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A Dynamic Model

for Predicting Off-gas Mole Fraction from the Nitrifying Activated Sludge Process

A thesis submitted in partial satisfaction

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by

Shao-Yuan Leu

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The thesis of Shao-Yuan Leu is approved

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Jennifer A. Jay

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Keith D. Stolzenbach

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Michael K. Stenstrom

University of California Los Angeles

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ABSTRACT OF THE THESIS

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by

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Professor Michael K. Stenstrom

The activated sludge process is the most popular method for providing secondary treatment of municipal wastewaters. The primary energy requirement is aeration and often the aeration system uses more than 50% of the electrical energy of a treatment plant. The need for nutrient removal such as ammonia increases the energy requirement, since the ammonia must also be oxidized. Ammonia is important to remove since the discharged ammonia may cause high biological oxygen demand (BOD) in receiving waters and is toxic to aquatic life. Removing ammonia in the

activated sludge process places greater constraints on the process, such as a longer mean cell retention time, need for higher temperatures and dissolved oxygen concentrations, and more neutral pH. As a consequence of the need to remove ammonia, treatment plants need to be upgrade to meet the more stringent conditions. Upgrading the aeration system is one of the most critical needs.

Aeration systems are quantified and designed using clean water data. The conversion of clean water conditions to process conditions is difficult and sometimes unreliable. Conversion requires accurate correction factors, which are hard to estimate, and can not be determined in real-time. As a consequence, process water testing is used, and off-gas testing is the most commonly used method of process water testing. An off-gas test is an analysis method with no such shortcomings. By analyzing the off-gas right from the process water with simple devices, oxygen transfer efficiency can be correctly and effectively estimated, and the treatment performance can be easily understood.

The classical method of off-gas testing ignores the carbon dioxide content in the off-gas. Since the by-products of oxidizing carbonaceous and nitrogenous compounds are different, it is possible to use the carbon dioxide mole fraction to estimate nitrification performance. This thesis develops a dynamic model to simulate off-gas mole fraction of a nitrifying ASP for various process conditions. The relationship between nitrification, oxygen transfer, carbon dioxide production, and pH was investigated. It is concluded that the relative mole fraction of oxygen and carbon dioxide in the off-gas can be used to estimate nitrification efficiency.

1. INTRODUCION

The activated sludge process is the most common treatment processes for municipal wastewaters, especially for large cities. Under appropriate conditions, pollutants that exert biological oxygen demand (BOD), including carbonaceous and nitrogenous compounds, can be removed by the microorganisms in the activated sludge. However, because of the variation of the influent wastewater flow and composition, the operation and performance of the activated sludge process vary. There are many criteria for providing a suitable habitat for microorganisms, especially for nitrifying bacteria, which must be carefully maintained, such as proper pH, temperature, sufficient oxygen supply and high sludge retention time (SRT).

An important aspect of process operation is the oxygen transfer efficiency (OTE), which impacts not only nitrification but also energy conservation. If sufficient oxygen can not be supplied, a proper bacteria population cannot be maintained and the failure of nitrification may easily occur. Days or weeks can be required to recover the bacteria population. During this period, the effluent may still contain substantial amount of nitrogenous compounds which could cause serious environmental problems.

In recent years, fine-pore diffusers have been used to reduce energy consumption and provide higher oxygen transfer rates. Unfortunately, fine pore diffusers suffer from fouling or scaling and the lifetime of fine-pore diffusers is hard to estimate. Diffusers made from both ceramic and synthetic membranes are susceptible to fouling. Fouled diffusers suffer a significant drop in OTE. If this situation is not corrected in a short period, greater air flow rate, which represents more energy and operation costs, will be required, eliminating the benefits of fine-pore diffusers.

To avoid this problem, better OTE analysis methods have been developed, which can provide real-time data. Several major strategies for estimating OTE have been applied, which are the clean water test, various process water tests, material balance methods, and the off-gas test. Among these tests, the off-gas test has the benefits of accuracy and requires a short test interval. The off-gas method is now being frequently used to assess aeration system performance.

In this thesis, the possibility of estimating nitrification efficiency using off-gas test results was investigated. Since the by-products of the treatment of carbonaceous and nitrogenous compounds in activated sludge processes (ASP) are different, this difference, if measurable in the off-gas, can become the basis for a new method of analyzing nitrification efficiency.

The proposed method is based upon the differences in carbon dioxide production, as shown in Figure 1. The molar fraction of carbon dioxide in the off-gas should be greater if nitrification is limited, or the ratio of nitrogenous compounds and total BOD is smaller. For verifying this assumption, a mathematical model of ASP was built to simulate the temporal concentrations of the major components in wastewater and its off-gas, including the temporal concentrations of substrate, biomass in the biological phase, oxygen, carbon dioxide, ammonia, nitrite, nitrate, alkalinity and pH in the liquid phase, and oxygen, carbon dioxide, and nitrogen in the gas phase. The model simulations and trends from full-scale treatment plant were compared and a probable operation strategy is suggested.

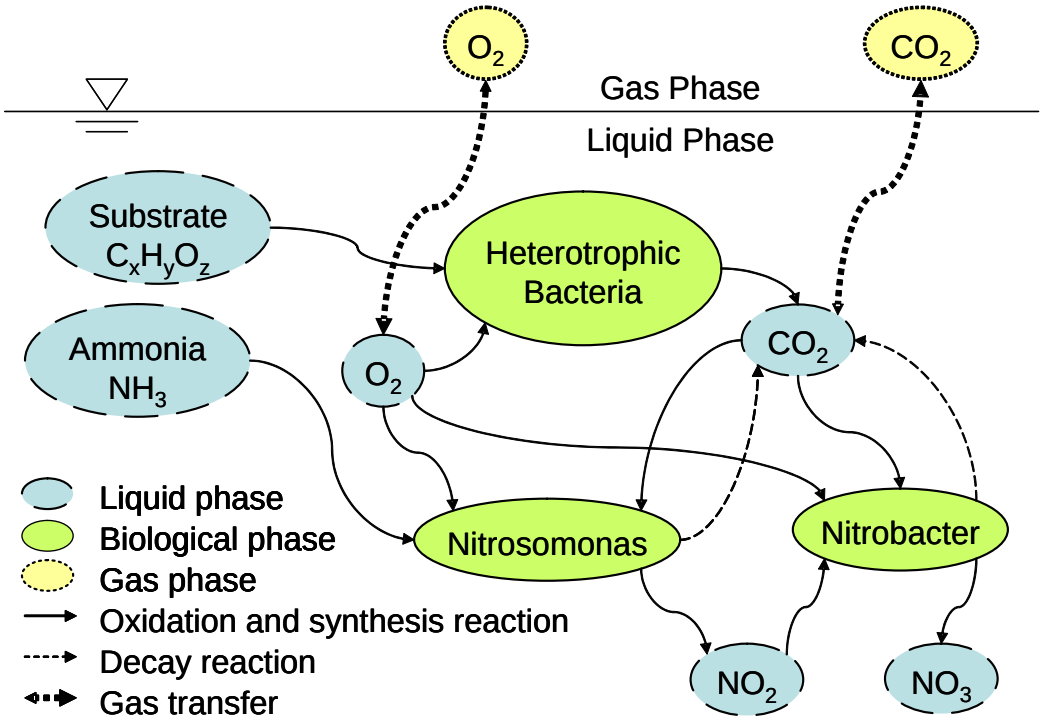

Figure 1. A sketch of basic reactions in ASP

2. LITERATURE REVIEW

2.1 Development of general activated sludge dynamic models

With improving computer technology, mathematical modeling has become one of the most helpful tools for environmental researchers to understand the long-term or temporal situation in a biological treatment process. With a suitable model, engineers or operators can easily predict the probable results and make a decision without using trial and error on doing experiments; since only personal computers are required. This approach is economical and avoids the risk of violating a permit if an experiment fails.

The fundamental theorem of activated sludge model is based on mass conservation equation (Accumulation = Inflow – Outflow ± Reaction). To simplify the calculation, the reactor is assumed to be a continuous flow stirred tank reactor (CFSTR) followed by a clarifier (Figure 2), which functions as a liquid-solid separator. Also, all the reactions are assumed to occur only in the aeration tank, and the clarifier is treated as a 'zero-volume' container.

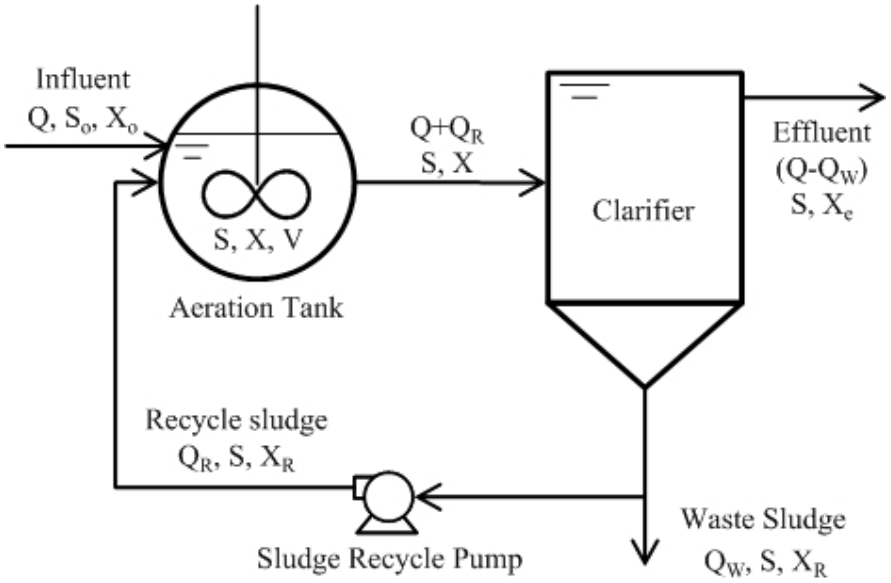

Figure 2. Schematic diagram of reactor system (Metcalf and Eddy, 2003)

The basic mass balance equation of cell accumulation can be expressed as:

$$\frac{dX}{dt}\cdot V = QX_o - \left[(Q - Q_W)X_e - Q_W X_R\right] + r_g V \qquad (1)$$

where

X = cell concentration in the tank (M/L^3)

X_o = the influent cell concentration (M/L^3)

X_e = the effluent cell concentration (M/L^3)

X_R = recycle sludge concentration (M/L^3)

V = tank volume (L^3)

Q = flow rate (L^3/T)

Q_W = disposed sludge flow rate (L^3/T)

r_g = reaction rate ($1/T$)

The reaction rate (r_g) in this equation represents the net rate of microbial production. It consists of several terms including cell growth and decay rates. The microbial growth kinetics was reported by Monod (1942). In his research, he found that the cell growth rate was affected by the substrate concentration in the reactor. As the substrate increased concentration, the biomass growth rate was increased proportionally, and then saturated at a maximum value as the substrate continued to increase (Figure 3). This phenomenon could be expressed as the simple function showing in equation, which is now commonly known as the Monod function. The net microbial production rate including the Monod function and first-order decay rate can be written as:

$$r_g = \frac{\hat{\mu}_S XS}{Ks + S} - Kd \cdot X \qquad (2)$$

where

$\hat{\mu}_S$ = maximum biomass growth rate (1/T)

S = substrate concentration (M/L^3)

Ks = half-velocity coefficient, the concentration of substrate when half maximum specific substrate rate is achieved (M/L^3)

Kd = decay rate (1/T)

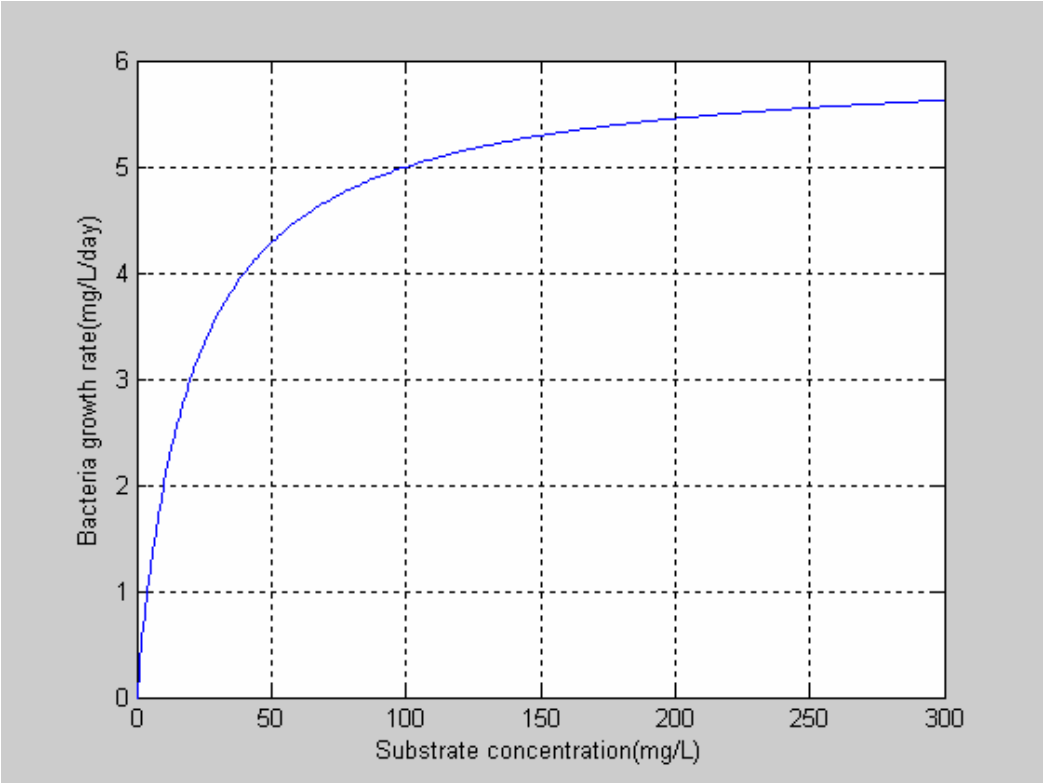

Figure 3. Relationship between substrate concentration and biomass growth rate

Since the utilization rate of substrate is proportional to the cell growth rate, it can also be calculated from Monod function as well. The mass balance of substrate can be expressed as:

$$\frac{dS}{dt} \cdot V = QS_O - QS \pm V\frac{r}{Y} \tag{3}$$

where

S_O = the influent cell concentration (M/L^3)

$$r = \frac{\hat{\mu}_S S}{Ks + S} \cdot X = \text{net cell growth rate } (1/T) \tag{4}$$

Y = mass yield (mass cell / mass substrate)

2.1.1 Steady-state model

Analytical solutions of non-linear ordinary differential equations (ODE) are generally not available; hence time dependent simulation of the mass balance equations of ASP was not possible. Only steady-state solutions were available. At steady-state, the accumulation rate in mass balance equations (1) and (3) are equal to zero; therefore the ODE can be reduced to algebraic equations and can be easily solved. For example, the ODE of cell growth and substrate utilization can be reduced and expressed as two functions (Metcalf and Eddy, 2003):

$$S = \frac{Ks\left[1 + Kd \cdot SRT\right]}{SRT \cdot \left(Yk - Kd\right) - 1} \quad (5)$$

$$X = \left(\frac{SRT}{\tau}\right) \cdot \left[\frac{Y \cdot \left(S_o - S\right)}{1 + Kd \cdot SRT}\right] \quad (6)$$

SRT = sludge retention time (T)

$\tau = \frac{V}{Q}$ = hydraulic retention time (T)

From the steady-state model, the basic pattern or correlation between substrate and biomass concentration over sludge retention time (SRT) can be understood. As shown in Figure 4, microorganisms can be "washed out" when the SRT is low; and therefore no substrate is consumed. The optimal sludge retention time for an ASP can be determined using this model if the influent conditions are stable.

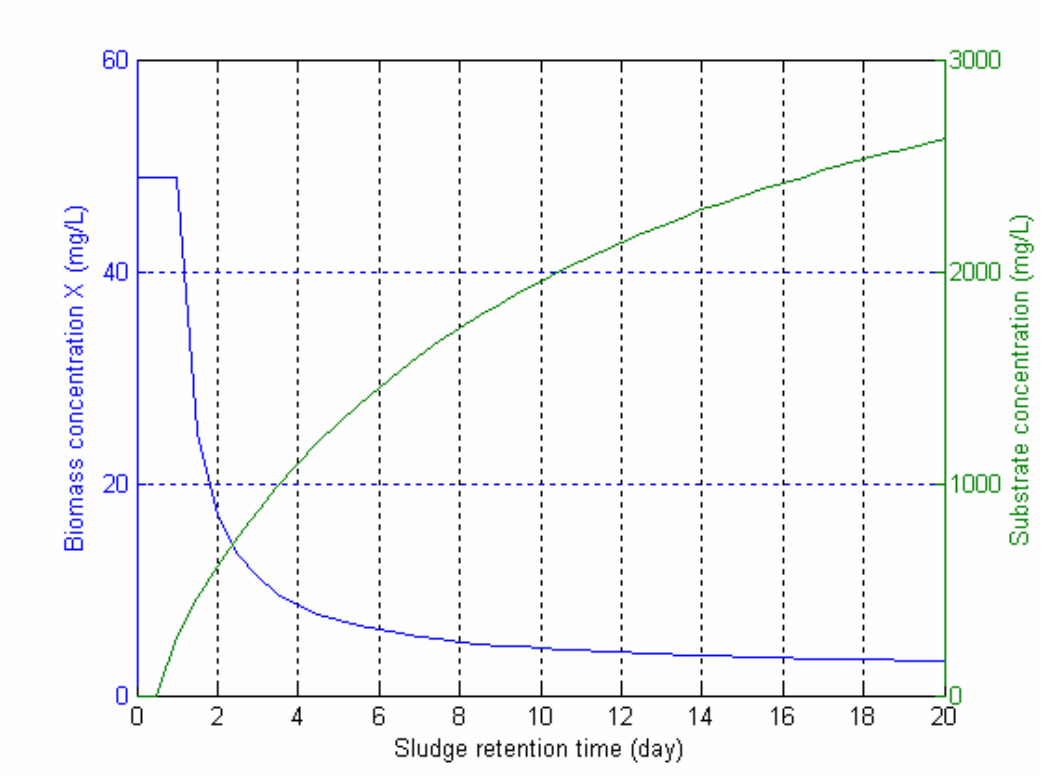

Figure 4. Steady-state simulation of substrate and biomass concentration

2.1.2 Dynamic model

After the popular use of computers, ODEs could be solved numerically, which allow researchers to use dynamic models. The earliest dynamic model for a biological wastewater treatment process was developed by Andrews (1972). In his model, a computer program called CSMP/360 (Speckhart, and Green, 1976) was utilized to numerically solve the ODEs of substrate and cell mass balances. From his research, the concepts of developing an ASP model and control strategies were then built. The benefits of simulation models were also realized.

In 1983, the International Association on Water Quality (IAWQ) established an international research group to develop a general ASP model. Different approaches were suggested and discussed among researchers. For example, substrate was found

to be consumed in different rates in activated sludge. Some of the substrate could be utilized by microorganism rapidly in cell synthesis but others could not. Clifft and Andrews (1981) suggested a pattern between the substrate reduction, the growth of microorganism and oxygen consumption as Figure 5 (Patry and Chapman, 1989).

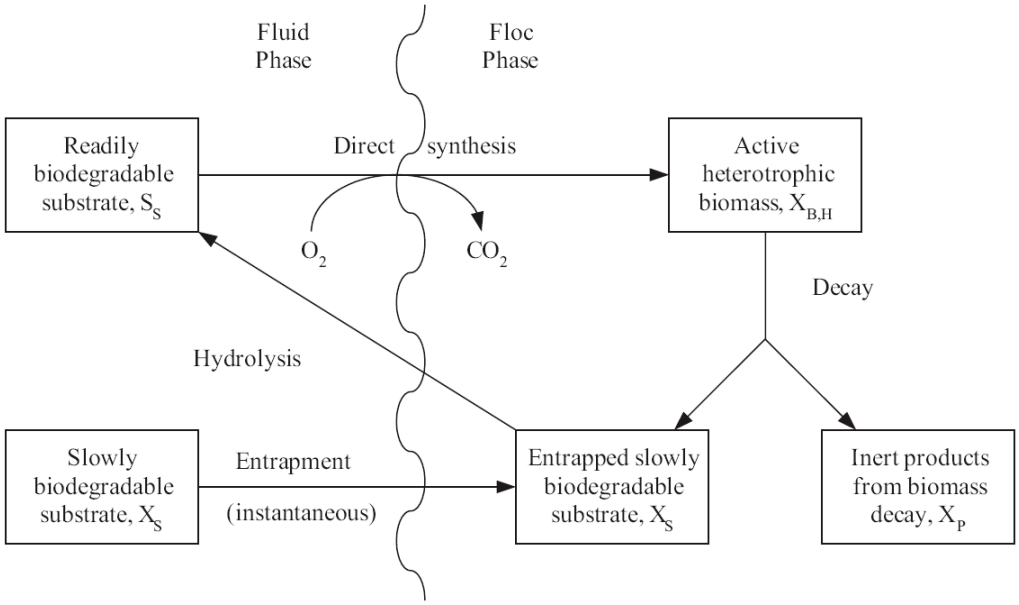

Figure 5. Flow diagrams of the Clifft and Andrews Activated Sludge Model (Patry and Chapman, 1989)

Different solubilities of substrates were assumed and particulate substrate storage with later conversion to active mass was considered. Dold and Marais (1986) proposed a different pattern in (Figure 6). In this report, the substrate was described by the reaction rate instead of solubility, because the term soluble had not been defined and may cause confusion.

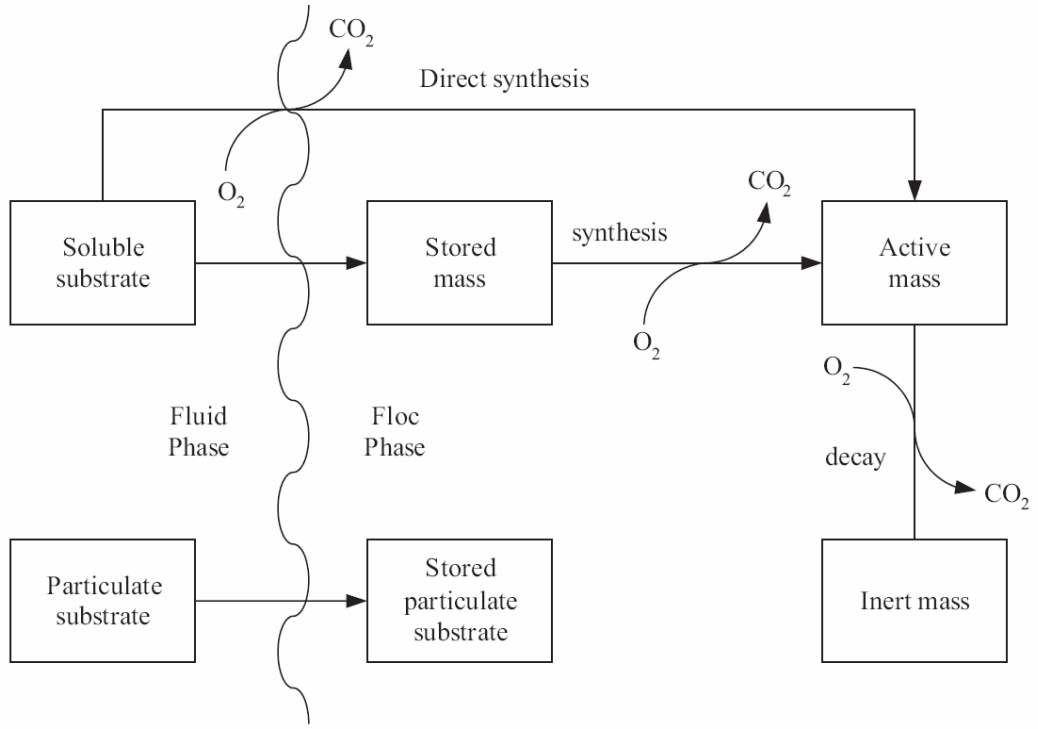

Figure 6. Flow diagram of the Dold and Marais Activated Sludge Model (Patry and Chapman, 1989)

To simplify the calculation, the storage mass step was removed since the slowly biodegradable substrate can be entrapped in the cells. The accuracy of Monod function for this dynamic model was also discussed, since it was measured from steady state conditions (Daigger and Grady, 1982). The stable enzyme system in the microorganisms indicated that the reaction rate could be still stable and this assumption was also accepted by IAWQ (Patry and Chapman, 1989). The final report of this general dynamic ASP model, namely Activated Model No. 1 or ASM1, was published in 1986. This model can be used to estimate the treatment efficiency of oxidation, nitrification and denitrification in a single sludge system. A total of eight essential processes were adopted in this model, including the growth of heterotrophic bacteria under aerobic or anoxic conditions, the growth of autotrophic bacteria under

aerobic conditions, the decay of heterotrophic and autotrophic bacteria, ammonification of soluble organic nitrogen, and the hydrolysis of organics and organic nitrogen.

As shown in Table 1, this model was proposed in a matrix form. The reaction kinetics of different components under different processes can be calculated from the matrix. For example, the reaction rate of readily biodegradable substrate which is presented in the second column can be calculated from the summation of the first, second, and seventh coefficients in the column times the process rates shown on the right side of table; hence, the dynamic behavior of readily biodegradable substrate can be simulated from the reaction kinetic and mass balance equations (Henze, 1987).

Based upon ASM1, ASM2 (Henze, 1995) and ASM3 (Gujer, 1999) were developed by the same IAWQ task group. In ASM2, phosphorus conservation was added to simulate the phosphorous removal process. Thus, variables of nutrient removal could be then simulated, including denitrification, the removal of phosphate, and phosphorus organisms (PAOs). Furthermore in ASM3, the phosphorus removal of ASM2 was not included, different approaches about bacteria decay were considered. Several calculations of ASM1 were neglected since a new approach about stored substrates was introduced. These models have supplied researchers with a tool for research, design, and education.

Table 1. Process kinetics and stoichiometry of ASM1

Component i →	1	2	3	4	5	6	7	8	9	10	11	12	13	Process rate,
Process j ↓	S_I	S_S	X_I	X_S	$X_{B,H}$	$X_{B,A}$	X_P	S_O	S_{NO}	S_{NH}	S_{ND}	X_{ND}	S_{ALK}	$(ML^{-3}T^{-1})$
1 Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$\frac{-i_{XB}}{14}$	R1
2 Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14.286Y_H}$	R2
3 Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$\frac{-i_{XB}}{14}-\frac{1}{7Y_A}$	R3
4 "Decay" of heterotrophs				$1-f_p$	-1		f_p					$-i_{XB}-f_p i_{XP}$		R4
5 "Decay" of autotrophs				$1-f_p$		-1	f_p					$-i_{XB}-f_p i_{XP}$		R5
6 Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$	R6
7 "Hydrolysis" of entrapped organics		1		-1										R7
8 "Hydrolysis" of entrapped organic nitrogen											1	-1		R8

Description:

S_I = Soluble inert organic
S_S = Readily biodegradable substrate
X_I = Particulate inert organic matter
X_S = Slowly biodegradable substrate
$X_{B,H}$ = Active heterotrophic biomass
$X_{B,A}$ = Active autotrophic biomass
X_P = Particulate products arising from biomass decay
S_O = Oxygen
S_{NO} = Nitrate and nitrite nitrogen
S_{NH} = NH4++NH nitrogen
S_{ND} = Soluble biodegradable organic nitrogen
X_{ND} = Particulate biodegradable organic nitrogen
S_{ALK} = Alkalinity

$$R1 = \hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_{B,H}$$

$$R2 = \hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_g X_{B,H}$$

$$R3 = \hat{\mu}_H\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_{B,A}$$

$$R4 = b_H X_{B,H}$$

$$R5 = b_A X_{B,A}$$

$$R6 = k_a S_{ND} X_{B,H}$$

$$R7 = k_h \frac{X_S/X_{B,H}}{K_X+(X_S/X_{B,H})}\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{N,O}}{K_{NO}+S_{NO}}\right)\right]X_{B,H}$$

$$R8 = \rho_T(X_{ND}/X_S)$$

The ASM models do not calculate pH which can greatly affect biological treatment. Nitrification efficiency (biological conversion of ammonia to nitrite and nitrate) may be considerably affected by pH. Grunditz and Dalhammar (2001) investigated the pure culture behavior of the two main nitrifying bacteria groups at different pHs. They suggested that pH in the tank should be maintained between 7 and 9, which conforms to well-known experimental observations (Painter, 1970). Therefore, simulating pH change in the ASP is desirable. Also, since the distribution of dissolved carbon dioxide (H_2CO_3) and bicarbonate (HCO_3^-) is different at different pHs, the solubility of CO_2 will change with pH as well. Thus if estimating dissolved carbon dioxide concentration is required, correct pH values have to be obtained (Pratt, 2003).

Unlike the substrates and microorganisms, pH can not be calculated from mass balance equation. To calculate pH, an alkalinity balance must be used. In ASM1 (Henze, 1987), alkalinity was calculated from the charge balance equation. This estimation is inconvenient since the charge balance can only be applied when all the ion concentrations, including organics and metals, can be measured. To solve this problem, Serralta (2004) developed a different pH model based on different concept. This model was extended from ASM2d and the alkalinity was basically calculated from proton balance. Consequently, the input data for this simulation were reduced to only the influent pH and carbonate alkalinity, which are much easier to collect from treatment plants. This approach has been applied in simulating the treatment performance of high purity oxygen (HPO) activated sludge process (Stenstrom et al.,1989 and Tzeng et al., 2003).

2.2 Gas transfer theories

Oxygen supply is the most important element in a secondary activated sludge treatment process, and may be as much as 70% of the operation cost (Krause, 2002). Since the transfer rate must satisfy the oxygen uptake rate, oxygen transfer analysis is always an essential step estimating ASP efficiency. The current oxygen transfer theory for wastewater treatment purpose is basically developed from the gas transfer model reported by Lewis and Whitman (1924). In this model, gas molecules are assumed to diffuse across two stagnant films which exist at the interface between gas and liquid phases; one film is in the gas phase side and the other is in the liquid phase side (Figure 7).

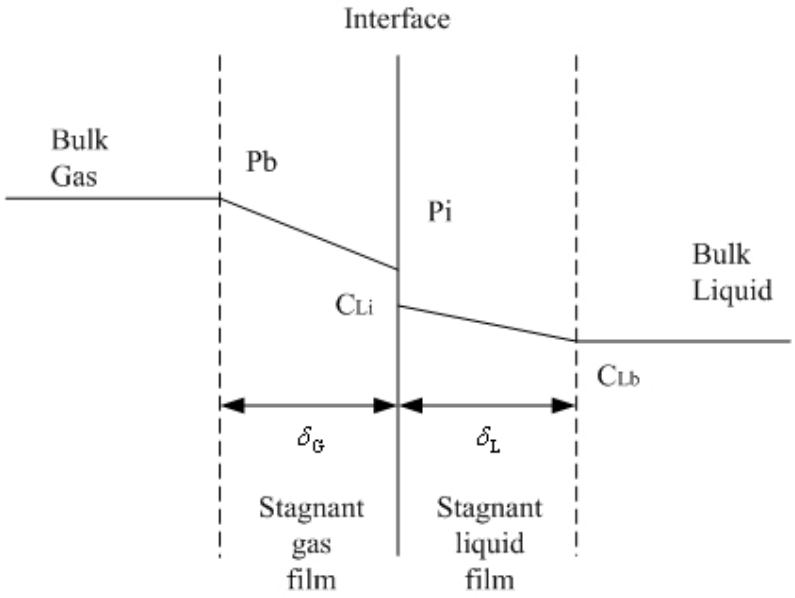

Figure 7. Sketch of double film theory

Different diffusion rates can be observed in the two different films. Depending on the solubility of gas to the liquid, one of the films can sometimes be neglected. For highly soluble gases, for example ammonia to water, the diffusion rate of gas

molecules in the gas phase is much smaller than in the liquid phase; therefore, the gas film becomes the limiting factor and the liquid film can be neglected. In contrast, oxygen is a sparingly dissolved gas in water and the diffusion rate in the liquid phase is small; the total diffusion rate is controlled by the film in the liquid phase and the gas phase film becomes negligible. By this assumption, the oxygen accumulation rate in a non-steady state batch reactor can be calculated from an oxygen transfer coefficient, which can be expressed as:

$$\frac{dC}{dt} = K_L a \cdot \left(C_\infty^* - C \right) \tag{7}$$

where

$K_L a$ = mass transfer coefficient (T^{-1})

C_∞^* = saturation dissolved oxygen concentration (M/L^3)

In real cases, $K_L a$ and C_∞^* may be vary as a function of different process conditions. For example, coefficient K_L could be affected by the change of temperature, bubble size, and the maturity of the stagnant film between liquid and gas phase; also, different C_∞^* may be observed at different depths of the aeration tank, because the capacity of saturated dissolved oxygen in water can be affected by partial pressure (Stenstrom, 1979). However, the two parameters are generally considered as constants to simplify the calculation in a model. In addition, since depending on operation strategies and aeration devices, significant difference can be observed for different designs. Estimating $K_L a$ and C_∞^* from the aeration devices of different plants is necessary.

Based upon oxygen transfer theory, clean water non-steady state testing is one of the most essential methods to estimate these two coefficients. In this test, a part of the aeration system and DO sensor are set up in a small batch reactor. By physical or chemical method, the DO can be stripped; then, $K_L a$ can be calculated from measuring DO recovery rate and the coefficient C_∞^*, which can be applied from references or the steady state DO concentration measurement (ASCE, 1993).

Furthermore, to correctly estimate transfer in a treatment process, the "clean water" test results must be converted to "wastewater" or process rates by conversion factors. Converting for the effects of temperature DO concentration, barometric pressure and ionic strength are straight forward. Accounting for the effects of surface active agents in the process is usually difficult. Hwang and Stenstrom (1985) reported that several variables may significantly influence the alpha factor, which accounts for the effect of contaminants on K_L and area. The overall process rate depends on air flow rate, liquid depth, tank geometry, and water quality. Another strategy is to conduct a process water test, which uses process water is a full scale evaluation. However, since it is difficult to measure the oxygen uptake rate from a real treatment process, and because the process must exist in order for it to be tested, process water testing is generally not used for treatment plant design or real-time estimation of treatment performance.

To estimate the gas transfer coefficient $K_L a$ of other gases, for example carbon dioxide, the surface renewal theory which proposed by Dankwertz (1951) is used. This theory is applicable to a surface that is renewed continuously (no stagnant films). Therefore, the K_L of a gas can be expressed as:

$$K_L = -\sqrt{D \cdot rc} \tag{8}$$

where

D = diffusion coefficient

rc = surface renewal rate

If the value rc in one reactor is a constant, this term can be canceled out by combining two surface renewal equations of oxygen and carbon dioxide. Thus, $K_L a_{CO_2}$ can be estimated from:

$$K_L a_{CO_2} = K_L a \sqrt{\frac{D_{CO_2}}{D_{O_2}}} \tag{9}$$

Therefore, if the oxygen transfer coefficient is known, the transfer rates of other gases, such as CO_2 and N_2 can be estimated. If the system is less turbulent, the correlation between transfer rates varies from the square root of the diffusivity ratios, and ranges from 0.5 to 1.0. Hsieh at al (1993a,b) discusses this relationship in greater detail.

2.3 Introduction to off-gas testing

As mentioned in the former section, present oxygen transfer estimation strategies, including clean and process water test, are all still problematic. Especially for large-scale treatment plants, it is difficult to gather the instantaneous information on the process via the laboratory experiments. Since the problems might not be easily solved, different estimating approaches should be considered. The off-gas test has few of these shortcomings, and has become an appropriate alternative.

The basic concept of off-gas test is to estimate the oxygen consumption from comparing the gas composition in the supplied air and the off-gas. Because the information of off-gas is directly gathered from the processing aeration systems, errors from conversion and estimation can be avoided, and real-time data can be also obtained. The modern off-gas analysis was developed by Redmon et al. (1983). In the analysis process, off-gas collected from a floating hood on the surface of aeration basin is treated to remove CO_2 and water vapor, and the oxygen molar fraction is measured by an oxygen sensor (Figure 8).

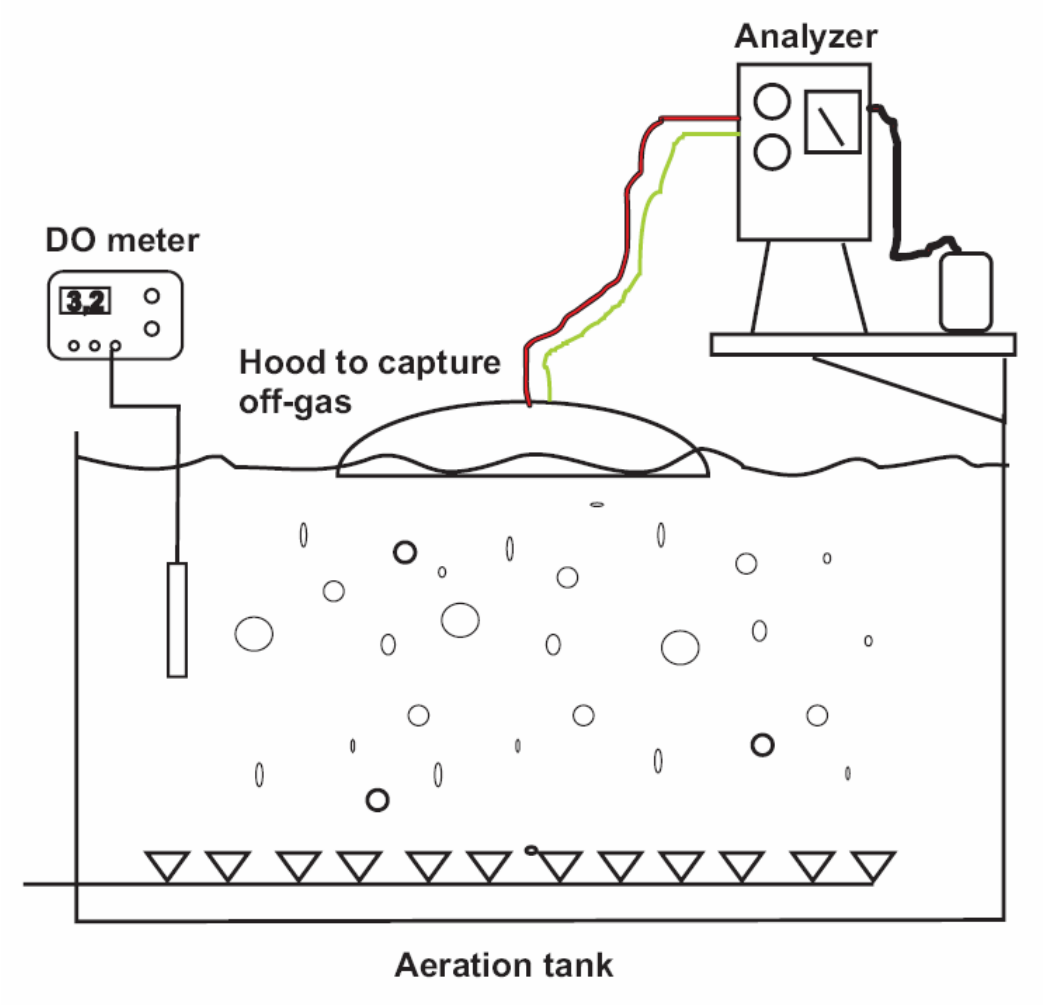

Figure 8. Off-gas test Equipment (Stenstrom,2004)

To eliminate the errors from estimating total gas mass flow rate, oxygen fraction is calculated by the total molar oxygen divided by total molar inert gases, which are non-reactive gases in the wastewater and the amount of inert gases is always fixed. The oxygen transfer efficiency can be calculated as:

$$\mathrm{OTE} = \frac{\mathrm{mass}O_2\mathrm{in} - \mathrm{mass}O_2\mathrm{out}}{\mathrm{mass}O_2\mathrm{in}} \tag{10}$$

$$= \frac{\mathrm{Gi}\left(\mathrm{M_o}/\mathrm{M_i}\right)\mathrm{MR_{o/i}} - \mathrm{Gi}\left(\mathrm{M_o}/\mathrm{M_i}\right)\mathrm{MR_{og/i}}}{\mathrm{Gi}\left(\mathrm{M_o}/\mathrm{M_i}\right)\mathrm{MR_{o/i}}} \tag{11}$$

$$= \frac{\mathrm{MR_{o/i}} - \mathrm{MR_{og/i}}}{\mathrm{MR_{o/i}}} \tag{12}$$

where

Gi = mass flow rate of inert gas (M/L^3)

M_o = molecular weight of oxygen

M_i = molecular weight of inert gas

$MR_{o/i}$ = mole ratio of oxygen to inert gas in air

$MR_{og/i}$ = mole ratio of oxygen to inert gas in off-gas

also,

$$\mathrm{MR_{o/i}} = \frac{Y_R}{1 - Y_R - Y_{CO_2(R)} - Y_{W(R)}} \tag{13}$$

$$\mathrm{MR_{og/i}} = \frac{Y_{og}}{1 - Y_{og} - Y_{CO_2(og)} - Y_{W(og)}} \tag{14}$$

$Y_{CO_2(R)}$ = mole fraction of CO_2 in reference gas

$Y_{CO_2(og)}$ = mole fraction of CO_2 in off-gas

$Y_{W(R)}$ = mole fraction of water vapor in reference gas

$Y_{W(og)}$ = mole fraction of water vapor in off-gas

The off-gas test is an important analysis method for estimating total oxygen transfer efficiency because of its accuracy and efficiency. Libra (2002) applied this method to compare the performance of several different aeration devices. Krause (2003) used both unsteady-state clean water test and off-gas test to estimate the treatment efficiency of full-scale membrane bioreactors. Furthermore, off-gas analysis has been shown as an appropriate analysis strategy for estimating reactions in small-scale ASP processes. In combination with pH analysis, a new method, online titrimetric and off-gas analysis (TOGS), was developed to correctly estimating not only substrate consumption but also nitrification (Pratt et al., 2003). Therefore, even though the real cases are always more complex, the possibility of an online nitrification estimating strategy for real ASP may be possible from off-gas testing.

3. MODEL DEVELOPMENT

The fundamental structure of the dynamic model is based on both the general activated sludge process ASP models of Andrews and IAWQ ASM model. The purpose of this dynamic model is to simulate and understand the relationship between nitrification efficiency and off-gas composition in the ASP. In this model, nine ordinary differential equations were used, and the corresponding parameter values (Appendix B) were adopted from literature references (Poduska and Andrews, 1975, Metcalf and Eddy, 2003). The dynamic behavior of the biological and liquid phases was simulated, including the temporal status of substrate, biomass, oxygen, carbon dioxide, ammonia, nitrite, nitrate and alkalinity. The new capabilities added in this research is the alkalinity balance and dissolved gas balances, which allow the pH to be calculated from a quadratic function of alkalinity, concentration distribution of ammonia, and carbon dioxide. Also, the dynamic gas phase composition (off-gas), and nitrification efficiency are simulated from the gas-liquid equilibrium.

3.1 Stoichiometry

Several reactions can occur simultaneously in the reactor, including substrate reduction, nitrification, and biomass decay. Each reaction will impact the effluent composition.

In general, the total BOD in domestic wastewater consists of two major kinds of pollutants, which are substrate, the carbonaceous compounds, and ammonia, the nitrogenous compounds. In the activated sludge process, carbonaceous compounds are consumed by heterotrophic bacteria. This reaction is rapid and the biomass production may be 30 to 70% of the BOD mass.

Unlike carbonaceous substrate reduction, longer reaction time and stricter conditions are required for nitrification. Effluent ammonia concentration may still remain at high concentration even after most carbonaceous compounds have been oxidized. However, the oxygen demand for nitrification is still significant and not ignorable (Poduska and Andrews, 1975). Longer sludge retention time is required to achieve nitrification.

In this model, to simplify the calculation, the general formula $C_5H_7NO_2$ is used to represent all the bacteria species, although heterotrophic bacteria and nitrifying bacteria may be a little different in composition.

3.1.1 Net equation of cell growth and substrate reduction

The net equation is also the heterotrophic bacteria growth reaction, which is calculated from the combination of respiration reaction and synthesis reactions. A portion of the substrate is utilized for growth and the remainder is oxidized to produce energy. The faction of the substrate used for growth is called the yield, *Y*, and is usually considered constant. The molar reaction and production of the biomass or other compounds can be determined by balancing the respiration and synthesis reactions. For convenience equation 15 can be used for substrate expressed as $C_\alpha H_\beta O_\gamma$ with molar biomass yield *Y* using $C_5H_7NO_2$ for cell mass.

$$C_\alpha H_\beta O_\gamma + Y NH_4^+ + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{4} - 5Y\right) O_2 \rightarrow Y C_5H_7NO_2 + (\alpha - 5Y) CO_2 + \left(\frac{\beta}{2} - 2Y\right) H_2O + Y H^+ \quad (15)$$

where

Y = molar biomass yield

Therefore, if we assume the basic formula of substrate is $C_8H_{12}O_4$, and the biomass molar yield is 0.609, which equal to mass yield 0.4, then the reaction equation can be expressed as:

$$C_8H_{12}O_4 + 0.609NH_4^+ + 5.955O_2 \rightarrow 0.609C_5H_7NO_2 + 4.955CO_2 + 4.782H_2O + 0.609H^+ \quad (16)$$

3.1.2 Nitrification

Ammonia serves as both a nutrient and energy source for nitrifying bacteria. Two different nitrifying microorganism genera are responsible for nitrification and both are autotrophic, obligatory aerobic (Poduska and Andrews, 1975). First, ammonia is oxidized to nitrite by Nitrosomonas (Equation 17); then, nitrite is oxidized to nitrate by Nitrobacter (Equation 19). For both reactions, the major portion of energy produced from nitrification is used for cell metabolism, which results in a low biomass yield.

Ammonia oxidation equation (Nitrosomonas growth reaction):

$$NH_4^+ + 5Y_{NS}CO_2 + \left(\frac{3}{2} - \frac{13}{2}Y_{NS}\right)O_2 \xrightarrow{\text{Nitrosomonas}} Y_{NS}C_5H_7NO_2 + (1-Y_{NS})NO_2^- + (2-Y_{NS})H^+ + (1-3Y_{NS})H_2O \quad (17)$$

where

Y_{NS} = Molar yield of Nitrosomonas

If Poduska's data (1975) are used for Y_{NS} (0.006 moles cells/moles ammonia), the net reaction equation can be expressed as:

$$NH_4^+ + 0.031CO_2 + 1.460O_2 \xrightarrow{\text{Nitrosomonas}} 0.006C_5H_7NO_2 + 0.994NO_2^- + 1.993H^+ + 0.982H_2O \quad (18)$$

Similarly, the nitrite oxidation reaction (Nitrobacter growth reaction) is:

$$NO_2^- + 5Y_{NB}CO_2 + 3Y_{NB}H_2O + \left(\frac{1}{2} - 7Y_{NB}\right)O_2 + Y_{NB}H^+ \xrightarrow{\text{Nitrobacter}} Y_{NB}C_5H_7NO_2 + (1 - Y_{NB})NO_3^- \quad (19)$$

Poduska found the molar yield of Nitrobacter to be 0.0025 (mole Nitrobacter / mole nitrite), the equation can be expressed as:

$$NO_2^- + 0.0124CO_2 + 0.0074H_2O + 0.4827O_2 + 0.0026H^+ \xrightarrow{\text{Nitrobacter}} 0.0025C_5H_7NO_2 + 0.9975NO_3^- \quad (20)$$

3.1.3 Biomass decay reaction

Biomass decays and is oxidized to produce carbon dioxide and ammonia. This effect may be considerable, especially at longer SRT.

$$C_5H_7NO_2 + 5O_2 + H^+ \rightarrow 5CO_2 + 2H_2O + NH_4^+ \quad (21)$$

3.2 BIOLOGICAL PHASE

In the biological phase, microorganisms consume the pollutants and accumulate in the sludge. Ordinary differential equations are used to model the dynamic conditions of the concentration of the substrate and three different microorganism populations, including heterotrophic bacteria, Nitrosomonas, and Nitrobacter.

3.2.1 Effluent substrate concentration — S

Equation 22 shows the balance for heterotrophic substrate:

$$\frac{dS}{dt} = \frac{Q}{V} \cdot (S_o - S) - \frac{\mu_1}{Y_{MASS}} \cdot X \tag{22}$$

where

μ_1 = Monod growth rate function (T^{-1})

Y_{MASS} = theoretical yield coefficient (includes no decay)

S_o = influent substrate (M/L^3)

Q = flow rate (L^3/T)

V = aeration tank volume (L^3)

X = heterotrophic bacteria concentration (mass/volume)

To include the effects of low DO concentrations, double Monod-type growth rate kinetics were used as follows (Stenstrom and Poduska, 1980):

$$\mu_1 = \frac{\hat{\mu}_S \cdot S}{(K_S + S)} \cdot \frac{DO}{(DO + K_{SDO})}, \tag{23}$$

where

$\hat{\mu}_S$ = maximum cell growth rate (T^{-1})

K_S = half velocity coefficient (M/L^3)

DO = dissolved oxygen concentration (M/L^3)

K_{SDO} = half saturation coefficient (M/L^3)

3.2.2 Biomass concentration — X

The biomass balance equation is similar to substrate balance (24). The difference between these two equations the biomass growth rate (μ_1) which is positive, and because of biomass is decay, a negative first-order decay rate (K_D) is added. The recycle sludge is also included using a term p.

$$\frac{dX}{dt} = \left(p + \mu_1 - K_D\right) \cdot X, \tag{24}$$

where

p = recycle term (T^{-1})

K_D = decay coefficient (T^{-1})

The sludge recycle rate and wasting can be calculated from the tank volume, the recycle flow rate and the sludge discharge rate:

$$p = -\frac{Q_W}{V} \cdot \frac{\left(Q + Q_R\right)}{Q_R} \tag{25}$$

where

Q_W = waste sludge flow rate (L^3/T)

Q_R = sludge recycle flow rate (L^3/T)

Using equation 25 simplifies the simulation by assuming that the secondary clarifier is overloaded.

3.2.3 Nitrosomonas concentration and Nitrobacter concentration — Xns & Xnb

The material balance equations for both Nitrosomonas and Nitrobacter are the same as heterotrophic bacteria, and differ only by parameter values (growth rate μ and decay rate K_D).

$$\frac{dX_{NS}}{dt} = \left(p + \mu_2 - K_{DNS}\right) \cdot X_{NS}, \tag{26}$$

$$\frac{dX_{NB}}{dt} = \left(p + \mu_3 - K_{DNB}\right) \cdot X_{NB}, \tag{27}$$

For the cell growth rate, double Monod-functions were used and are similar to heterotrophic biomass growth equation. The only differences are the nutrient terms here represent total ammonia and nitrite concentrations:

$$\mu_2 = \frac{\hat{\mu}_{NS} \cdot N_{NH_3-N}}{\left(K_{NS} + N_{(NH_3)_T-N}\right)} \cdot \frac{DO}{\left(DO + K_{SDO}\right)}, \tag{28}$$

$$\mu_3 = \frac{\hat{\mu}_{NB} \cdot N_{NO_2^- -N}}{\left(K_{NB} + N_{NO_2^- -N}\right)} \cdot \frac{DO}{\left(DO + K_{SDO}\right)}, \tag{29}$$

where

$\hat{\mu}_{NS}$ = maximum Nitrosomonas growth rate (T^{-1})

$\hat{\mu}_{NB}$ = maximum Nitrobacter growth rate (T^{-1})

$N_{(NH_3)_T-N}$ = total ammonia concentration (M/L^3)

$N_{NO_2^- -N}$ = nitrite concentration (M/L^3)

3.3. LIQUID PHASE

All the compounds flowing in or being released by microorganisms may be dissolved in the liquid phase or stripped to the gas phase. The material balance equation of each compound in the liquid phase is based on the same concepts as the biological phase. However, unlike the biomass balance, more reactions may affect the material balance. For example, ammonia is not only being oxidized by nitrifiers, but is also required in the synthesis of heterotrophic bacteria. Each term of reaction rate in material balance equation of any compound in the liquid phase can be determined from either the biomass growth rate or the biomass decay rate multiplied by a coefficient calculated from stoichiometry.

3.3.1 Dissolved oxygen — DO

Dissolved oxygen is supplied by aeration systems and consumed by bacteria. Therefore, the oxygen transfer rate is a positive term in the balance equation. Also, since oxygen is consumed in the growth and decay reactions of all three bacteria species, six negative terms are added into the balance equation as well. The dissolved oxygen material balance can be expressed as:

$$\frac{dDO}{dt} = \frac{Q}{V} \cdot (DO_o - DO) + \gamma_{DOTR} - \gamma_{DO1} - \gamma_{DO2} - \gamma_{DO3} - \gamma_{DO4} - \gamma_{DO5} - \gamma_{DO6} \qquad (30)$$

where

DO_o = influent dissolved oxygen concentration (M/L^3)

γ_{DOTR} = oxygen transfer rate ($M/L^3/T$)

γ_{DO1} = oxygen reducing rate in heterotrophic bacteria growth reaction ($M/L^3/T$)

γ_{DO2} = oxygen reducing rate in heterotrophic bacteria decay reaction ($M/L^3/T$)

Υ_{DO3} = oxygen reducing rate in Nitrosomonas growth reaction ($M/L^3/T$)

Υ_{DO4} = oxygen reducing rate in Nitrosomonas decay reaction ($M/L^3/T$)

Υ_{DO5} = oxygen reducing rate in Nitrobacter growth reaction ($M/L^3/T$)

Υ_{DO6} = oxygen reducing rate in Nitrobacter decay reaction ($M/L^3/T$)

The oxygen transfer rate can be expressed as:

$$\Upsilon_{DOTR} = K_L a \cdot (DO_S - DO), \tag{31}$$

where

$K_L a$ = volumetric oxygen transfer coefficient (T^{-1})

DO_S = saturated dissolved oxygen concentration (M/L^3)

The oxygen reduction rates of cell growth and decay reactions can be expressed as:

$$\Upsilon_{DO1} = \frac{Y_2}{Y_1} \cdot \mu_1 \cdot X \tag{32}$$

$$\Upsilon_{DO2} = Y_3 \cdot K_D \cdot X \tag{33}$$

$$\Upsilon_{DO3} = \frac{Y_{NS2}}{Y_{NS1}} \cdot \mu_2 \cdot X_{NS} \tag{34}$$

$$\Upsilon_{DO4} = Y_{NS3} \cdot K_{DNS} \cdot X_{NS} \tag{35}$$

$$\Upsilon_{DO5} = \frac{Y_{NB2}}{Y_{NB1}} \cdot \mu_3 \cdot X_{NB} \tag{36}$$

$$\Upsilon_{DO6} = Y_{NB3} \cdot K_{DNB} \cdot X_{NB} \tag{37}$$

where

$$Y_1 = \frac{Y_{MASS}}{1 + K_D \cdot HRT} \tag{38}$$

Y_1 = mass observed yield for heterotrophic bacteria growth reaction (mass heterotrophic bacteria VSS / mass substrate)

Y_2 = oxygen demand for heterotrophic bacteria growth reaction (mass oxygen / mass substrate)

Y_3 = oxygen demand for heterotrophic bacteria decay reaction (mass oxygen / mass heterotrophic bacteria biomass)

Y_{NS1} = mass observed yield of Nitrosomonas growth reaction (mass Nitrosomonas VSS / mass NH_4-N)

Y_{NS2} = oxygen demand of Nitrosomonas growth reaction (mass oxygen / mass NH_4-N)

Y_{NS3} = oxygen demand of Nitrosomonas decay reaction (mass oxygen / mass Nitrosomonas biomass)

Y_{NB1} = mass observed yield of Nitrobacter growth reaction (mass Nitrosomonas VSS / mass NO_2^--N)

Y_{NB2} = oxygen demand of Nitrobacter growth reaction (mass oxygen / mass NO_2^--N)

Y_{NB3} = oxygen demand of Nitrobacter decay reaction (mass oxygen / mass Nitrobacter biomass)

3.3.2 Dissolved carbon dioxide — DCD

Similar to dissolved oxygen balance, there is one stripping term and six reaction terms in the carbon dioxide balance. The reaction terms include both consumption and production of dissolved carbon dioxide, and the total can be either positive or negative. The carbon dioxide balance can be expressed as:

$$\frac{dDCD}{dt} = \frac{Q}{V}\cdot\left(DCD_o - DCD\right) + \Upsilon_{CDSTRP} + \Upsilon_{DCD1} + \Upsilon_{DCD2} - \Upsilon_{DCD3} + \Upsilon_{DCD4} - \Upsilon_{DCD5} + \Upsilon_{DCD6}, \quad (39)$$

where

DCD_o = influent dissolved CO_2 concentration (M/L^3)

Υ_{CDSTRP} = CO_2 stripping rate ($M/L^3/T$)

Υ_{DCD1} = CO_2 producing rate in heterotrophic bacteria growth reaction ($M/L^3/T$)

Υ_{DCD2} = CO_2 producing rate in heterotrophic bacteria decay reaction ($M/L^3/T$)

Υ_{DCD3} = CO_2 reducing rate in Nitrosomonas growth reaction ($M/L^3/T$)

Υ_{DCD4} = CO_2 producing rate in Nitrosomonas decay reaction ($M/L^3/T$)

Υ_{DCD5} = CO_2 reducing rate in Nitrobacter growth reaction ($M/L^3/T$)

Υ_{DCD6} = CO_2 producing rate in Nitrobacter decay reaction ($M/L^3/T$)

The dissolved carbon dioxide stripping rate can be expressed as:

$$\Upsilon_{CDSTRP} = K_L a_{CO_2}\cdot\left(DCD_S - DCD\cdot f_{CO_2}\right) \quad (40)$$

$K_L a_{CO_2}$ = transfer rate of CO_2 (T^{-1})

DCD_S = saturated CO_2 concentration (M/L^3)

$$f_{CO_2} = \frac{[H_2CO_3]}{[H_2CO_2]+[HCO_3^-]+[CO_3^{2-}]} \quad (41)$$

= molar fraction of H_2CO_3 in total dissolved CO_2

The reaction rates can be expressed as:

$$\Upsilon_{DCD1} = \frac{Y_4}{Y_1} \cdot \mu_1 \cdot X \tag{42}$$

$$\Upsilon_{DCD2} = Y_5 \cdot K_D \cdot X \tag{43}$$

$$\Upsilon_{DCD3} = \frac{Y_{NS4}}{Y_{NS1}} \cdot \mu_2 \cdot X_{NS} \tag{44}$$

$$\Upsilon_{DCD4} = Y_{NS5} \cdot K_{DNS} \cdot X_{NS} \tag{45}$$

$$\Upsilon_{DCD5} = \frac{Y_{NB4}}{Y_{NB1}} \cdot \mu_3 \cdot X_{NB} \tag{46}$$

$$\Upsilon_{DCD6} = Y_{NB5} \cdot K_{DNB} \cdot X_{NB} \tag{47}$$

where

Y_4 = CO_2 production in heterotrophic bacteria growth reaction (mass CO2 / mass substrate)

Y_5 = CO_2 production in heterotrophic bacteria decay reaction (mass CO2 / mass heterotrophic bacteria biomass)

Y_{NS4} = CO_2 demand in Nitrosomonas growth reaction (mass CO2 / mass NH_4-N)

Y_{NS5} = CO_2 production in Nitrosomonas decay reaction (mass CO2 / mass Nitrosomonas)

Y_{NB4} = CO_2 demand in Nitrobacter growth reaction (mass CO2 / mass NO_2^--N)

Y_{NB5} = CO_2 production in Nitrobacter decay reaction (mass CO2 / mass Nitrobacter)

3.3.3 Ammonia — $N_{(NH_3)_T-N}$

Since ammonia is highly soluble at neutral pH, the ammonia stripping rate is negligible in the material balance. The ammonia balance can be expressed as:

$$\frac{dN_{(NH_3)_T-N}}{dt} = \frac{Q}{V}\cdot\left(N_{o(NH_3)_T-N} - N_{(NH_3)_T-N}\right) - \Upsilon_{NH_3 1} + \Upsilon_{NH_3 2} - \Upsilon_{NH_3 3} + \Upsilon_{NH_3 4} + \Upsilon_{NH_3 5} \quad (48)$$

where

$\Upsilon_{NH_3 1}$ = ammonia reducing rate in heterotrophic bacteria growth reaction ($M/L^3/T$)

$\Upsilon_{NH_3 2}$ = ammonia producing rate in heterotrophic bacteria decay reaction ($M/L^3/T$)

$\Upsilon_{NH_3 3}$ = ammonia reducing rate in Nitrosomonas growth reaction ($M/L^3/T$)

$\Upsilon_{NH_3 4}$ = ammonia producing rate in Nitrosomonas decay reaction ($M/L^3/T$)

$\Upsilon_{NH_3 5}$ = ammonia producing rate in Nitrobacter decay reaction ($M/L^3/T$)

The reaction rates can be calculated from the equations:

$$\Upsilon_{NH_3 1} = \frac{Y_6}{Y_1}\cdot\mu_1\cdot X \quad (49)$$

$$\Upsilon_{NH_3 2} = Y_7\cdot K_D\cdot X \quad (50)$$

$$\Upsilon_{NH_3 3} = \frac{1}{Y_{NS}}\cdot\mu_2\cdot X_{NS} \quad (51)$$

$$\Upsilon_{NH_3 4} = Y_{NS6}\cdot K_{DNS}\cdot X_{NS} \quad (52)$$

$$\Upsilon_{NH_3 5} = Y_{NB6}\cdot K_{DNB}\cdot X_{NB} \quad (53)$$

where

Y_6 = ammonia demand in heterotrophic bacteria growth reaction (mass NH_4-N / mass substrate)

Y_7 = ammonia production in heterotrophic bacteria decay reaction (mass NH_4-N / mass heterotrophic bacteria biomass)

Y_{NS6} = ammonia production in Nitrosomonas decay reaction (mass NH_4-N / mass Nitrosomonas biomass)

Y_{NB6} = ammonia production in Nitrosomonas decay reaction (mass NH_4-N / mass Nitrosomonas biomass)

3.3.4 Nitrite — $N_{NO_2^- -N}$

Nitrite can only be accumulated from the influent, the ammonia oxidation reaction and reduced from the nitrite oxidation reaction. The mass balance of nitrite can be expressed as:

$$\frac{dN_{NO_2^- -N}}{dt} = \frac{Q}{V} \cdot \left(N_{o\,NO_2^- -N} - N_{NO_2^- -N} \right) + \Upsilon_{NO_2 1} - \Upsilon_{NO_2 2} \tag{54}$$

where

$\Upsilon_{NO_2 1}$ = nitrite producing rate in ammonia oxidation reaction ($M/L^3/T$)

$\Upsilon_{NO_2 2}$ = nitrite reducing rate in Nitrobacter growth reaction ($M/L^3/T$)

The reaction rates can be calculated from the equations:

$$\Upsilon_{NO_2 1} = \frac{Y_{NS7}}{Y_{NS1}} \cdot \mu_2 \cdot X_{NS} \tag{55}$$

$$\Upsilon_{NO_2 2} = \frac{1}{Y_{NB}} \cdot \mu_3 \cdot X_{NB} \tag{56}$$

where

Y_{NS7} = nitrite production in ammonia oxidation reaction (mass NO_2-N / mass NH_4-N)

3.3.5 Nitrate — N_{NO_3-N}

The Nitrobacter growth reaction is the only reaction that produces nitrate and denitrification is ignored. Therefore the mass balance becomes:

$$\frac{dN_{NO_3-N}}{dt} = \frac{Q}{V} \cdot \left(N_{oNO_3-N} - N_{NO_3-N} \right) + \Upsilon_{NO_3 1} \tag{57}$$

where

$\Upsilon_{NO_2 1}$ = nitrate production rate in Nitrobacter growth reaction ($M/L^3/T$)

The reaction rate can be calculated from the equation:

$$\Upsilon_{NO_2 1} = \frac{Y_{NB7}}{Y_{NB1}} \cdot \mu_3 \cdot X_{NB} \tag{58}$$

where

Y_{NB7} = nitrate production in Nitrobacter growth reaction (mass NO_3–N / mass NO_2-N)

3.3.6 Alkalinity — Z

The aeration tank must be maintained near neutral pH and must be modeled in order to predict the dissolved carbon dioxide stripping rate. To modeling the time varying pH, an alkalinity balance is applied in this model. The alkalinity is calculated by the charge balance of several ions. As shown in equation (22), the hydrogen ion molar concentration appears as a negative term when calculating the alkalinity; alkalinity is consumed when hydrogen ions are produced.

$$Z = [HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+]+[NH_3]-F_1[NO_2^-]+F_2\,[NO_3^-] \tag{59}$$

where

F_1 = Mole ratio of hydrogen ion and nitrite in ammonia oxidation reaction

F_2 = Mole ratio of hydrogen ion and nitrate in nitrite oxidation reaction

Hydrogen ions are produced in the ammonia oxidation reaction (3). Therefore as soon as the ammonia is oxidized to nitrite, the alkalinity decreases. In addition, the decreasing rate of alkalinity can be calculated from the nitrite concentration since the molar production of hydrogen ion is proportional to the production of nitrite. The ratio of molar concentration of hydrogen ion and nitrite, coefficient F_1, can be calculated using stoichiometry.

Similarly, the nitrite oxidation reaction, which is also the nitrate production reaction, can affect the alkalinity balance. The difference is in the nitrite oxidation reaction (4) consumes a hydrogen, which means the conversion of nitrite to nitrate restores some of the alkalinity. From the concept of alkalinity balance, the dynamic behavior of alkalinity can be expressed as:

$$\frac{dZ}{dt} = \frac{Q}{V} \cdot \left[(Z_o - Z) + \frac{\gamma_{Z1} - \gamma_{Z2} + \gamma_{Z3}}{Mw - N} \right] \tag{60}$$

where

$$\gamma_{Z1} = \left(f_{NH_3} \cdot N_{(NH_3)_T - N} - N_{0(NH_3)_T - N} \right) = \text{alkalinity coefficient of ammonia hydrolysis} \tag{61}$$

$$\gamma_{Z2} = F_1 \cdot \left(N_{0_{NO_2^- - N}} - N_{NO_2^- - N} \right) = \text{alkalinity coefficient from ammonia oxidation} \tag{62}$$

$$\gamma_{Z3} = F_2 \cdot \left(N_{0NO_3 - N} - N_{NO_3 - N} \right) = \text{alkalinity coefficient from nitrite oxidation} \tag{63}$$

$$f_{NH_3} = \frac{1}{1 + \frac{[H^+]}{K_{NH_3}}} = \text{molar fraction of } [NH_3] \text{ in the total ammonia concentration} \tag{64}$$

$Mw - N$ = molecular weight of nitrogen

3.3.7 pH

The pH value can be calculated from the quadratic function consists of alkalinity and the molar concentration of ammonia and carbon dioxide:

$$[H^+]^2 + [H^+] \cdot \left(Z - f_{NH_3} \cdot N_{(NH_3)_T - N} \right) - K_W - \left(K_1 + \frac{2K_1K_2}{[H^+]} \right) \cdot f_{CO_2} \cdot DCD = 0 \quad (65)$$

where

K_W= ion product in water

K_1= first Keq for carbon dioxide

K_2= second Keq for carbon dioxide

3.4 GAS PHASE

In activated sludge process, the gas phase composition can most easily be measured using off-gas analysis, because the aeration tank is open to the atmosphere. If the off-gas mole is assume to be in equilibrium with the liquid phase, which means that the mass transfer reactions are rapid compared to the biological reactions, then off-gas data can be calculated based on the known gas flow rate and the stripping rate calculated from the liquid phases.

3.4.1 Oxygen molar flow rate — O2og

The oxygen flow rate can be calculated as:

$$O_2og = \frac{D_{O_2} \cdot Qg \cdot Y_{O_2}i - K_La \cdot V \cdot (DOs - DO)}{Mw - O_2} \quad (66)$$

where

D_{O_2} = oxygen gas density (M/L^3)

Qg = gas flow rate from diffusers (L^3/T)

$Y_{O_2 i}$ = oxygen molar fraction in inlet gas

$Mw - O_2$ = molecular weight of oxygen

3.4.2 Carbon dioxide molar flow rate — CDog

Similarly, the calculation of carbon dioxide flow rate can be expressed as:

$$CDog = \frac{D_{CO_2} \cdot Qg \cdot Y_{CO_2 i} - K_L a_{CO_2} \cdot V \cdot (DCDs - DCD \cdot f_{CO_2})}{Mw - CO_2} \quad (67)$$

where

D_{CO_2} = carbon dioxide gas density (M/L3)

$Y_{CO_2 i}$ = carbon dioxide molar fraction in inlet gas

$Mw - CO_2$ = molecular weight of carbon dioxide

3.4.3 Nitrogen molar flow rate — N_2og

Since nitrogen gas does not react in the aeration tank, the nitrogen gas flow rate is just the inlet nitrogen flow rate:

$$N_2 og = \frac{D_{N_2} \cdot Qg \cdot Y_{N_2}}{Mw - N_2} \quad (68)$$

D_{N_2} = nitrogen gas density (M/L^3)

$Y_{N_2} \approx 1 - Y_{O_2} - Y_{CO_2}$ = nitrogen molar fraction in inlet gas

$Mw - N_2$ = molecular weight of nitrogen gas

3.4.4 Molar fraction of carbon dioxide in off-gas

As mentioned in the former chapter, off-gas analysis allows the mole fractions of both oxygen and carbon dioxide to be measured. The oxygen mole fraction is always measured since it is used to calculate the oxygen transfer rate. The carbon dioxide mole fraction is usually ignored. It can be calculated as follows:

$$Y_{cdog} = \frac{CDog}{O_2og + CDog + N_2og} = \text{Molar fraction of carbon dioxide in off-gas} \qquad (69)$$

The carbon dioxide mole fraction will vary independently of the oxygen transfer rate since the there are several carbon dioxide production and consumption terms. The carbon dioxide mole fraction will be used later to assess the rates of nitrification as compared to the rate of carbonaceous oxidation.

3.5 PROGRAM

The model was developed based upon Matlab 6.5 (MathWorks, Natick, Massachusetts). Function ode45 (Runge-Kutta variable step integration) was applied to calculate the numerical solution of all ODEs (Appendix C).

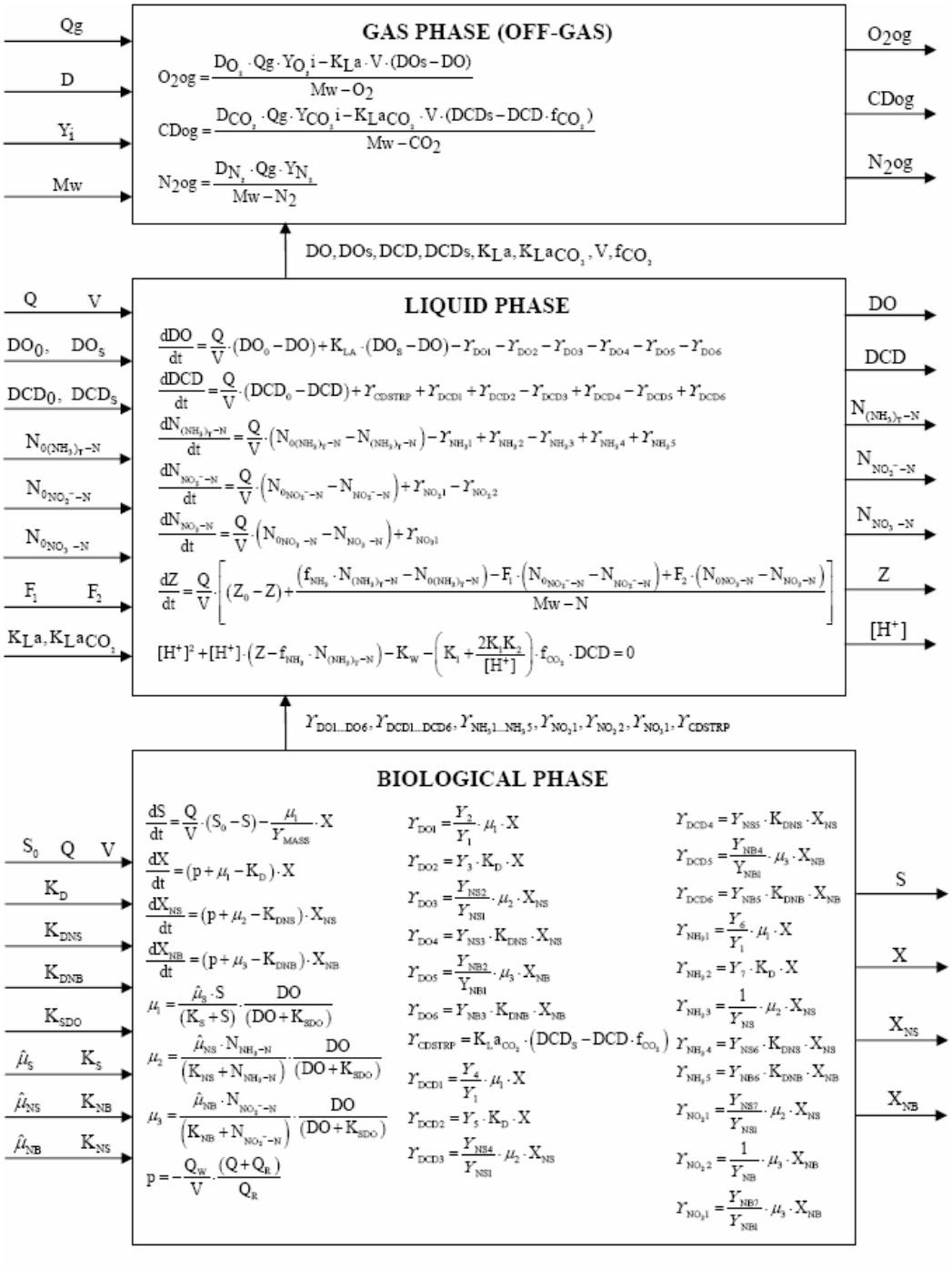

Figure 9. Model flow diagram

4. RESULTS AND DISCUSSION

4.1 Model validation

To validate the functions of the model, several basic simulations were performed. An initial value problem was worked first. The initial conditions for substrates (both ammonia and COD) were assumed to be equal to the influent concentrations and only a small or seed biomass concentration was assumed. Under this initial condition, both substrates should decline over time and the biomass should increase to the steady state condition. This condition may represent the start up of a new activated sludge process. Figure 9 shows the simulation results for ammonia, nitrite, and nitrate and Figure 11 shows the biomasses and the COD.

Figure 9 shows two distinct changes in ammonia concentration. The initial rapid decrease in ammonia is due to heterotrophic uptake. The initial uptake occurs in the first day. Corresponding trends are shown in Figure 11. There is a rapid decrease in substrate and an increase in heterotrophic biomass (X). The second, more gradual decrease in ammonia occurs because of nitrification and is accompanied by the production of nitrite and nitrate. The nitrite initially accumulates but decreases after the nitrite oxidizing biomass (Nitrobacter) increases. Eventually there are low effluent ammonia, substrate and nitrite concentrations. Nitrite is always low in uninhibited nitrifying cultures, since the nitrite oxidation rate is greater than the ammonia oxidation rate (Poduska and Andrews, 1975). Steady state occurs after approximately eight days.

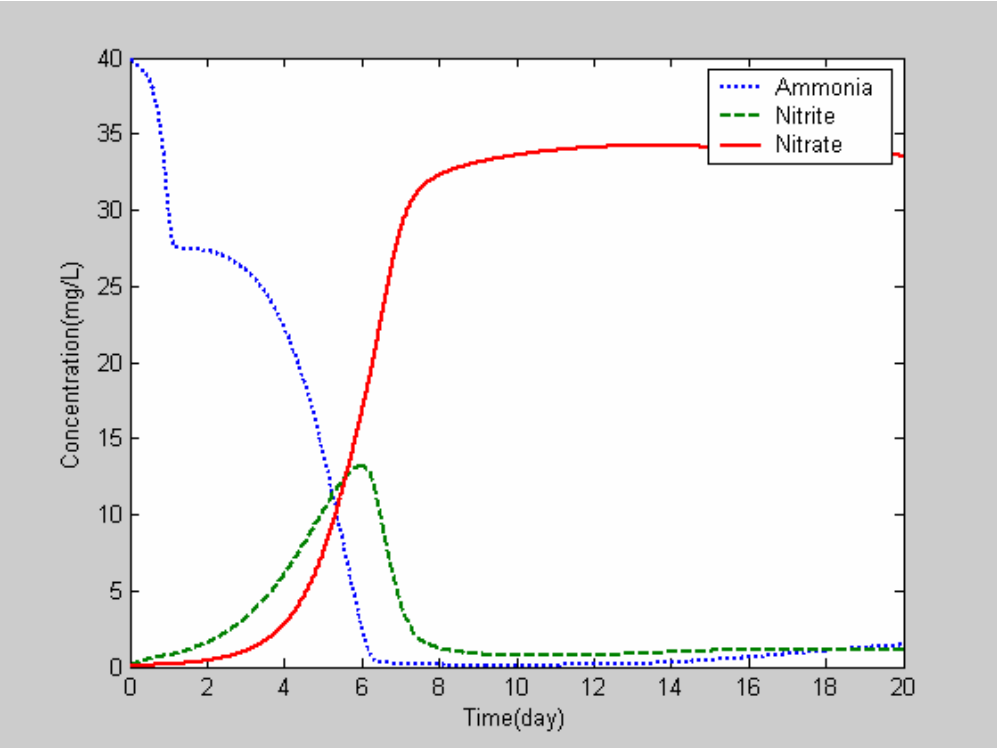

Figure 10. Model simulation of nitrification status (initial condition = inflow values)

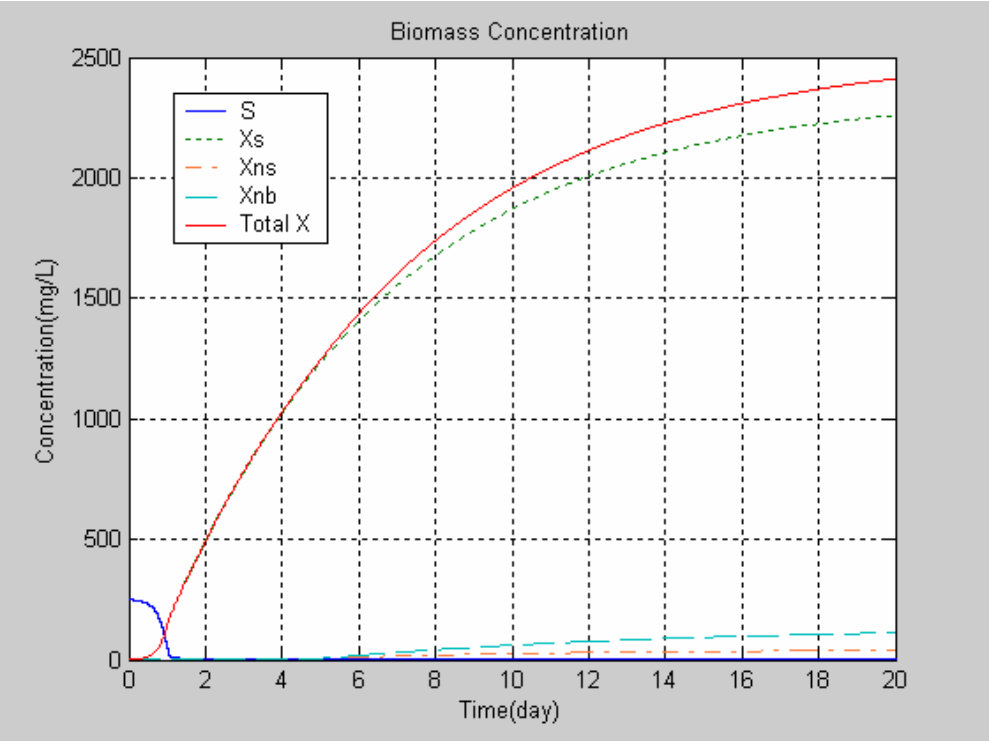

Figure 11. Model simulation of substrate and different bacteria populations

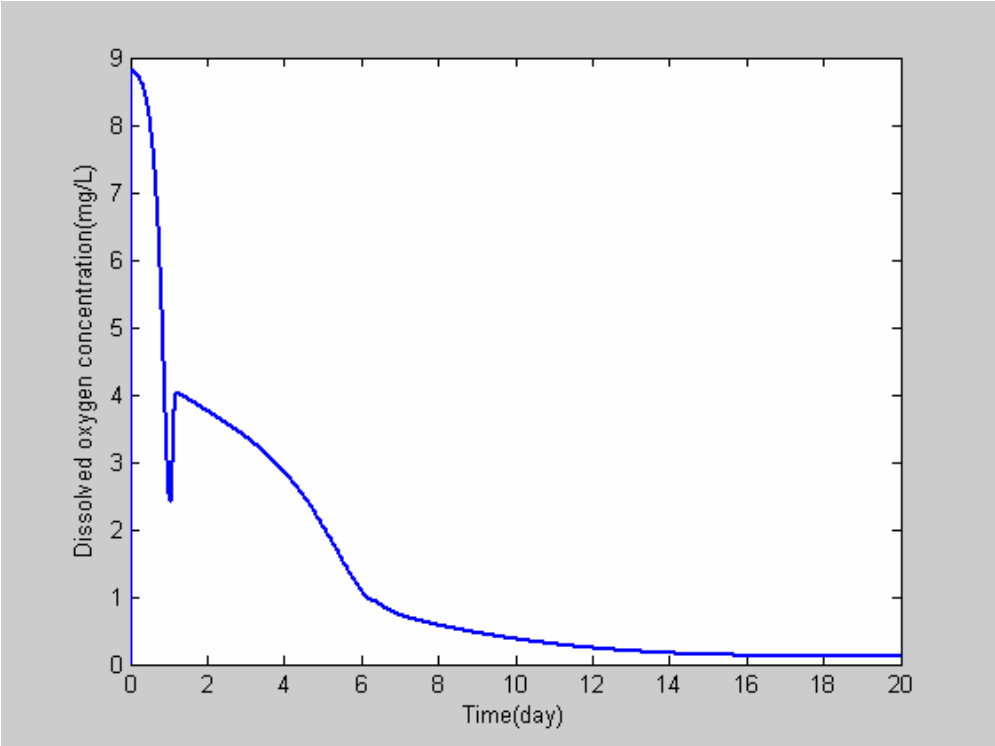

Figure 12. Model simulation of dissolved oxygen (initial condition = inflow values)

Figure 12 shows the dissolved oxygen concentration for the same conditions. There is an initial, rapid decline in DO as the heterotrophic organisms consume oxygen as metabolize the initial, high substrate concentration. The initial substrate is exhausted after approximately 1.5 days, and the DO increases. After approximately 2 days, the nitrifiers begin to oxidize significant quantities of ammonia and nitrite, and suppress the DO again. Eventually the DO concentration reaches a steady state value of approximately 0.3 mg/L. The simulation shows well established trends observed in treatment plants and with other models. A simple steady state balance on oxygen demand, assuming the stoichiometric amounts for ammonia (4.5 mg DO/mg-N) and substrate (1.1 mg/mg) and accounting for excess sludge production (1.42 mg O2/mg X) closes to within ±1%.

Another strategy to check the simulation accuracy is by changing certain input parameters and verifying the trends in output values. Increasing the gas transfer coefficient $K_L a$, should increase the oxygen uptake rate until the DO concentration exceeds the K_{SDO}. After exceeding the value of K_{SDO}, the oxygen uptake rate is nearly constant since the oxidation rates are no longer affected by DO concentration. Simultaneously, dissolved carbon dioxide will stripped more effectively by the higher mass transfer coefficient, and the pH rise. Simulation results confirmed these expected trends.

4.2 Application to Off-gas testing

Pratt and Gapes (2003) used off-gas analysis to estimate performance of biological wastewater treatment in small-scale batch bioreactors. They called their method on-line titrimetric and off-gas analysis (TOGA). Hydrogen ion production rate (HPR) was measured by simultaneously monitoring pH and carbon dioxide production (CPR) rates. Carbon dioxide was monitored in the off-gas using a mass spectrometer. By knowing HPR and CPR, the transfer rate of oxygen, nitrogen and carbon dioxide was calculated using stoichiometry. They demonstrated their methodology in a closed system for certain carbonaceous and nitrogenous compounds.

In large-scale treatment processes, operating conditions will be far more complicated. Aeration tanks are so large that collecting and analyzing the total outflow gas is generally not possible. To overcome the difficulties associated with full scale application of the technique, the traditional off-gas method (Redmon, 1983) can be used, except that carbon dioxide can be measured. This allows the carbon dioxide production to be monitored as a function of location in the aeration tank, and can be estimated for the entire tank using a flow-weighted average of off-gas flux and carbon dioxide mole fraction. The pH of the mixed liquor will change, which can be measured locally with a pH meter. The model can be used to compare observed data and theory. The equilibrium assumptions for the gases can also be evaluated.

To confirm the possibility nitrification estimation from off-gas test, several tests were applied in the model. The molar fraction of carbon dioxide in the off-gas was simulated based upon different strength of nitrogenous components in a fixed total BOD wastewater. For instance, the oxygen demand for nitrification is 4.5 mg O_2 per

mg ammonia-nitrogen. For the substrate, approximately around 1.1 mass of oxygen per unit of nonstructural substrate (the portion of substrate which is not utilized for biomass reproduction) is consumed. The total oxygen demand constant of the wastewater can be maintained at a constant value by changing the relative amounts of oxygen demand from substrate and ammonia. The carbon dioxide production rates will be different.

Figure 13 shows the simulation results. The horizontal axis shows the fraction of oxygen demand that is attributed to ammonia oxidation. It is observed that the mole fraction of carbon dioxide in the off-gas decreases linearly, as expected. This simulation suggests that the relative rate of ammonia oxidation can be estimated from the off-gas mole fractions.

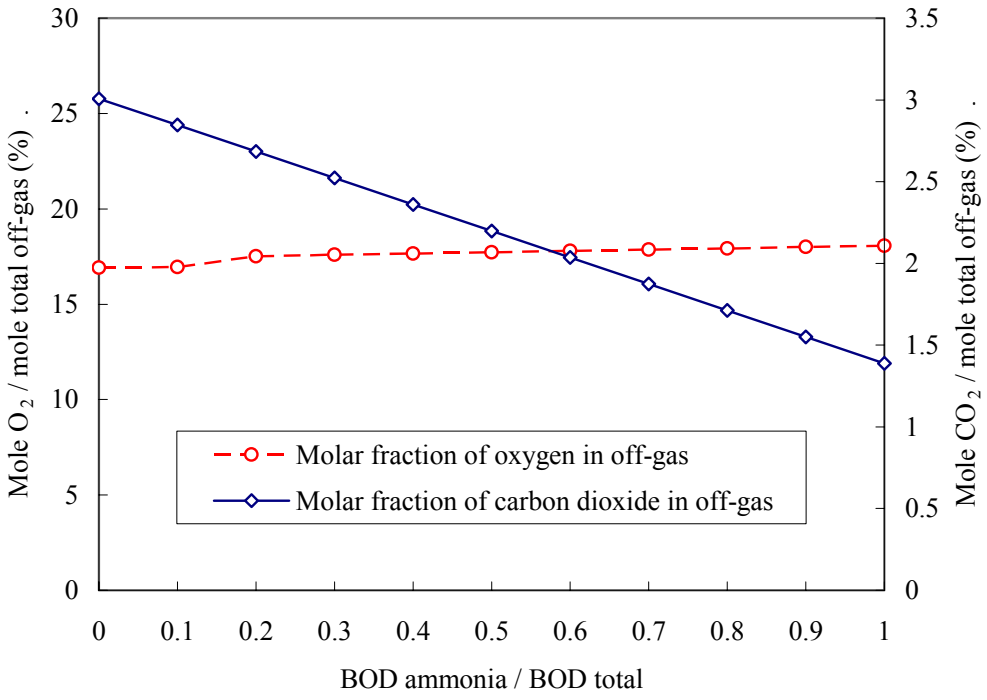

Figure 13. The simulation of off-gas molar fraction of CO_2 and ammonia strength

One of the major uncertainties of off-gas test is the gas-liquid equilibrium. As mentioned before, the oxygen transfer rate in this model is calculated from the summation of saturation concentration and dissolved concentration times transfer coefficient (equation 31). Estimation error may occur if the dissolved oxygen concentration approaches the saturated concentration (Krause, 2003). On the other hand, similar problem may occur in the case of carbon dioxide estimation. The carbon dioxide concentration will always be supersaturated in the liquid phase and must be stripped (equation 40). If the stripping rate is not sufficiently high, the off-gas carbon dioxide mole fraction will not accurately estimate the carbon dioxide production rate. The stripping rate will be highly dependent on $K_L a$.

When $K_L a$ is high, the dissolved oxygen in the liquid will be high, because the oxygen transfer rate is high to sustain the consumption rate. Hence, the dissolved carbon dioxide is more likely to be stripped from liquid phase as fast as it is produced. In contrast, at low $K_L a$, DO should be lower and therefore dissolved CO_2 would be greater; also, the partial pressure of CO_2 in off-gas would be lower because less CO_2 is stripped.

A way of testing the degree of supersaturation is to apply Henry's law. The model provides all the parameters and concentrations to use Henry's law. By comparing the results using Henry's law to the calculated off-gas concentrations, the nearness of the system to equilibrium can be determined. Under low $K_L a$, dissolved CO_2 concentration will be super saturated since it is much higher than the estimated value calculated from the Henry's constant and partial pressure. The difference of dissolved CO_2 calculated from two approaches under various $K_L a$ is shown in Figure

14. It can be seen that the degree of super saturation decreases within increasing increase of $K_L a$. When $K_L a$ is lower than approximately 150 day^{-1}, the difference between the two approaches does not drop significantly with increasing $K_L a$. As $K_L a$ increases to the range from 150 day^{-1} to 480 day^{-1}, the difference of two approaches drops exponentially, and then equilibrium shows up as $K_L a$ greater than 480 day^{-1}. This difference might be still quite significant since in the real case $K_L a$ rarely exceeds 480 day^{-1} (20 day^{-1}). Therefore, further investigate for convergent factors or different estimating strategy will be necessary.

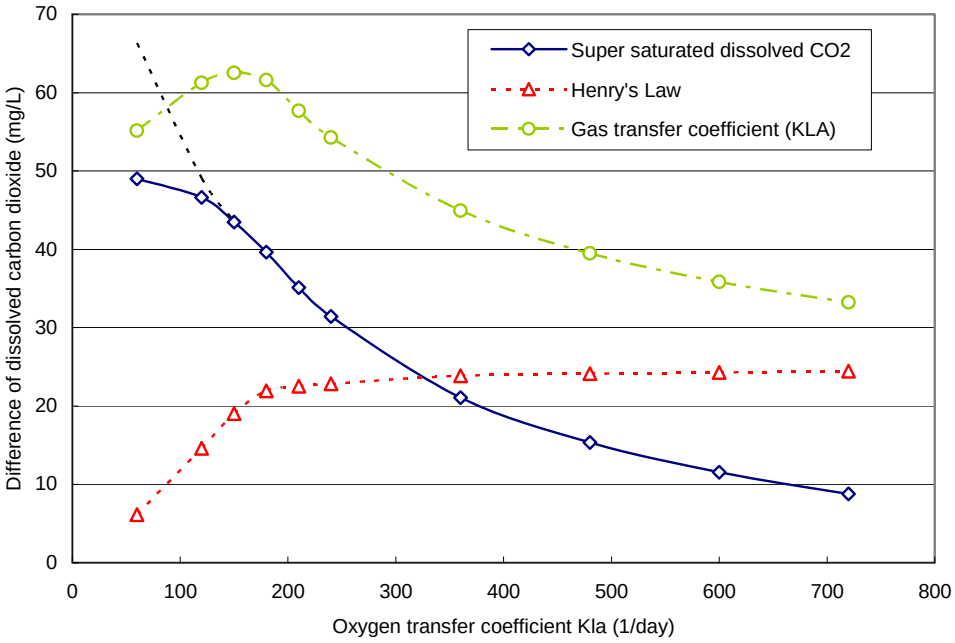

Figure 14. The difference of dissolved CO_2 estimation between gas transfer approach and Henry's law approach versus $K_L a$

5. CONCLUSIONS

A dynamic model simulating the several components in an activated sludge wastewater treatment process was developed. The target components or properties include carbonaceous pollutants (substrate), nitrogenous pollutants (ammonia, nitrite, and nitrate), heterotrophic bacteria concentration, nitrifying bacteria (Nitrosomonas and Nitrobacter) concentrations, gas and liquid phase oxygen concentrations, gas and liquid phase carbon dioxide concentrations, alkalinity, and pH. From references and simulation tests, the simulation results were shown to be reasonable. The model can be used as a tool for evaluating several phenomena including nitrification, oxygen consumption, carbon dioxide production, and pH change.

Based upon the model simulation, the linear relationship between CO_2 production and the ratio of ammonia and total pollutants suggest that estimating nitrification efficiency from an off-gas test might be possible. Further work is required to develop and validate the approach.

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APPENDIX A. — Definition of parameters

Symbol	Definition
CDog	carbon dioxide molar flow rate in off-gas (mole CO_2/T)
DCD	dissolved carbon dioxide concentration (M/L^3)
D_{CO_2}	carbon dioxide gas density (M/L^3)
D_{N_2}	nitrogen gas density (M/L^3)
DO	dissolved oxygen concentration (M/L^3)
D_{O_2}	oxygen gas density (M/L^3)
F_1	mole ratio of hydrogen ion and nitrite in ammonia oxidation reaction
F_2	mole ratio of hydrogen ion and nitrate in nitrite oxidation reaction
K_1	first Keq for carbon dioxide
K_2	second Keq for carbon dioxide
K_D	decay coefficient (T^{-1})
K_La	volumetric oxygen transfer coefficient (T^{-1})
$K_La_{CO_2}$	CO_2 transfer rate (T^{-1})
K_S	half velocity coefficient (M/L^3)
K_{SDO}	half saturation coefficient (M/L^3)
K_W	ion product in water
$Mw-CO_2$	molecular weight of carbon dioxide
$Mw-N$	molecular weight of nitrogen
$Mw-N_2$	molecular weight of nitrogen gas
$Mw-O_2$	molecular weight of oxygen
N_2og	nitrogen gas molar flow rate (mole N_2/T)
$N_{(NH_3)_T-N}$	ammonia concentration (M/L^3)
$N_{(NH_3)_T-N}$	total ammonia concentration (M/L^3)
$N_{NO_2^--N}$	nitrite concentration (M/L^3)
O_2og	oxygen molar flow rate in off-gas (mole O_2/T)
Q	average flow rate (L^3/T)
Qg	gas flow rate from diffusers (L^3/T)
Q_R	sludge recycle flow rate (L^3/T)
Q_W	discharged sludge flow rate (L^3/T)
S	substrate concentration (M/L^3)
SRT	Sludge retention time (T)
V	aeration tank volume (L^3)

X	heterotrophic bacteria concentration (mass/volume)
$Y_{CO_2}i$	carbon dioxide molar fraction in inlet gas
Y_{N_2}	nitrogen molar fraction in inlet gas
$Y_{O_2}i$	oxygen molar fraction in inlet gas
Z	alkalinity (Mole/L^3)
f_{CO_2}	molar fraction of H_2CO_3 in total dissolved CO_2
f_{NH_3}	molar fraction of $[NH_3]$ in the total ammonia concentration
p	recycle coefficient (T^{-1})
γ_{CDSTRP}	CO_2 stripping rate (M/L^3/T)
γ_{DCD1}	CO_2 producing rate in heterotrophic bacteria growth reaction (M/L^3/T)
γ_{DCD2}	CO_2 producing rate in heterotrophic bacteria decay reaction (M/L^3/T)
γ_{DCD3}	CO_2 reducing rate in Nitrosomonas growth reaction (M/L^3/T)
γ_{DCD4}	CO_2 producing rate in Nitrosomonas decay reaction (M/L^3/T)
γ_{DCD5}	CO_2 reducing rate in Nitrobacter growth reaction (M/L^3/T)
γ_{DCD6}	CO_2 producing rate in Nitrobacter decay reaction (M/L^3/T)
γ_{DOTR}	oxygen transfer rate (M/L^3/T)
γ_{DO1}	oxygen reducing rate in heterotrophic bacteria growth reaction (M/L^3/T)
γ_{DO2}	oxygen reducing rate in heterotrophic bacteria decay reaction (M/L^3/T)
γ_{DO3}	oxygen reducing rate in Nitrosomonas growth reaction (M/L^3/T)
γ_{DO4}	oxygen reducing rate in Nitrosomonas decay reaction (M/L^3/T)
γ_{DO5}	oxygen reducing rate in Nitrobacter growth reaction (M/L^3/T)
γ_{DO6}	oxygen reducing rate in Nitrobacter decay reaction (M/L^3/T)
$\gamma_{NH_3 1}$	ammonia reducing rate in heterotrophic bacteria growth reaction (M/L^3/T)
$\gamma_{NH_3 2}$	ammonia producing rate in heterotrophic bacteria decay reaction (M/L^3/T)
$\gamma_{NH_3 3}$	ammonia reducing rate in Nitrosomonas growth reaction (M/L^3/T)
$\gamma_{NH_3 4}$	ammonia producing rate in Nitrosomonas decay reaction (M/L^3/T)
$\gamma_{NH_3 5}$	ammonia producing rate in Nitrobacter decay reaction (M/L^3/T)
$\gamma_{NO_2 1}$	nitrite producing rate in ammonia oxidation reaction (M/L^3/T)
$\gamma_{NO_2 2}$	nitrite reducing rate in Nitrobacter growth reaction (M/L^3/T)
$\gamma_{NO_2 1}$	nitrate production rate in Nitrobacter growth reaction (M/L^3/T)
γ_{Z1}	alkalinity coefficient of ammonia hydrolysis (mole/L^3/T)
γ_{Z2}	alkalinity coefficient from ammonia oxidation (mole/L^3/T)

Y_{Z3} = alkalinity coefficient from nitrite oxidation (mole/L^3/T)

$\hat{\mu}_{NS}$ maximum Nitrosomonas growth rate (T^{-1})

$\hat{\mu}_{NB}$ maximum Nitrobacter growth rate (T^{-1})

$\hat{\mu}_{S}$ maximum cell growth rate (T^{-1})

Y_1 mass observed yield for heterotrophic bacteria growth reaction (mass heterotrophic bacteria VSS / mass substrate)

Y_2 oxygen demand for heterotrophic bacteria growth reaction (mass oxygen / mass substrate)

Y_3 oxygen demand for heterotrophic bacteria decay reaction (mass oxygen / mass heterotrophic bacteria biomass)

Y_4 CO_2 production in heterotrophic bacteria growth reaction (mass CO_2 / mass COD)

Y_5 CO_2 production in heterotrophic bacteria decay reaction (mass CO_2 / mass heterotrophic bacteria biomass)

Y_6 ammonia demand in heterotrophic bacteria growth reaction (mass NH_4-N / mass substrate)

Y_7 ammonia production in heterotrophic bacteria decay reaction (mass NH_4-N / mass heterotrophic bacteria biomass)

Y_{NB} molar yield coefficient of Nitrobacter with no decay (mole Nitrobacter VSS / mole NO_2^--N)

Y_{NB1} mass observed yield of Nitrobacter growth reaction (mass Nitrobacter VSS / mass NO_2^--N)

Y_{NB2} oxygen demand of Nitrobacter growth reaction (mass oxygen / mass NO_2^--N)

Y_{NB3} oxygen demand of Nitrobacter decay reaction (mass oxygen / mass Nitrobacter biomass)

Y_{NB4} CO_2 demand in Nitrobacter growth reaction (mass CO_2 / mass NO_2^--N)

Y_{NB5} CO_2 production in Nitrobacter decay reaction (mass CO_2 / mass Nitrobacter)

Y_{NB6} ammonia production in Nitrobacter decay reaction (mass NH_4-N / mass Nitrobacter biomass)

Y_{NB7} nitrate production in Nitrobacter growth reaction (mass NO_3–N / mass NO_2-N)

Y_{NS} molar yield coefficient of Nitrosomonas with no decay (mole Nitrosomonas VSS / mole NO_2--N)

Y_{NS1} mass observed yield of Nitrosomonas growth reaction (mass Nitrosomonas VSS / mass NH_4-N)

Y_{NS2} oxygen demand of Nitrosomonas growth reaction (mass oxygen / mass NH_4-N)

Y_{NS3} oxygen demand of Nitrosomonas decay reaction (mass oxygen / mass Nitrosomonas biomass)

Y_{NS4} CO_2 demand in Nitrosomonas growth reaction (mass CO_2 / mass NH_4-N)

Y_{NS5} CO_2 production in Nitrosomonas decay reaction (mass CO_2 / mass Nitrosomonas)

Y_{NS6}	ammonia production in Nitrosomonas decay reaction (mass NH_4-N / mass Nitrosomonas biomass)
Y_{NS7}	nitrite production in ammonia oxidation reaction (mass NO_2-N / mass NH_4-N)
Y_{MASS}	heterotrophic bacteria yield coefficient with no decay (mass biomass / mass substrate)
o	as subscript, influent condition of compounds
S	as subscript, saturated concentration of a gas

APPENDIX B. — Reference parameter values

Parameter	Value	Unit
D_{CO_2}	1.25	g/L
D_{N_2}	1.25	g/L
D_{O_2}	1.29	g/L
K_1	$10^{-6.35}$	
K_2	$10^{-10.33}$	
K_D	0.12	day^{-1}
K_La	240	day^{-1}
K_S	20	mgbCOD/L
K_{SDO}	0.5	mgDO/L
K_W	10^{-14}	
$Mw-CO_2$	44	g/mole CO_2
$Mw-N$	14	g/mole N
$Mw-O_2$	32	g/mole O_2
$Y_{CO_2}i$	0.0003	molar CO_2/molar inlet gas
Y_{N_2}	0.7803	molar CO_2/molar inlet gas
$Y_{O_2}i$	0.2099	molar CO_2/molar inlet gas
$\hat{\mu}_S$	6	day^{-1}
$\hat{\mu}_{NS}$	1.08	day^{-1}
$\hat{\mu}_{NB}$	1.44	day^{-1}
Y_{MASS}	0.4	heterotrophic bacteria yield coefficient with no decay (mass biomass / mass substrate)
Y_{NB}	0.12	mass observed yield of Nitrobacter growth reaction (mass Nitrosomonas VSS / mass NO_2^--N)
Y_{NS}	0.05	mass observed yield of Nitrosomonas growth reaction (mass Nitrosomonas VSS / mass NH_4-N)

APPENDIX C. — Matlab code

C.1. Main program

```
clc
clear

% Influent Conditions
S0=250; % Average Influent COD (mg/L)
X0=1; % Seed Concentration (mg/L)
DO0=0; % Influent Dissolved Oxygen Concentration (mg/L)
NH40=40; % Influent Ammonia Concentration (mgNH4-N/L)
NO20=0.01; % Influent Nitrite Concentration (mgNO2-N/L)
NO30=0.01; % Influent Nitrate Concentration (mgNO3-N/L)
Xns0=0.1; % Influent Nitrosomonas Concentration (mg/L)
Xnb0=0.1; % Influent Nitrobacter Concentration (mg/L)
CaCO30=450; % Influent Alkalinity as CaCO3 (mg/L)
Z0=CaCO30/50/1000; % Influent Alkalinity (M)
H0=10^(-7); % Influent Hydrogen Ion Concentration (M)
DCD0=0.716; % Influent Carbon Dioxide Concentration (mg/L)

% Initial Conditions
Si=4.42; % Initial COD (mg/L)
Xi=2527.47; % Initial Biomass Concentration (mg/L)
DOi=0.08; % Initial Dissolved Oxygen Concentration (mg/L)
NH4i=5.1546; % Initial Ammonia Concentration (mgNH4-N/L)
NO2i=0.9769; % Initial Nitrite Concentration (mgNO2-N/L)
NO3i=30.817; % Initial Nitrate Concentration (mgNO3-N/L)
Xnsi=42.384; % Seed Concentration of Nitrosomonas (mg/L)
Xnbi=127.69; % Seed Concentration of Nitrobacter (mg/L)
Zi=0.00025; % Initial Alkalinity (M)
DCDi=20.688; % Initial Carbon Dioxide Concentration (mg/L)

% Dissociation Constants
Kw=10^(-14); % pkw=14.943-4.2467e-02*temp+1.8234e-04*temp^2
K1=10^(-6.35); % pk1=6.5793-1.3525e-02*temp+1.8126e-04*temp^2
K2=10^(-10.33); % pk2=10.629-1.5054e-02*temp+1.2074e-04*temp^2
KNH3=10^(-9.24); % pknh3=pkw-10.059-3.1956e-02*temp
fNH3=1/(1+H0/KNH3);
fHCO3=1/(1+K2/H0+H0/K1);
fCO3=1/(1+H0/K2+(H0)^2/K1/K2);
fCO2=1/(1+K1/H0+K1*K2/(H0^2));

% Loop for pH calculation and ODE Solving
H0=10^(-7); % Guess of hydrogen ion concentration (M)
for i=0:1:199 % [0 timeend] is devided into n parts, if n=10 then the maximun i is 99
since timeend=100/10=10(days)
```

```
tspan=[i i+1]/10; % For ode45 tspan=[0 timeend];
j=i+1;            % For specifying the location of data in the matrix
  time2(j)=i/10;% Only for Hi since the length of matrix Hi is different with y
                % After ode45, the length of y is greater then Hi
  % Global data
    global fCO2 fNH3
    if j<=1 % First series of Hi and ode claculation (Data come from initial condition)
        Hi(j)=H0; % Initial guess for [H+]
        options = odeset('RelTol',1e-4,'AbsTol',[1e-4 1e-4 1e-4 1e-4 1e-4 1e-4 1e-4 1e-4
                                                 1e-4 1e-4]);
        [t,y]=ode45(@cstr13_dynamic,tspan,[Si Xi DOi DCDi NH4i NO2i NO3i Xnsi
Xnbi Zi],options,S0, X0, DO0, DCD0, NH40, NO20, NO30, Xns0, Xnb0, Z0);
        time=t;   % Build a new matrix "time" for continuously counting each part of "t"
                    for next series
        yacc=y;   % Save all the data from ode to matrix "yacc" since the data in matrix
                    "y" will be replaced in next series
        a=2*K1*K2/Hi(j);
        b=yacc(length(y),10)-fNH3*yacc(length(y),5)/14000;
        c=-Kw-(K1+a)*yacc(length(y),4)/44000;
    else          % Continuous series
        fNH3=1/(1+Hf/KNH3);
        fCO2=1/(1+K1/Hf+K1*K2/(Hf^2));
        if j==2
         long1=length(y); % Save the length of matrix y
         longacc=long1;
        end
        Hi(j)=(-b+(b^2-4*c)^(1/2))/2;
        options = odeset('RelTol',1e-4,'AbsTol',[1e-4 1e-4 1e-4 1e-4 1e-4 1e-4 1e-4 1e-4
                                                 1e-4 1e-4]);
        z=longacc;
        [t,y]=ode45(@cstr13_dynamic,tspan,[yacc(z,1) yacc(z,2) yacc(z,3) yacc(z,4)
yacc(z,5) yacc(z,6) yacc(z,7) yacc(z,8) yacc(z,9) yacc(z,10)],options,S0, X0, DO0,
DCD0, NH40, NO20, NO30, Xns0, Xnb0, Z0);
        long2=length(y);
        longacc=longacc+long2;
        x=longacc-long2+1;
        z=longacc;
        time(x:z,:)=t;
        yacc(x:z,:)=y;
        a=2*K1*K2/Hi(j);
        b=yacc(longacc,10)-fNH3*yacc(longacc,5)/14000;
        c=-Kw-(K1+a)*yacc(longacc,4)/44000;
     end
        Hf=Hi(j);
end
% Off-gas calculation (gas flow rate is known)
Do2=1.29; % Density of oxygen (g/L)
```

```
Dco2=1.25; % Density of carbon dioxide (g/L)
Dn2=1.25; % Density of nitrogen (g/L)
Yo2i=0.2099; % Oxygen mole fraction in inlet gas
Yco2i=0.0003; % Carbon dioxide mole fraction in inlet gas
Yn2=1-Yo2i-Yco2i; % Inert gases mole fraction in inlet/outlet gas
Qg=0.833*5000; % Total volumetric gas flow rate of inlet gas (L/s)

% Global data
global DOs DCDs KLA KLAco2 V temp
% Oxygen mole flow rate in dry off-gas (mole/s)
O2og=(Do2*Qg*Yo2i-KLA*V*(DOs-yacc(longacc,3))/86400000)/32;
% Carbon dioxide mole flow rate in dry off-gas (mole/s)
CDog=(Dco2*Qg*Yco2i-KLAco2*V*(DCDs-yacc(longacc,4)*fCO2)/86400000)/44;
% Nitrogen mole flow rate in dry off-gas (mole/s)
N2og=Dn2*Qg*Yn2/28;
% Total gas mole flow rate in dry off-gas (mole/s)
Tg=O2og+CDog+N2og;
% Mole fraction of oxygen in dry off-gas
Yo2og=O2og/Tg;
% Mole fraction of carbon dioxide in dry off-gas
Ycdog=CDog/Tg;
% Mole fraction of inert gases in dry off-gas
Yn2og=N2og/Tg;

% Equilibrium check
Patm=1; % Atomosphere pressure
R=8.2056*10^(-5); % Ideal gas constant
beta=0.99; % Gas transfer effiecincy coefficient
% Henry's law coefficient for CO2
Heco2=(0.72206+0.02969*temp+2.6693*temp^2)/(55555*44*beta);
% Water vapor partial pressure (atm)
Ph2o=(5.0538-0.021092*temp+0.030783*temp^2)/760;
% Partial pressure of CO2 in dry off-gas
Pco2=(Patm-Ph2o)*Ycdog   % Partial pressure of CO2 in atmosphere
DCD1=Pco2/Heco2;
DCD2=yacc(longacc,4)
pH=Hi(200);
DO=yacc(longacc,3);
% Oxygen transfer efficiency OTE (mass oxygen transfered/ mass oxgen flow in)
% Eo2=KLA*V*(DOs-yacc(longacc,3))/86400000/Do2/Qg/Yo2i;

% Total biomass
X=yacc(:,2)+yacc(:,8)+yacc(:,9);

% Daigrams
figure(1)
plot(time,yacc(:,1));
```

```
xlabel('Time(day)')
ylabel('Substrate concentration(mg/L)')
title('X Concentration')
grid

figure(2)
plot(time,yacc(:,3));
xlabel('Time(day)')
ylabel('Dissolved oxygen concentration(mg/L)')

figure(3)
[AX,H1,H2] = plotyy(time,yacc(:,3),time,yacc(:,4),'plot');
set(get(AX(1),'Ylabel'),'String','Dissolved Oxygen Concentration (mg/L)')
set(get(AX(2),'Ylabel'),'String','Carbondyoxide Concentration (mg/L)')
xlabel('time(day)')
title('O2,CO2 Concentration')
grid

figure(4)
plot(time,yacc(:,5),':',time,yacc(:,6),'--',time,yacc(:,7));
xlabel('time(day)')
ylabel('concentration(mg/L)')
legend('Ammonia','Nitrite','Nitrate');
title('Ammonia, Nitrite and Nitrate Concentration')
grid

figure(5)
plot(time,yacc(:,2),':',time,yacc(:,8),'-.',time,yacc(:,9),'--',time,X)
xlabel('Time(day)')
ylabel('Concentration(mg/L)')
legend('Xs','Xns','Xnb','Total X');
title('Biomass Concentration')
grid

figure(6)
plot(time,yacc(:,10))
xlabel('time(day)')
ylabel('ALk')
title('Alk vs time')
grid

figure(7)
semilogy(time2,Hi)
xlabel('time(day)')
ylabel('log[H+]')
title('pH vs time')
grid
```

C. 2. Function file

```
function dy=cstr13(t, y, S0, X0, DO0, DCD0, NH40, NO20, NO30, Xns0, Xnb0, Z0)
global fCO2 fNH3 DOs DCDs KLA KLAco2 V temp

% Background Data
% a=8; % Carbon number in substrate empirical formula "CaHbOc"
% b=12; % Hydrogen number in substrate empirical formula "CaHbOc"
% c=4; % Oxygen number in substrate empirical formula "CaHbOc"
% Mw=12*a+b+16*c; % Molecular weight of substrate
Ymass=0.4; % Yield coefficient with no decay (mass biomass/mass COD)
V=6623750; % Aeration tank volume (L)
Q=26495000; % Average flow rate (L/day)
HRT=V/Q; % Hydraulic retention time (day)
temp=25; % Water temperature (drgree C)
uMax=6; % Maximum cell growth rate (massVSS/massVSS/day)
Ks=20; % Half velocity coefficient (mgbCOD/L)
Kd=0.12; % Decay coefficient (massVSS/massVSS/day)
DOs=9.09; % Saturated oxygen concentration (mg/L)
KLA=840; % Volumetric oxygen transfer coefficient (1/day)
KsDO=0.5; % Half saturation coefficient (mgDO/L)
KLAco2=0.836*KLA; % Volumetric carbon dioxide transfer coefficient (1/day)
KLAn2=0.943*KLA; % Volumetric nitrogen transfer coefficient (1/day)
DCDs=0.716; % 5.5555*10^4*44/Heco2*Pco2*beta; % Saturated carbon dioxide
concentration (mg/L)

% Sludge Recycle Coefficient
SRT=20; % Biomass Retention Time (day)
R=0.80; % Sludge Recycle Percentage (%)
Qr=R*Q; % Sludge Recycle Flow Rate (L/day)
Qw=Qr*V/SRT/(Q+Qr);     % Discharged Sludge Flow Rate (L/day)

% Coefficient Calculation for Substrate
% Molar Yield with No Decay (mole biomass/mole COD)
Y=0.609;
% Molar Observed Yield (mole biomass/mole COD)
Yobs=0.591;
% Mass Observed Yield (mass biomass/mass COD)
Y1=0.388; % Y1=Ymass/(1+Kd*HRT);
% Oxygen Requirement of Synthesis Reaction (mass oxygen/mass COD)
Y2=1.125;
% Decay Oxygen Requirement (mass oxygen/mass biomass)
Y3=1.42;
% Carbon Dioxide Production Coefficient (mass CO2/mass COD)
Y4=1.291;
% Carbon Dioxide Production Coefficient (mass CO2/mass Biomass)
Y5=1.947;
```

```
% Ammonia Consumming Coefficient in Synthesis Reaction (mass NH4-N/ mass
VSS)
Y6=0.048;
% Ammonia Production Coefficient in Decay Reaction (mass NH4-N/mass Substrate)
Y7=0.124;

% Nitrification - Nitrosomonas
% Maximum Nitrosomonas Growth Rate (massVSS/massVSS/day)
uMns=1.08;
% Nitrosomonas Half Velocity Coefficient (mgNH4-N/L)
Kns=0.063;
% Nitrosomonas Decay Coefficient (massVSS/massVSS/day)
Kdns=0.12;
% Mass Yield of Nitrosomonas (massVSS/massNH4 utilized)
Yns=0.05;
% Mass Observed Yield of Nitrosomonas (massVSS/massNH4-N utilized)
Yns1=0.05;
% Oxygen Requirement for ammonium oxidation reaction (massO2/massNH4-N)
Yns2=3.337;
% Oxygen requirement for Nitrosomonas decay reaction (massO2/mass nitrosomonas
biomass)
Yns3=Y3;
% Carbon dioxide requirement for ammonium oxidation reaction
(massCO2/massNH4-N)
Yns4=0.0974;
% Carbon dioxide production for ammonium oxidation reaction (massCO2/mass
nitrosomonas biomass)
Yns5=Y5;
% Ammonia production coefficient in Nitrosomonas decay reaction (massNH4-
N/mass nitrosomonas biomass)
Yns6=0.124;
% Nitrite production coefficient in ammonium oxidation reaction (massNO2-
N/massNH4-N)
Yns7=0.9938;

% Nitrification - Nitrobacter
% Maximum Nitrobacter Growth Rate (massVSS/massVSS/day)
uMnb=1.44;
% Nitrobacter Half Velocity Coefficient (mgNH4-N/L)
Knb=0.74;
% Decay Coefficient of Nitrobacter (massVSS/massVSS/day)
Kdnb=0.08;
% Mass Yield of Nitrobacter
Ynb=0.12;
% Mass Observed Yield of Nitrobacter (mass biomass/mass COD)
Ynb1=0.12;
```

```
% Oxygen requirement for nitrite oxidation reaction (massO2/massNO2-N)
Ynb2=1.1033;
% Oxygen requirement for Nitrobacters decay reaction (massO2/mass nitrobacters
biomass)
Ynb3=Y3;
% Carbon dioxide requirement for nitrite oxidation reaction (massCO2/massNO2-N)
Ynb4=0.039;
% Carbon dioxide production in nitrite oxidation reaction (massCO2/mass
nitrosomonas biomass)
Ynb5=Y5;
% Ammonia production in Nitrobacter decay reaction (massNH4-N/mass Nitrobacter
biomass)
Ynb6=Y6;
% Nitrate production in nitrite oxidation reaction (massNO3-N/massNO2-N)
Ynb7=0.9975;

% Coefficients for alkalinity and pH calculation
% Hydrogen ion reduction coefficient in ammonia oxidation
F1=1.993/0.9938;
% Hydrogen ion production coefficient in nitrite oxidation
F2=0.0026/0.9975;

% ODE Formula
dy=zeros(10,1);
mu1=uMax*y(1)*y(2)/(Ks+y(1))*y(3)/(KsDO+y(3));
mu2=uMns*y(5)*y(8)/(Kns+y(5))*y(3)/(KsDO+y(3));
mu3=uMnb*y(6)*y(9)/(Knb+y(6))*y(3)/(KsDO+y(3));
% Recycle coefficient
p=-Qw/V*(Q+Qr)/Qr;

% Liquid and biological phase
% Effulent Substrate Concentration(mg/L) S=y(1)
dy(1)=1/HRT*(S0-y(1))-mu1/Ymass;
% Biomass Concentration (mg/L) X=y(2)
dy(2)=p*y(2)+mu1-Kd*y(2);
% Dissolved Oxygen Concentration (mg/L) DO=y(3)
dy(3)=1/HRT*(DO0-y(3))+KLA*(DOs-y(3))-Y2*mu1/Y1-Y3*Kd*y(2)-
Yns2*mu2/Yns1-Yns3*Kdns*y(8)-Ynb2*mu3/Ynb1-Ynb3*Kdnb*y(9);
% Carbon Dioxide Concentration (mg/L) DCO2=y(4)
dy(4)=1/HRT*(DCD0-y(4))+KLAco2*(DCDs-
y(4)*fCO2)+Y4*mu1/Y1+Y5*Kd*y(2)-Yns4*mu2/Yns1+Yns5*Kdns*y(8)-
Ynb4*mu3/Ynb1+Ynb5*Kdnb*y(9);
% Ammonia Concentration (mg/L) NH4=y(5)
dy(5)=1/HRT*(NH40-y(5))-Y6*mu1/Y1-
mu2/Yns+Y7*Kd*y(2)+Yns6*Kdns*y(8)+Ynb6*Kdnb*y(9);
% Nitrite Concentration (mg/L) NO2=y(6)
dy(6)=1/HRT*(NO20-y(6))-mu3/Ynb+Yns7/Yns1*mu2;
```

```
% Nitrate Concentration (mg/L) NO3=y(7)
dy(7)=1/HRT*(NO30-y(7))+Ynb7/Ynb1*mu3;
% Nitrosomonas Concentration (mg/L) Xns=y(8)
dy(8)=p*y(8)+mu2-Kdns*y(8);
% Nitrobacter Concentration (mg/L) Xnb=y(9)
dy(9)=p*y(9)+mu3-Kdnb*y(9);
% Alkalinity Balance (M) Z=y(10)
dy(10)=1/HRT*(Z0-y(10))+1/HRT/14000*((fNH3*y(5)-NH40)-F1*(NO20-
y(6))+F2*(NO30-y(7)));
```