLVSS and enhances the decaying of biomass newly formed from the production of degradable COD by ozonation.

On Table 6 it can be seen that most of the significant parameters are operational and ozone, and that most of the non-significant parameters are biological. The yield is considered an operational parameter because it can be manipulated by changing the configuration of the system from aerobic to anoxic or anaerobic.

The segregation of parameters observed in Table 6 indicates that to be able to make a better prediction of the reduction in sludge production in an ozonated system it is not important to have a precise value of the biological parameters but it is important to have precise values of the operational parameters and the ozonation parameters. Generally the operational parameters are already known in an established biological wastewater system, leaving for investigation of the ozonation parameters for each specific site. The required ozonation tests can be performed at a laboratory scale level.

5.4.3) Design and Operation Guidelines

From the previous analysis and result interpretation, design and operational guidelines can be drawn for practitioners to take into account for the implementation of the ozone technology.

5.4.3.1) Operational Parameters

The installation of ozone technology requires the increase of the solid retention time (SRT) of the biological reactor to increase the mixed liquor suspended solids to secure operational levels. The higher is the increase of the SRT the higher will be the ozone technology efficiency in the reduction of excess biosolids production. Wastewater treatment plants with a high solid retention time are good candidates for the installation of the ozone technology.

A high particulate inert solids fraction of the wastewater treatment plant influent improves the efficiency of the reduction of excess biosolids production. A change in the wastewater treatment composition can change the amount of excess biosolids produced and the amount of ozone required to achieve a given excess biosolids reduction. For this reason a continuous monitoring of the wastewater treatment influent composition is highly suggested.

A higher temperature favors a higher efficiency of the reduction of excess biosolids production requiring less ozone to achieve a given excess biosolids reduction. As the temperature is a parameter that varies through the seasons it should be closely monitored and projected to anticipate and correct any change in the wastewater treatment plant operation.

A change in the configuration of the biological reactor, from an aerobic system to an anoxic or anaerobic system will reduce the overall yield of the system. This decrease of the system overall yield will reduce the amount of excess biosolids produced.

5.4.3.2) Ozone Parameters

The ozone parameters are intrinsic to of the characteristics of the biosolids found in every wastewater treatment plant. Different wastewater treatment plants will have a different reaction depending on the sludge characteristic and the ozone dose applied. A high particulate biodegradable ozone fraction (f^{t}_{XS}, f^{i}_{XS}), a low inactivation/transformation ratio $(bo_{3\,factor})$ and a high soluble inert ozone fraction (f^{t}_{SI}, f^{i}_{SI}) will increase the reduction of the excess biosolids production. The most important factor is the particulate biodegradable ozone fraction, followed by the inactivation/transformation ratio and finally the soluble inert ozone fraction. The ideal ozone dose that can maximize the excess biosolids reduction potential o a wastewater treatment plant can be found by laboratory scale experiments.

5.4.3.3) Biological Parameters

As the biological parameters are a characteristic of the biological community present in the reactor, it cannot be changed by process modifications. In this manner the only action to be taken is to find the most accurate value of these parameters. From all the biological parameters the decay rate is the only one that will have a significant impact in the accurate prediction of the reduction of the biosolids production. These values can be determined through laboratory experiments.

5.5) Conclusions

- The IWA-ASM3 extension model shows that the operational parameters and the ozone parameters have the greatest sensitivity/impact over the sludge production ratio slope.
- Biological parameters are not significant in the prediction of the sludge reduction in an ozonated system.
- The result of the global sensitivity analysis encourages focusing the efforts of the modelling of an ozonated system on the investigation of the ozone parameters over the biological parameters. Operational parameters are generally already available in established systems.
- The understanding of the ozonation system and the parameters that govern it imposes a challenge on practitioners on the design, retrofit and operation of biological wastewater treatment plants.

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Appendix A

Table A1: Statistic tests of 13 positive scenarios for ozonated reactor

SN	Program parameters			Major axis test (MA)					
				Ozonated Reactor Inventory					
	$f_{XI,inf}$	$ko_{3,reacted\ factor}$	f_{SS}^{t}	b_1	b_0	CI b_1		CI b_0	
1	0.230	2.370	0.200	0.9184	0.3280	0.6990	1.1992	-0.8337	1.2358
2	0.230	2.420	0.200	0.9248	0.3123	0.7053	1.2057	-0.8500	1.2203
3	0.230	2.470	0.200	0.9310	0.2971	0.7114	1.2121	-0.8661	1.2055
4	0.235	2.370	0.200	0.9272	0.3221	0.7058	1.2113	-0.8537	1.2383
5	0.235	2.420	0.200	0.9336	0.3063	0.7122	1.2179	-0.8701	1.2227
6	0.235	2.470	0.200	0.9399	0.2909	0.7183	1.2244	-0.8863	1.2078
7	0.240	2.370	0.200	0.9360	0.3162	0.7125	1.2236	-0.8741	1.2410
8	0.240	2.420	0.200	0.9425	0.3002	0.7189	1.2303	-0.8907	1.2252
9	0.240	2.470	0.200	0.9488	0.2847	0.7251	1.2368	-0.9069	1.2102
10	0.240	2.499	0.200	0.9523	0.2761	0.7286	1.2405	-0.9161	1.2019
11	0.230	2.020	0.300	0.9914	0.1382	0.7700	1.2758	-1.0386	1.0545
12	0.230	2.048	0.300	0.9957	0.1273	0.7740	1.2804	-1.0509	1.0444
*13	0.230	2.034	0.302	0.9957	0.1270	0.7741	1.2805	-1.0513	1.0441

SN: scenario number
CI: 95% confidence interval
*13: best solution
$ko_{3,reacted\ factor} = ko_{3,reacted}/ko_{3,solubilization}$
MA test: $Y = b_1 \times X + b_0$

Table A2: Statistic tests of 13 positive scenarios for ozonated reactor

	Major axis test (MA)						Ordinary least square test (OLS)		Student T-test (T-test)	
SN	Ozonated reactor wastage						Ozonated reactor inventory	Ozonated reactor wastage	Ozonated reactor inventory	Ozonated reactor wastage
	b_1	b_0	CI b_1		CI b_0				$t_{0.05,33} = 2.03$	$t_{0.05,37} = 2.021$
1	0.8961	0.0894	0.4203	1.7989	-0.2622	0.2747	0.6473	0.2092	-0.0794	1.7426
2	0.8983	0.0895	0.4192	1.8131	-0.2668	0.2760	0.6502	0.2072	0.0089	1.7695
3	0.9006	0.0894	0.4182	1.8277	-0.2716	0.2773	0.6529	0.2053	0.0955	1.7956
4	0.9111	0.0868	0.4285	1.8400	-0.2750	0.2747	0.6469	0.2085	0.1717	1.8483
5	0.9134	0.0868	0.4274	1.8551	-0.2799	0.2760	0.6498	0.2065	0.2612	1.8751
6	0.9157	0.0867	0.4264	1.8703	-0.2850	0.2773	0.6525	0.2046	0.3489	1.9011
7	0.9262	0.0841	0.4369	1.8817	-0.2880	0.2746	0.6463	0.2079	0.4213	1.9533
8	0.9286	0.0840	0.7186	1.3011	-0.0610	0.1658	0.6493	0.2059	0.5123	1.9799
9	0.9312	0.0839	0.4350	1.9135	-0.2986	0.2772	0.6520	0.2040	0.6009	2.0059
10	0.9326	0.0839	0.4345	1.9228	-0.3017	0.2779	0.6535	0.2030	0.6513	2.0207
11	0.9125	0.0919	0.4028	1.9476	-0.3112	0.2904	0.6762	0.1885	0.8686	2.0053
12	0.9142	0.0918	0.4021	1.9593	-0.3152	0.2912	0.6776	0.1873	0.9250	2.0207
*13	0.9957	0.1270	0.7741	1.2805	-1.0513	1.0441	0.6776	0.1873	0.9252	2.0205

SN: scenario number

CI: 95% confidence interval

*13: best solution

MA test: $Y = b_1 \times X + b_0$

OLS test: R^2 value

t-test: t-test for paired samples with 95% confidence

In appendix A it can be seen the statistical results for 13 simulated scenarios, including the best solution (scenario 13). The statistical test includes the maximum axis test (MA), the t-student test (t-test) and the ordinary least square test (OLS). The MA test includes the coefficient b_1 that represents the correlation between the simulation results and the collected data, and an intercept b_0 that represents any bias between the simulation results and the collected data. It can be observed that in the MA test results all the selected scenarios had a b_1 coefficient higher than 0.89 and a b_0 intercept less than 0.32, which shows a good fit of the simulation results with the pilot plant data. The ideal values of this test are 1 for the slope coefficient b_1 that represents a perfect correlation between the simulation results and the data, and 0 for the intercept b_0 that represents non-bias between the simulation results and the data. These values are included in the 95% confidence interval of all the scenarios. The t-test also gave positive results for all the 13 selected scenarios ranging from -0.0794 to 0.20205. The 95% confidence interval for this test for the inventory and wastage of the ozonated system are ±2.03 and ±2.021 respectively. This means that any scenario that has a t-test value within this confidence interval does not have a significant difference between the simulation result and the measured data. In addition the OLS coefficient was also calculated for each scenario. As it can be observed the results of the OLS test show very low values that would suggest a poor correlation between the simulation results and the data. This is not the case as the OLS test is not the appropriate method to be used, as explained before, and the interpretation of its results could lead to interpretation errors.