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To My Dear Farhood

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Abstract

A membrane activated sludge bench-scale system was used to treat a complex synthetic wastewater over a wide range of operating conditions ranging 1 to 15 day(s) solids retention time (SRT) and 4 to 12 hours hydraulic retention time (HRT). Although the membrane reactor was able to provide good to excellent separation of particulates from the liquid in the mixed liquor over these operating conditions, the membrane failed, primarily due to clogging at operating conditions outside of these ranges. Various techniques, such as coagulant addition, were attempted to further expand the operating range but they failed. All runs were conducted until steady state conditions existed at which time data for modelling were collected. Performance of the system primarily for carbon and nitrogen removal is described for conditions where solids loss or clogging was nonproblematic.

Different mathematical models to predict the behaviour of an activated sludge system and to estimate stoichiometric and kinetics parameters are presented. After gathering enough experimental data, modeling was done, first with simple models such as the Lawrence and McCarty model and the Goodman and Englande model and expanded for International Water Association (IWA) more complicated models (ASM1, ASM2 and ASM3). In addition, a simple empirical model for carbon removal was proposed.

For IWA models, modeling of carbon was first completed and after that, nitrogen was added to the model. In this way, the number of parameters involved in each stage was decreased. The oxygen concentration in the system was high enough for the system to be under aerobic condition, as a result anoxic and anaerobic processes have been ignored in modeling. The AQUASIM 2.1 program has been utilized for parameter estimation when the number of parameters was more than five and a grid search technique was used for four or less parameters. Parameter ranges were defined according to the literature and engineering judgment.

Although all models provide excellent predictions of biomass growth, the Goodman and Englande model was the best. Foretelling of substrate removal is good according to models that are a function of biomass concentration. However, the improvement is not too significant; ASM3 was the best model. Due to the complexity of nitrogen processes and less precision in measuring its components, nitrogen models performed at a moderate level and need more investigation.

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Notation

The following symbols are used in this thesis

Glossary

b_A	decay coefficient for autotrophic biomass
b_H	decay coefficient for heterotrophic biomass
b_{STO}	aerobic respiration rate for X_{STO}
d	day
E	quantity of substrate eliminated per unit of biomass in view of ensuring maintenance
f_i	inert fraction of influent
f_{ndi}	inert inorganic fraction of biomass
f_{nd}	non-biodegradable fraction of biomass
f_{SI}	fraction of inert COD in particulate substrate
f_P	fraction of biomass leading to particulate products
f_{XI}	fraction of inert COD generated in biomass lysis
g	gram
h	hour
i_{NBM}	nitrogen content of biomass X_{BA}, X_{BH}
i_{NSI}	nitrogen content of inert soluble substrate S_I
i_{NSS}	nitrogen content of soluble substrate S_S
i_{NXS}	nitrogen content of inert particulate substrate X_S
i_{XB}	mass of nitrogen per mass of COD in biomass
i_{XP}	mass of nitrogen per mass of COD in products from biomass
k	maximum velocity constant
k_a	ammonification rate
k_d	endogenous decay coefficient of active biomass
k_e	endogenous decay coefficient
K_m	overall substrate removal rate

K_{NH}	ammonia half-saturation coefficient for autotrophic biomass
K_{NO}	nitrate half-saturation coefficient for denitrifying heterotrophic biomass
K_{OA}	oxygen half-saturation coefficient for autotrophic biomass
K_{OH}	oxygen half-saturation coefficient for heterotrophic biomass
K_S	half-velocity constant
K_{STO}	half-velocity constant for X_{STO}
k_{STO}	storage rate constant
K_X	half-velocity coefficient for hydrolysis
k_h	maximum specific hydrolysis rate
Q	flow rate
Q_r	recycle flow rate
Q_W	sludge wasting rate
r_S	rate of substrate removal
r_X	the net growth rate of microorganisms
r_{Xe}	endogenous decay rate
r_{XP}	production of biomass from substrate removal
S	total substrate
S_O	oxygen concentration
S_{ALK}	alkalinity- Molar units
S_I	soluble inert organic matter
S_{ND}	soluble biodegradable organic nitrogen
S_{NH}	ammonia and ammonium nitrogen
S_{NO}	nitrate and nitrite nitrogen
S_S	soluble substrate
t	time
U	food: microorganism
V	volume of aeration basin
X_a	active biomass
X_{BA}	active autotrophic biomass
X_{BH}	active heterotrophic biomass
X_I	particulate inert organic matter

X_{ND}	particulate biodegradable organic nitrogen
X_P	particulate products arising from biomass decay
X_S	slowly biodegradable substrate
X_{STO}	organics stored by heterotrophs
X_i	influent suspended solids concentration
X_{Ti}	inert suspended solids concentration
X_V	biomass concentration in the system
X_{V0}	biomass concentration in influent
X_{Ve}	biomass concentration in effluent
X_{Vr}	recycled biomass concentration
Y	growth yield
Y_A	yield for autotrophic biomass
Y_H	yield for heterotrophic biomass
Y_{STO}	aerobic yield of stored product per S_S
η_g	correction factor for $\hat{\mu}_H$ under anoxic conditions
η_h	correction factor for hydrolysis under anoxic conditions
μ	specific growth rate
$\hat{\mu}$	maximum specific growth rate
$\hat{\mu}_A$	maximum specific growth rate for autotrophic biomass
$\hat{\mu}_H$	maximum specific growth rate for heterotrophic biomass
θ_d	hydraulic retention time
θ_X	solids retention time

Dimensions

L	length; liter
M	mass
T	time

Abbreviations

ASM1	activated sludge model No. 1

ASM2	activated sludge model No. 2
ASM3	activated sludge model No. 3
ATP	adenosine tri-phosphate
BOD	biological oxygen demand
CAS	conventional activated sludge
COD	chemical oxygen demand
DO	dissolved oxygen
FS	fixed solids
FDS	fixed dissolved solids
FSS	fixed suspended solids
HRT	hydraulic retention time
IWAPRC	International Association of Water Pollution Research and Control
IWA	International Water Association
MBR	membrane bioreactor
MCASP	membrane-coupled activated sludge process
MLSS	mixed liquor suspended solids
PAO	phosphorus accumulating organisms
PHA	poly-hydroxy-alkanoic acids
PHB	poly-β-hydroxy-butyrate
RAS	recycled activated sludge
SMBR	submerged membrane bioreactor
SMP	soluble microbial products
SRT	solids retention time
TS	total solids
TDS	total dissolved solids
TSS	total suspended solids
VS	volatile solids
VDS	volatile dissolved solids
VSS	volatile suspended solids
WWTP	wastewater treatment plant

Chapter 1

Introduction

The main purpose of biological wastewater treatment is the degradation of organic matter and converting it into harmless products through biochemical oxidation. One of the common systems for biological treatment is activated sludge, which has wide application as an effective means of wastewater treatment and is used for biological treatment of both municipal and industrial wastewaters. A large amount of biomass (sludge) is formed in an activated sludge process. It is a very effective system when the sludge settles well but its performance deteriorates with poor settling sludge.

Membranes are finding different applications in wastewater treatment. Membrane technologies applied in treatment of wastewater solve the settling problem in many situations. They are used with aerobic or anaerobic bioreactors to separate treated wastewater from the biomass and other solids in suspension. With a membrane reactor, the secondary clarifier can be eliminated and the system is able to operate at a higher mixed liquor suspended solids (MLSS) concentration that provides some advantages for the system. These are

1) Lower hydraulic retention time (HRT).
2) Longer solids retention time (SRT) resulting in less sludge production
3) High quality effluent [low turbidity, bacteria, total suspended solids (TSS) and biological oxygen demand (BOD)].
4) Less space

After developing a system that has good performance, it is necessary to develop a mathematical model that describes the behaviour of the system. Mathematical modeling of wastewater treatment has three major goals. First, modeling can offer an overall conceptual understanding to researchers and extend their knowledge. Second designers have the tools to evaluate a wide range of system variables to find optimal designs in which the process objectives can be achieved at lowest cost, and finally the modeling can help operators of wastewater treatment plants (WWTP) by optimizing the operation or adjusting some operating parameters for desired performance. Consequently, a significant evolution in modeling practice was experienced in the last four or five decades, from a single component model (McKinney, 1962) to complicated models including many components and different processes (Henze et al., 1995) that describe combined carbon, nitrogen and phosphorus removal.

Many studies have been done on modeling activated sludge but membrane bioreactors are a relatively new variation in activated sludge treatment. There is a need to develop parameters for models in membrane biotreatment systems. Moreover, a comparison of simple and complex models applied to systems operating over a wide variety of conditions is an exercise that will illustrate the robustness and predictive power among various models.

The objectives of this thesis are

1) To set up a porous pot membrane activated sludge system and find suitable operating conditions for the system.
2) To apply three levels of models: Lawrence and McCarty (simple), Goodman and Englande (intermediate) and IWA (complex) models (ASM1, ASM2 and ASM3) for the system and find the best model for the system. A comparison of the models in terms of experimental and data reduction efforts required for additional predictive benefits will also be performed.
3) To estimate stoichiometric and kinetic parameters of all models over a wide range of operating conditions.

Chapter 2

Literature Review

2.1 General

The concept of using air for wastewater treatment dates back to the nineteenth century. In 1912, experiments indicated that aeration of sewage for a short time in a tank containing slabs of slate produced a compact brown growth on the slate and a clear nonnitrified effluent. Arden and Lockett (1914) studied the effect of reuse of flocculent solids, activated sludge, in sewage treatment by aeration. Activated sludge greatly increased the purification potential beyond simple aeration. They concluded that average strength Manchester, England sewage could yield a clear, well-oxidized effluent upon aeration in contact with activated sludge for a period of six to nine hours. This period was adopted as a design parameter in future WWTPs.

More studies were undertaken in the United States (Mohlmann, 1917) where activated sludge was confirmed to be the essential factor for sewage stabilization within a six hour aeration period. Other experiments also demonstrated that the air volume supplied for the process should be between 7 and 11 m^3 of air/m^3 of sewage. This became the second key design parameter for years. Because of the flocculent properties of the activated sludge and its clarifying power, efforts were directed towards using the process under continuous flow conditions. By 1917, two small-scale continuous flow plants and one large continuous flow plant were put into operation. Successful experiences with these plants led to the construction of other major plants, which were soon in operation. Several installations were put into operation in the 1920s; however, the process was only used on a widespread basis from the1940s (Orhon and Artan, 1994).

Investigators noted that the amount of biodegradable organics applied to a biological system affected the rate of metabolism. They changed different parameters of the system and investigated their effects on the process. Initial design methods were entirely empirical in nature. Some of these empirical parameters include organic loading, hydraulic loading, reaction time and others. Today, the design of activated sludge utilizes empirical as well as logical parameters based on biological kinetic equations to express growth of biomass and substrate removal rates. These equations include biological coefficients, food-to-microorganism ratio, the mean cell residence time or SRT, the mean waste residence time or HRT and more.

During past years design equations have been developed based on fundamental and scientific concepts of mass balance and microbial growth kinetics. This chapter discusses some of the most widely used of these models. These are the Lawrence and McCarty model (1970), Goodman and Englande model (1974), and the IWA activated sludge models (ASMs): ASM1 (Henze et al., 1987), ASM2 (Henze et al., 1995) and ASM3 (Gujer et al., 1999).

2.2 Mechanism of Biological Reaction

In biological wastewater treatment, biological groups including bacteria, fungi, protozoa, rotifers and nematodes, convert part of soluble organic substrates to new cells while the remainder is oxidized to simple products.

Reaction kinetics involves two basic processes: microbial growth and microbial decay. Monod (1949) used a low amount of biomass and substrate in excess to study these two processes in a batch reactor. Substrate and nutrients are present in excess and only a very small population of biomass exists. The results of his experiment are shown in Fig. 2.1. It shows four different growth phases for biomass growth and decay and amount of substrate in the system.

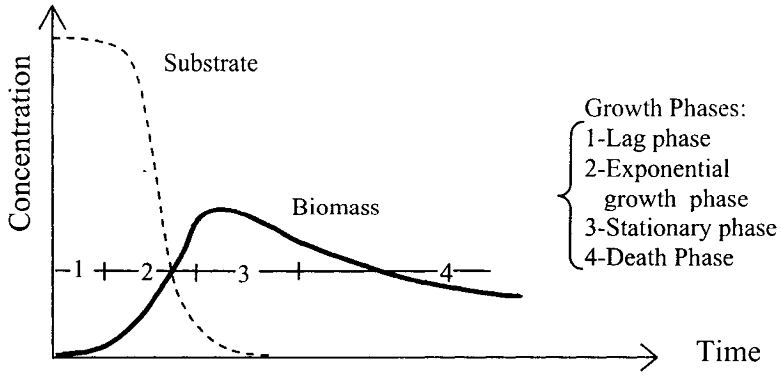


Fig. 2.1 Biomass Growth Phases (Metcalf and Eddy, 2003)

1) Lag phase: Bacteria adapt to a new environment.
2) Exponential phase: Bacteria grow with a maximum specific growth rate, as there is no limitation due to substrate or nutrients. With unlimited substrate and nutrients, the only factor that affects the rate of exponential growth is temperature.
3) Stationary phase: The rate of reproduction is balanced by the death rate.
4) Death or endogenous decay phase: The microbial density decreases rapidly with a high microorganism death rate due to decrease of available substrate.

These phases have different durations depending on the species and medium.

2.2.1 Studies of Substrate Removal

Investigators have suggested different mathematical models to describe substrate removal. In this section, some important ones will be explained.

Monod (1949) suggested the following equation for substrate removal:

$$r_S = \frac{dS_{Se}}{dt} = -\frac{kS_{Se}}{K_S + S_{Se}} \tag{2.1}$$

and the modified Monod equation,

$$r_S = \frac{dS_{Se}}{dt} = -\frac{kX_V S_{Se}}{K_S + S_{Se}} \tag{2.2}$$

where:

k = maximum velocity constant (T^{-1} or $M\ L^{-3}\ T^{-1}$)

K_S = half-velocity constant ($M\ L^{-3}$)

X_V = concentration of biomass ($M\ L^{-3}$)

S_{Se} = concentration of soluble substrate in the reactor ($M\ L^{-3}$)

r_S = rate of substrate removal ($M\ L^{-3}\ T^{-1}$)

McKinney (1962) used a first-order rate with respect to substrate only to describe substrate removal. It is

$$r_S = \frac{dS_{Se}}{dt} = -kS_{Se} \tag{2.3}$$

Eckenfelder (1966) suggested a first-order function of S_e and X_V for the substrate removal mechanism. It is

$$r_S = \frac{dS_e}{dt} = -kX_V S_{Se} \tag{2.4}$$

2.2.2 Studies of Biological Growth of Biomass

One of the most famous rate expressions for microorganism growth was suggested by Monod (1949). He experimentally found that

$$\frac{1}{X_V} \cdot \frac{dX_V}{dt} = \mu = \hat{\mu}\frac{S_{Se}}{K_S + S_{Se}} \tag{2.5}$$

where

μ = specific growth rate (T^{-1})

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

Specific growth rate versus concentration of growth limiting substrate is illustrated in Fig. 2.2.

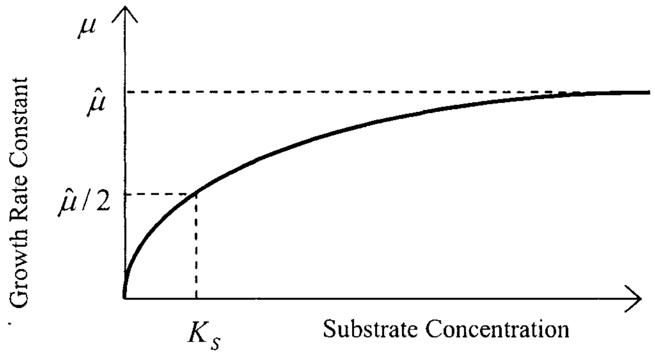


Fig. 2.2 Growth Rate vs. Substrate Concentration (Reynolds and Richards, 1996)

Monod (1949) defined the growth yield Y to estimate the amount of cell synthesis as

$$Y = \frac{\text{amount of bacteria formed}}{\text{amount of substrate removed}} \tag{2.6}$$

Therefore, the production of biomass can be described by

$$r_{XP} = -Yr_S \tag{2.7}$$

where

r_{XP} = production of biomass from substrate removal (M L^{-3} T^{-1})

r_S = rate of substrate removal (M L^{-3} T^{-1})

The common equation is used to describe microbial growth during the exponential growth phase is

$$r_{XP} = \mu X_V \tag{2.8}$$

Substituting the Monod equation into Eq. 2.8,

$$r_{XP} = \mu X_V = \frac{\hat{\mu} S_{Se} X_V}{K_S + S_{Se}} \tag{2.9}$$

The total growth rate is limited by substrate concentration and it is proportional to the concentration of biomass. Comparing Eqs. 2.9 and 2.7 and defining $k = \hat{\mu}/Y$ results in the modified Monod equation (Eq. 2.2).

It is necessary to find an equation that describes growth rate when raw wastewater enters the system. Garret and Sawyer (1952), Gaudy and Gaudy (1971) and Andrews (1971) studied mixed cultures and found that the Monod equation is applicable to a mixed culture. The Monod equation is still the most widely used equation to describe biological growth.

Nitrogen and phosphorus are required for the synthesis of new biomass. If the proper amount of nutrients is not present in the system, the removal of organic matter will not be completed. Geol and Gaudy (1969) studied the effect of nitrogen and Schaezler (1969) studied the effect of phosphorus on biological growth. The rule of thumb suggested for the ratio of chemical oxygen demand (COD): N: P is 100: 5: 1 for aerobic processes based on a sludge composition of $C_5H_7NO_2$ (Droste, 1997).

A number of environmental factors affect the efficiency of the system. Temperature and pH are two of the most important factors. The temperature effect on the substrate removal rate depends on the combined effect of $\hat{\mu}$, K_S and Y (Arceivala, 1981). He showed that $\hat{\mu}$ increases with temperature between 10 and 30°C; K_S decreases slightly from 10 to 20°C, then increases substantially up to 30°C and Y increases from 10 to 20°C, but decreases thereafter. Ramalho (1977) found that the optimum pH for growth of bacteria is between 6.5 and 7.5. Organisms cannot usually tolerate pH levels above 9 or below 5 (Eckenfelder, 1966).

The Monod equation shows good agreement with experimental results for readily biodegradable substrates but not with slowly biodegradable substrates (large molecules or particulate matter), since those substrates need to be hydrolysed first. Hydrolysis is rate limiting thus it is important to be modeled as a separate entity. Dold et al. (1980) suggested the following equation to model slowly biodegradable substrate.

$$\frac{dX_S}{dt} = -k_h \frac{X_S / X_a}{K_X + X_S / X_a} X_a \tag{2.10}$$

in which

X_S = slowly biodegradable substrate concentration (M L^{-3})

X_a = active biomass concentration (M L^{-3})

k_h = maximum specific hydrolysis rate (T^{-1})

K_X = half-velocity coefficient for hydrolysis [M(COD)/M(COD)]

An important characteristic of this expression is that even though the rate is first-order with respect to the active biomass concentration, it is controlled by the ratio of particulate substrate concentration to active biomass concentration, rather than by the particulate substrate concentration alone. This is necessary because the reaction is thought to be surface mediated, depending on the presence of extra-cellular enzymes whose quantity will be proportional to the biomass concentration (Grady et al., 1999).

2.2.3 Endogenous Metabolism

When the system operates under substrate-limited conditions, the decay of biomass becomes significant. This phenomenon is called endogenous decay and it can be expressed by a first-order equation as

$$r_{Xe} = -k_e X_V \tag{2.11}$$

in which

r_{Xe} = endogenous decay rate (M L^{-3} T^{-1})

k_e = endogenous decay coefficient (T^{-1}),

Arceivala (1981) showed k_e increases between 10 and 30°C.

2.2.4 Net Growth Rate

The net growth rate of microorganisms is the sum of growth and decay phenomena. It is

$$r_X = -Yr_S - k_e X_V \tag{2.12}$$

in which

r_X = the net growth rate of microorganisms (M L^{-3} T^{-1})

2.3 *Models of Biological Systems*

2.3.1 Lawrence and McCarty Model

Lawrence and McCarty (1970) suggested a treatment model for gross COD or BOD removal. They used two basic equations, Eqs. 2.2 and 2.12. An essential assumption in this model is that microbial growth is limited by the availability of one substrate or a group of substances. All other growth requirements are available in excess. An activated sludge system and reactions in the Lawrence and McCarty model are illustrated in Fig. 2.3.

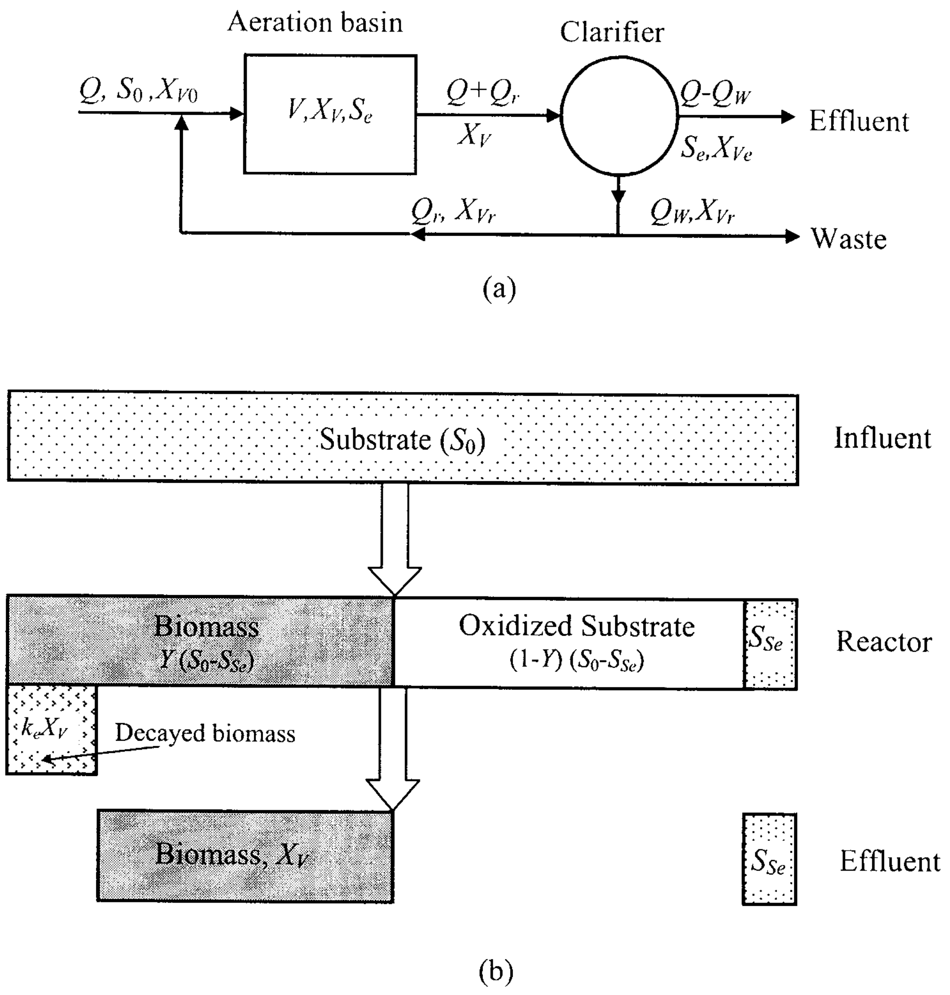


Fig. 2.3 Lawrence and McCarty Model; (a) System; (b) Reactions

A mass balance for the changing rate of substrate mass and microbial mass in the system is written as:

$$QS_0 + Q_r S_{Se} - (Q + Q_r) S_{Se} + r_S V = \frac{dS_{Se}}{dt} V \tag{2.13}$$

$$QX_{V0} + Q_r X_{Vr} - (Q + Q_r) X_V + r_X V = \frac{dX_V}{dt} V \tag{2.14}$$

where

Q = flow rate ($L^3\ T^{-1}$)

Q_r = recycle flow rate ($L^3\ T^{-1}$)

V = volume of aeration basin (L^3)

X_{V0} = VSS concentration in influent (ML^{-3})

X_{Vr} = recycled VSS concentration (ML^{-3})

X_V = VSS concentration inside the reactor (ML^{-3})

Solids retention time, θ_X, and hydraulic retention time, θ_d, are defined as:

$$\theta_X = \frac{X_V V}{Q_W X_r + X_{Ve}(Q - Q_W)} \tag{2.15}$$

$$\theta_d = \frac{V}{Q} \tag{2.16}$$

where

Q_W = sludge wasting rate ($L^3\ T^{-1}$)

X_{Ve} = VSS concentration in clarified effluent (ML^{-3})

In practice, the sludge age can be maintained by controlling the sludge removal rate from the system. Substituting Eqs. 2.2 and 2.12 into Eqs. 2.13 and 2.14, assuming $X_{V0} = 0$ and steady state condition in which $dS_{Se}/dt = 0$ and $dX_V/dt = 0$ result in the system design parameters as

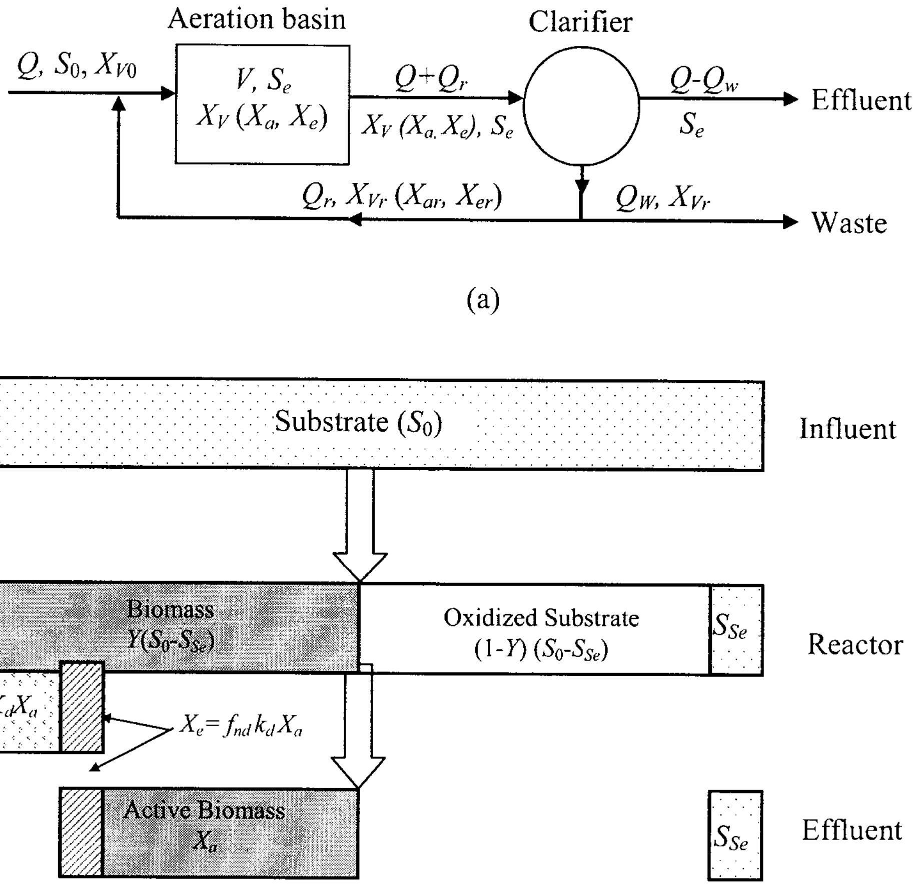
$$S_{Se} = \frac{KS_0(1 + k_e\theta_X)}{\theta_X(YK - k_e) - 1} \tag{2.17}$$

$$X_V = \frac{Y(S_0 - S_{Se})}{1 + k_e\theta_X} \cdot \frac{\theta_X}{\theta_d} \tag{2.18}$$

Lawrence and McCarty reported kinetic constants for several types of substrate biodegradation using a mixed culture. Their relationships do not satisfactorily correlate completely mixed activated sludge parameters when applied to a system under a food-limited condition, in order to achieve a low effluent BOD. But their model is very simple and useful in many cases.

2.3.2 Goodman and Englande Model

Goodman and Englande (1974) proposed a unified model for an activated sludge system by using the McKinney (1963) and Eckenfelder models (1966). They used first-order kinetics for substrate removal. An activated sludge system and reactions according to the Goodman and Englande model are illustrated in Fig. 2.4.



(b)

Fig. 2.4 Goodman and Englande Model; (a) System; (b) Reactions

Biomass (VSS) has been divided into three parts in this model: active mass (X_a), endogenous biomass (X_e) and inert solids (X_{Ti}). Active or viable biomass is the portion that is effectively engaged in biodegradation reactions. Active biomass is a non-linear function of sludge age. The active mass fraction decreases as the sludge age increases. In addition to X_a, there is organic debris in the system which is termed X_e. A significant amount of suspended organic material is dead biomass or associated with decay of biomass (endogenous biomass). Because X_e is a direct function of X_a, the total mass of VSS is related to the active mass.

The current design and simulation models invariably include active biomass as a fundamental parameter. Therefore, it is important to be able to measure active biomass in the lab. Adenosine triphosphate (ATP) and dehydrogenase activity measurement (Jorgensen et al., 1992; Weddle and Jenkins, 1971) are the best measures of active biomass but the procedures for determining ATP or dehydrogenase activity are difficult and complex. Therefore, VSS is commonly used as measure of biomass concentration. VSS is a measure of microorganism mass, which includes both the active and decayed portions. Guwy et al. (1998) determined activity of biomass with a catalase activity biomass monitor; it was correlated well with the respiration rate. Gronje et al. (2002) suggested a method for measuring active biomass, with the help of oxygen uptake rate, nitrate and nitrite measurements.

The substrate and active mass balances can be written as

$$QS_0 + Q_r S_{Se} - (Q + Q_r) S_{Se} + r_S V = \frac{dS_{Se}}{dt} V \tag{2.19}$$

$$QX_{a0} + Q_r X_{ar} - (Q + Q_r) X_a + r_X V = \frac{dX_a}{dt} V \tag{2.20}$$

They assumed $r_S = -K_m S_e$ and $X_{a0} = 0$. Net growth rate in this model is defined as

$$r_X = -Yr_S - k_d X_a \tag{2.21}$$

Solving Eq. 2.19 in a steady state condition results in

$$S_{Se} = \frac{S_0}{1 + K_m \theta_d} \tag{2.22}$$

where

k_d = biomass decay rate (T^{-1})

K_m = overall substrate removal rate (T^{-1})

Assuming steady state condition, Eq. 2.20 gives

$$X_a = \frac{Y(S_0 - S_{Se})}{1 + k_d\theta_X} \cdot \frac{\theta_X}{\theta_d} \tag{2.23}$$

They found X_e based on McKinney's work (1963) as

$$X_e = f_{nd}k_d\theta_X X_a \tag{2.24}$$

$$X_{Ti} = f_i X_i \frac{\theta_X}{\theta_d} + f_{ndi}(X_a + X_e) \tag{2.25}$$

where

X_{Ti} = inert suspended solids concentration (ML^{-3})

X_i = influent suspended solids concentration (ML^{-3})

f_i = inert fraction of influent (–)

f_{ndi} = inert inorganic fraction of biomass (–)

f_{nd} = non-biodegradable fraction of biomass (–)

$$X_T = X_{Ti} + X_a + X_e \tag{2.26}$$

where X_T = total biomass concentration (ML^{-3})

$$X_V = X_a + X_e \tag{2.27}$$

The Goodman and Englande model can predict the behaviour of the system more accurately than the Lawrence and McCarty model because it includes more details and parameters. But measurement of X_a is difficult in the lab.

2.4 IWA Models

2.4.1 General

The International Association of Water Pollution Research and Control (IWAPRC), currently the IWA, formed a task group in 1983 to promote the development and facilitate the application of practical models to the design and operation of biological wastewater treatment systems. The goal was to find a model capable of realistic prediction of performance of single sludge systems carrying out oxidation, nitrification and denitrification. ASM1 is the result of the group's efforts.

2.4.2 ASM1 Model

The task group proposed an activated sludge model designated ASM1 (Henze et al., 1986) that had foundations in the work of Dold et al. (1980), Cech et al. (1985) and Ekama et al. (1986) for a single sludge wastewater treatment systems carrying out carbon oxidation, nitrification and denitrification. ASM1 is expressed in a matrix format comprising 13 components, 8 process rates and 19 parameters.

In contrast to the uniform substrate classification in the earlier models, substrate in this model is classified into different types. Non-biodegradable organic matter usually passes through the system unchanged in form. It has two fractions: soluble and particulate (McKinney and Ooten, 1969). Inert soluble organic matter leaves the system with the same concentration that it entered. Inert suspended organic matter is removed from the system through sludge wastage.

Biodegradable organic matter can be divided into two fractions, readily biodegradable and slowly biodegradable. This division is made on biological response, not on physical separation (Ekama et al., 1986). Readily biodegradable organic matter is absorbed directly by microorganisms for synthesis but slowly biodegradable material through hydrolysis will be converted to readily biodegradable substrate. Growth can take place under aerobic or anoxic conditions. Some studies have been done for determining influent COD fractions (Ekama et al., 1986) and (Mino et al., 1995) and some methods (Germirli et al., 1991 and Orhon et al., 1993) have been developed for measuring inert soluble COD with less error than the task group suggested.

The model divides biomass into two categories: heterotrophs and autotrophs. Heterotrophic bacteria grow in both aerobic and anoxic environments by utilizing readily biodegradable substrate for carbon and energy. Heterotrophs grow in an anoxic condition by using nitrate nitrogen as an electron acceptor. Autotrophs only grow in an aerobic environment deriving their energy from the oxidation of ammonia. This classification allows for more detailed predictions of nitrification and denitrification. The carbon based processes involved in ASM1 for heterotrophs are illustrated in Fig. 2.5.

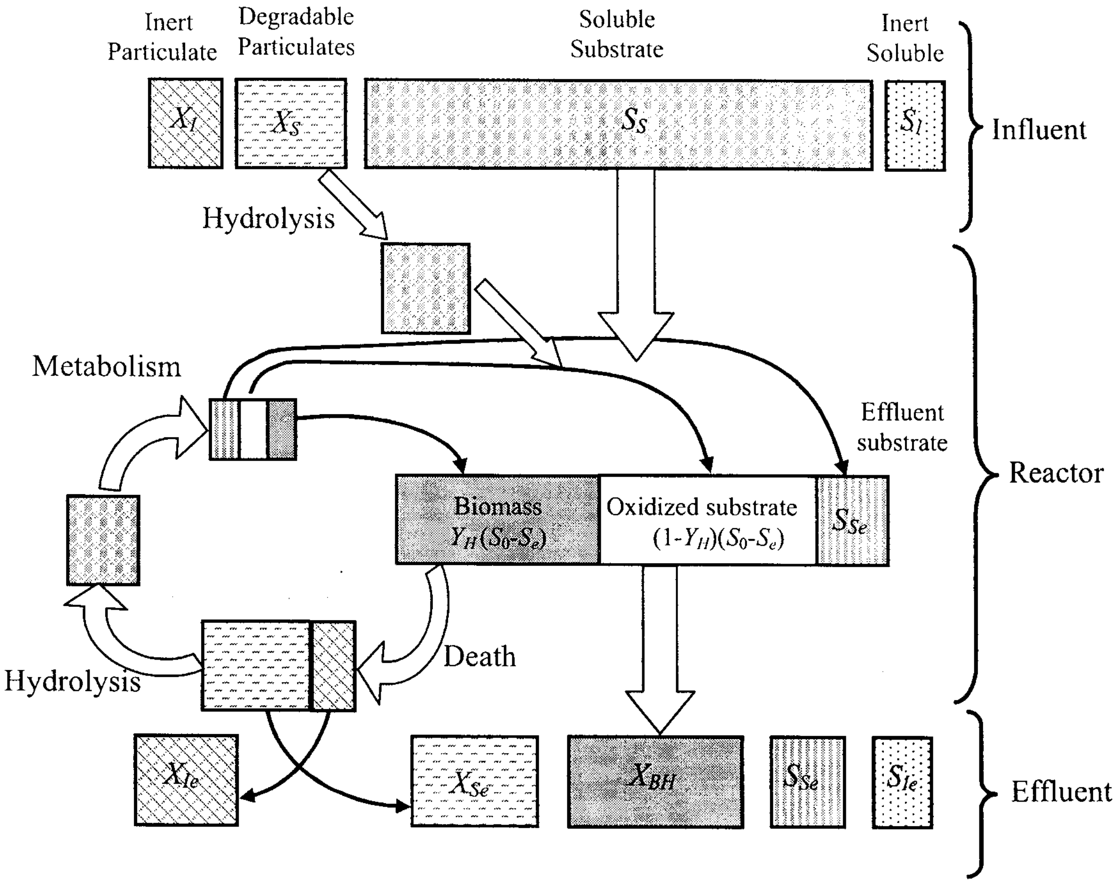


Fig. 2.5 ASM1 Model for Heterotrophic Biomass

COD was used for measuring organic matter because it provides a link between electron equivalents in the organic substrate, the biomass and oxygen utilized (Gaudy and Gaudy, 1971; Servizi and Bogan, 1963; and Payne, 1970). Electrons in a system cannot be created; this allows a mass (electron) balance to be made between the mass of influent COD and the sum of the masses of COD discharged in the effluent, COD in the sludge wastage and carbonaceous oxygen demand in the system.

Biomass is lost by decay (endogenous metabolism, death, predation and lysis). Decay happens when biomass converts to slowly biodegradable and particulate products, which are inert to further biological attack (Dold et al., 1980).

Nitrogenous matter can be divided into two categories: biodegradable and non-biodegradable each with further subdivision. Non-biodegradable nitrogenous matter includes soluble and particulate forms, where the soluble part is negligible (Henze et al., 1986). The biodegradable nitrogenous matter can be divided into ammonia, soluble organic nitrogen and particulate organic nitrogen. Heterotrophic bacteria use the soluble organic nitrogen and convert it to ammonia nitrogen that is the nitrogen source for growth of heterotrophic biomass. It is also the energy source for growth of autotrophic nitrifying bacteria. Drtil et al. (1992) measured kinetic constants of nitrification.

The following notations have been used in ASM1: Insoluble substrate (*X*) and soluble components (*S*), and subscripts of biomass (*B*), substrate (*S*) and oxygen (*O*).

Table 2.1 shows process kinetics and stoichiometry for carbon oxidation, nitrification and denitrification in ASM1.

The first step to set up the matrix is identifying the biological processes in the system. The index i was assigned to each component, after introducing components. The index j was assigned to each process. Then, stoichiometric and kinetic parameters are introduced.

The Monod-Herbert (1958) model was used for rate expressions. ρ is a process rate and ν_{ij} refers to stoichiometric coefficients (Henze et al,. 1986).

Table 2.1 ASM1, Process Kinetics and Stoichiometry (Henze et al., 2000)

j	Component → i Process ↓	1 S_I	2 S_S	3 X_I	4 X_S	5 X_{BH}	6 X_{BA}	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}	Process Rate, ρ_j [ML^{-3}T^{-1}]
1	Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\frac{i_{NBM}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)X_{BH}$
2	Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14\cdot 2.86Y_H}$ $-i_{XB}/14$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)$ $\times\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)\eta_g X_{BH}$
3	Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\hat{\mu}_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{OA}+S_O}\right)X_{BA}$
4	Decay of heterotrophs				$1-f_P$	−1		f_P					$i_{XB}\ f_p i_{Xp}$		$b_H X_{BH}$
5	Decay of autotrophs				$1-f_P$		−1	f_P					$i_{XB}\ f_p i_{Xp}$		$b_A X_{BA}$
6	Ammonification of soluble org. nitrogen										1	-1		$\frac{1}{14}$	$k_a S_{ND} X_{BH}$
7	Hydrolysis of entrapped organics		1		−1										$k_h\left(\frac{X_S/X_{BH}}{K_X+(X_S/X_{BH})}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}$
8	Hydrolysis of entrapped organic nitrogen											1	−1		$\rho_7(X_{ND}/X_S)$
	Observed conversion rates [ML^{-3}T^{-1}]	$r_i=\sum_j \nu_{ij}\rho_j$													

Components of Table 2.1 are:

S_I = soluble inert organic matter [(M (COD) L^{-3}]

S_S = readily biodegradable substrate [(M (COD) L^{-3}]

X_I = particulate inert organic matter [(M (COD) L^{-3}]

X_S = Slowly biodegradable substrate [(M (COD) L^{-3}]

X_{BH} = active heterotrophic biomass [(M (COD) L^{-3}]

X_{BA} = active autotrophic biomass [(M (COD) L^{-3}]

X_P = particulate products arising from biomass decay [(M (COD) L^{-3}]

S_O = oxygen (negative COD) [(M (–COD) L^{-3}]

S_{NO} = nitrate and nitrite nitrogen [(M (N) L^{-3}]

S_{NH} = ammonium and ammonia nitrogen [(M (N) L^{-3}]

S_{ND} = soluble biodegradable organic nitrogen [(M (N) L^{-3}]

X_{ND} = particulate biodegradable organic nitrogen [(M (N) L^{-3}]

S_{ALK} = Alkalinity-Molar units [Mol L^{-1}]

Stoichiometric parameters are:

Y_A = yield for autotrophic biomass [M (COD) / M (N)]

Y_H = yield for heterotrophic biomass [M (COD) / M (COD)]

f_P = fraction of biomass leading to particulate products (–)

i_{XB} = mass of nitrogen per mass of COD in biomass [M (N) / M (COD)]

i_{XP} = mass of nitrogen per mass of COD in products from biomass [M (N) / M (COD)]

Kinetic Parameters are

$\hat{\mu}_H$ = maximum specific growth rate for heterotrophic biomass (T^{-1})

K_S = half-saturation coefficient for heterotrophic biomass [M (COD) L^{-3}]

K_{OH} = oxygen half-saturation coefficient for heterotrophic biomass [M (O_2) L^{-3}]

K_{NO} = nitrate half-saturation coefficient for denitrifying heterotrophic biomass [M (NO_3) L^{-3}]

b_H = decay coefficient for heterotrophic biomass (T^{-1})

b_A = decay coefficient for autotrophic biomass (T^{-1})

η_g = correction factor for $\hat{\mu}_H$ under anoxic conditions (–)

η_h = correction factor for hydrolysis under anoxic conditions (–)

k_h = maximum specific hydrolysis rate[M (COD) / M (COD) T^{-1}]

K_X = half-saturation coefficient for hydrolysis of slowly biodegradable substrate [M (COD) / M (COD)]

$\hat{\mu}_A$ = maximum specific growth rate for autotrophic biomass (T^{-1})

K_{NH} = ammonia half-saturation coefficient for autotrophic biomass [M (NH_3) L^{-3}]

K_{OA} = oxygen half-saturation coefficient for autotrophic biomass [M (O_2) L^{-3}]

k_a = ammonification rate [L^3/M(COD) T^{-1}]

Some explanation about the table is necessary (Henze et al., 1986):

1) The i = 7 column contains the particulate products due to biomass decay (Kountz and Forney, 1959 and McKinney and Ooten, 1969). These forms are not completely inert to biological attack (Obayashi and Gaudy, 1973), but their destruction rate is very low. Introducing them into the model shows that not all biomass in the system is active (Weddle and Jenkins, 1971).
2) The 4.57 term in the stoichiometric coefficient for aerobic growth of autotrophs is theoretical oxygen demand associated with the oxidation of ammonia nitrogen to nitrate nitrogen.
3) The 2.86 term in the stoichiometric coefficient for anoxic growth of heterotrophic biomass is the oxygen equivalent for conversion of nitrate nitrogen to nitrogen gas and is included to maintain consistent units.
4) Nitrogen is necessary for cell synthesis and a term is added ($-i_{XB}$) for the nitrogen used during growth of both heterotrophs and autotrophs.
5) Total alkalinity provides information whereby undue changes in pH can be predicted.
6) The primary purpose of the oxygen term is a switching function that stops aerobic growth at low DO concentration and thus the value of K_{OH} is small.
7) The maximum growth rate under anoxic conditions is often less than that under aerobic conditions. There are two reasons: firstly, $\hat{\mu}_H$ is lower under anoxic conditions. Secondly, only a fraction of heterotrophic biomass is active under

anoxic conditions. Therefore the empirical coefficient, n_g is added to the rate expression, where $n_g < 1$ (Batchelor, 1982).

8) The approach used for modeling decay of the heterotrophic biomass is the death-regeneration concept of Dold et al. (1980).

ASM1 has some limitations and ASM3 was proposed to solve them. When ASM3 has been described, the limitations of ASM1 will be clear.

Different computer programs have been written since 1986 for simulation of the activated sludge process (Olsson and Newell, 1999).

2.4.2.1 Typical Values

The parameter values used by the task group or other researchers in the modeling studies are reported herein. Table 2.2 shows typical values parameters for domestic waste in the literature at neutral pH and 20°C. The values (Henze et al., 1986) in the second column (marked with an asterisk) were found when the temperature was 10°C. Values from Henze et al. (1997) are examples of standard constant sets used in computer models for domestic wastewater. The last column contains ranges of parameters that were defined for parameter estimation by Weijers and Vanrolleghem (1997).

By comparing the values of different parameters, it is realized that some of the parameters show little variation from waste to waste and if a measured value is not available it can be assumed. Those are Y_A, f_p, i_{XB}, i_{XP}, b_A, K_{OH}, K_{OA} and K_{NO} and their default values can be safely used (Henze et al., 1986). Weijers and Vanrolleghem (1997) studied the sensitivity of ASM1 to different parameters, the results of their studies were as follows:

1) In order to do a reliable sensitivity analysis optimal parameters are necessary because different sets of parameters lead to different sensitivity analyses.
2) The number of parameters should be decreased before starting parameter estimation. It is possible to estimate many parameters but a high number of parameters can result in unrealistic parameter estimation.
3) They found their model to be sensitive to $Y_A, \hat{\mu}_A$, k_h , f_p, b_H and η_g from most sensitive to least sensitive. The model is not sensitive to $\hat{\mu}_H$, K_S, b_A and k_a.

Table 2.2 Typical Parameter Values at Neutral pH at 20°C

Parameter	Unit	Henze (1986)	Henze* (1986)	Dold (1986)	Grady (1999)	Henze** (1997)				Weijers (1997)
						UCTAS	P111/7	EFOR/8	No.1/2	
Y_A	g cell COD formed (g N oxidized)$^{-1}$	0.24	0.24	0.15	0.24	0.15	0.24	0.24	0.24	0.1-0.25
Y_H	g cell COD formed (g COD oxidized)$^{-1}$	0.67	0.67	0.666	0.60	0.67	0.57	0.67	0.67	0.55-0.67
f_p	Nothing	0.08	0.08	0.08	0.08	0.08	0.1	0.08	0.08	0.08-0.2
i_{XB}	g N (g COD)$^{-1}$ in biomass	0.086	0.086	0.068	0.086	0.068	0.07	0.068	0.068	0.1-1.0
i_{XP}	g N (g COD)$^{-1}$ in endogenous mass	0.06	0.06	0.068	0.06	0.068	0.06	0.02	0.06	0.02-0.2
$\hat{\mu}_H$	day^{-1}	6.0	3.0	3.7	6.0	3.2	4.0	6.0	6.0	2-10
K_S	g COD m^{-3}	20.0	20.0	5.0	20.0	5.0	20.0	2.0	20.0	2.5-20
K_{OH}	g O_2 m^{-3}	0.20	0.20	0.002	0.10	0.002	0.25	0.2	0.2	0.1-0.5
K_{NO}	g NO_3-N m^{-3}	0.50	0.50	0.15	0.20	0.1	0.5	0.5	0.5	0.1-0.5
b_H	day^{-1}	0.62	0.20	0.62	0.41	0.62	0.5	0.62	0.62	0.1-1.5
b_A	day^{-1}	0.1		0.04	0.01	0.04	0.15	0.15	-	0.04-0.15
η_g	Nothing	0.8	0.8	0.85	0.8	0.33	0.8	0.8	0.8	0.6-1.0
η_h	Nothing	0.4	0.4	0.38	0.4	0.35	0.35	-	0.4	0.35-0.4
k_h	g slowly biodeg. COD (g cell COD. day)$^{-1}$	3.0	1.0	2.2	2.21	1.35	1.5	5.0	3.0	2.0-4.0
K_X	g slowly biodeg. COD (g cell COD)$^{-1}$	0.03	0.01	0.15	0.15	0.027	0.02	0.03	0.03	0.03-0.15
$\hat{\mu}_A$	day^{-1}	0.80	0.30	0.425	0.77	0.45	1.0	0.8	0.8	0.2-1.2
K_{NH}	g NH_3-N m^{-3}	1.0	1.0	1.0	1.0	0.002	0.5	0.4	0.4	0.8-1.0
K_{OA}	g O_2 m^{-3}	0.4	0.4	0.002	0.75	1.0	0.8	1.0	1.0	0.1-1.0
k_a	m^3(g cell COD.day)$^{-1}$	0.08	0.04	0.016	0.16	-	-	-	-	0.016-0.8

* Values at 10 °C

** Examples of standard constant sets used in computer models for activated sludge processes (at 20°C)

Comparing the studies of Henze et al. (1986) and Weijers and Vanrolleghem (1997) shows that there is not a unique expression for sensitivity analysis.

An important factor is that biomass grown under different configurations exhibits different values of $\hat{\mu}_H$ and K_S even though the reactors are operated at the same SRT, loading and other conditions. (Cech et al., 1985; Dold and Marais, 1986)

Comparing parameters at different temperatures shows that $\hat{\mu}_H$, b_H, k_h, K_X and $\hat{\mu}_A$ are sensitive to temperature. The other parameters are essentially almost independent of temperature.

Constraints are necessary to ensure that the simulation results have practical utility (Henze et al., 1986).

1) In conventional systems with an aeration basin followed by a clarifier, the net growth rate or SRT of biomass must be within the range that allows sludge with good settling characteristics to develop. Typically, the SRT should lie between 3 and 30 days.
2) The reactor configuration should be such that the active sludge concentration entering the settler is between 750 and 7500 g m^{-3} in order to achieve proper sludge settling.
3) The unaerated fraction of the reactor volume should not exceed 50% because larger fractions may cause deterioration of sludge settling characteristics.
4) The mixing intensity associated with oxygen transfer should not exceed 240 s^{-1} to prevent excessive floc shear. This must be considered during selection of the reactor sizes.

2.4.3 ASM2 Model

ASM2 (Henze et al., 1995) includes all the phenomena in ASM1; in addition, it incorporates biological phosphorus removal. A matrix of ASM2 and definition of symbols are presented in Appendix B. Some processes in ASM1 were simplified in ASM2 to minimize the size of the matrix. Ammonification of soluble organic nitrogen and hydrolysis of particulate organic nitrogen were removed. It is assumed that they occur in stoichiometric proportion to soluble substrate removal and hydrolysis of slowly biodegradable organic matter. Hydrolysis is divided into three processes under aerobic, anoxic and anaerobic conditions. In ASM1 inert soluble organic matter leaves the system at the same concentration that it enters; but in ASM2 it is also assumed to be produced in the process of hydrolysis of particulate substrates. Dinitrogen was added to model as a product of denitrification. Organic nitrogen was eliminated because of its difficulty of measurement. TSS was added to the model to include mineral particulate solids in the influent and poly-phosphates as a fraction of biomass that does not exert COD.

ASM2 includes fermentation, uptake of acetate for formation of poly-β-hydroxybutyrate (PHB) and other poly-hydroxy-alkanoic acids (PHA) and release of soluble phosphate from hydrolysis of polyphosphate. Readily biodegradable substrate is divided into readily fermentable substrate and fermentation products (acetate). Readily fermentable substrate produces acetate under anaerobic conditions and it is taken up by phosphorus accumulating organisms (PAO).

Heterotrophic bacteria ferment readily fermentable substrate and produce acetate but they do not grow under anaerobic conditions. ASM2 cannot model a totally anaerobic system but it is useful for an anaerobic zone in a system with aerobic and anoxic zones. ASM2 assumes PAO growth occurs under aerobic conditions (Grady et al., 1999).

ASM2D is based on ASM2 and is expanded to include the denitrifying activity of PAO. It includes two additional processes to account for the fact that PAO can use cell internal organic storage products for denitrification.

2.4.4 ASM3 Model

ASM3 (Gujer et al., 1999) was proposed because:

1) ASM1 cannot deal with nitrogen and alkalinity limitations of heterotrophic organisms.
2) Biodegradable soluble and particulate organic nitrogen, which are components of ASM1 model, are difficult to be measured.
3) In practice, specific values for ammonification kinetics cannot be found.
4) ASM1 differentiates inert particulate organic material depending on its origin, influent or biomass decay. It is impossible however to differentiate these two fractions in reality.

5) Hydrolysis dominates the prediction of oxygen consumption and denitrification by heterotrophic organisms. The kinetic parameters for this process are difficult to be quantified.
6) Lysis combined with hydrolysis and growth is used to describe the combined effects of endogenous respiration of the biomass (e.g., storage compounds, death, predation, lysis, etc.). This leads to difficulties in the evaluation of kinetic parameters.
7) The process of storage of poly-hydroxy-alkanoates, which is observed in activated sludge plants, is not included in ASM1.
8) ASM1 does not differentiate decay rates of nitrifiers under aerobic and anoxic conditions. At high SRTs and high fractions of anoxic reactor volumes, this leads to problems with the prediction of maximum nitrification rates.
9) The prediction of directly observable mixed liquor suspended solids (MLSS) is not allowable in ASM1.

Because of all these defects and the advance in experimental evidence on storage of organic compounds the task group has proposed ASM3. A matrix of ASM3 and definition of symbols are presented in Appendix B.

Koch et al. (2000) used data from WWTPs treating Swiss municipal diluted wastewater to calibrate ASM3. The most important parameters of ASM3 were estimated based on batch experiments with activated sludge from different WWTPs. They did sensitivity analysis to understand which parameters are more important. They determined those parameters (b_H, b_A, $\hat{\mu}_H$, $\hat{\mu}_A$, $K_{STO,}$ K_S) with the aid of available batch experiments, with multiple experiments at different temperatures or with activated sludge from different plants. The model uncertainty could be reduced by focusing on these parameters. The experiments that they used were designed to calibrate ASM1 and not ASM3. For accurate calibration of ASM3, more experiments will have to be performed in the future. As mentioned in ASM1 to do sensitivity analysis optimal parameters are necessary but it seems that they used some typical values to perform sensitivity analysis at the beginning.

Koch et al. (2001) made some simplification in ASM3 application but they did not explain how it was performed, only final equations and their primary assumptions were presented.

2.5 Membrane Bioreactor

The use of a membrane and an activated sludge tank for the separation of MLSS is called membrane-coupled activated sludge process (MCASP). The major difference of this system from a conventional activated sludge (CAS) process is in separation of the sludge from treated wastewater. Smith et al. (1969) described ultra-filtration as a replacement for sedimentation in an activated sludge system. In CAS solids that settle properly can be stored for a time in the clarifier and the rest leave the system with the effluent but with a membrane process, all parts of the MLSS that are larger than the pore size of membrane are retained. So the concentration of biomass and solids in effluent depends on membrane pore size. To maintain the necessary bacteria for the process, micro-filtration membranes with a maximum pore size of 0.4 μm are used. Hardt et al. (1970) achieved 98% COD removal with a MCASP.

This technology attracted Japanese engineers in the early 1980s, because it needs less space and land is valuable in Japan. In 1989, the Japanese government joined with many large companies to develop a high product quality process that could be suitable for water recycling. A flat plate immersed membrane bioreactor (MBR) was a result of that work (Churchouse and Wildgoose, 1999). There are over 500 commercial MBRs in operation worldwide with many more proposed or currently under construction (Stephenson et al., 2000).

There are two kinds of MCASP, with external membrane filtration and with internal membrane filtration. Japan has 66% of the world's processes. Approximately 55% of these commercial systems have an internal submerged membrane and the reminder have external membrane filtration.

MBR has been gaining a lot of attentions in wastewater treatment for better effluent quality and lower sludge production comparing to CAS. Many researchers report successful performance of MBR with different kinds of wastewater. However, only a few attempts to develop mathematical models for MBR have been made. Some studies on modeling will be reported in this part.

Chaize and Huyard (1991) studied MBR with an increase of biomass concentration in the aeration tank. It makes possible a low food to microorganism ratio and a reduction in sludge production. Two modeling approaches were tested, maintenance phenomena and single sludge simulation process. Both failed in predictions of organic and nitrogen removal.

Canales et al. (1994) showed that when SRT decreased, the biomass viability and the substrate to biomass conversion yield factor (Y) increased. By obtaining a high active biomass concentration, the MBR allowed treatment of synthetic wastewater loads up to 20 kg COD m^{-3} d^{-1} with a COD removal of about 95%.

Wisnieswsli et al. (1999) studied the kinetics of organic carbon removal by a mixed culture in a MBR. They found that $[(S_0 - S_e)/\theta_d - EX_V]Y = dX_V/dt$, in which the value of E (quantity of substrate eliminated per unit of biomass in view of ensuring maintenance) and Y measured for total cell recycling experiments and for experiments with various SRT remained constant and were found to equal 0.04 mg VSS /mg CODh^{-1} and 0.36 mg VSS/mg COD, respectively. Determining these two processes made it possible to anticipate the optimal biomass concentration for defined removal efficiency under different steady state conditions.

Ghyoot and Verstraete (2000) compared the performance of different two-stage systems for the treatment of synthetic wastewater. The first stage was a completely mixed reactor without sludge retention for the simulation of dispersed bacteria growth. The second stage was an activated sludge system in which growth of protozoa and metazoa was simulated. Solid- liquid separation was done by sedimentation (CAS) or submerged membrane bioreactor (SMBR). Good COD removal was obtained with both configurations. In the CAS configuration, excessive growth of filaments and flagellates in the first and second stage sometimes resulted in bulking sludge and erratic increase of suspended solids in the effluent. The MBR system yielded an effluent free of suspended solids. The sludge yield of the two-stage MBR system was 20-30% lower than that of the two-stage CAS system for similar conditions of solids retention time and organic loading rate. This was due to an increased quantity of predators in the two-stage MBR. In summary they found aerobic wastewater treatment with the two-stage membrane-assisted bioreactor resulted in a low sludge production and a stable effluent quality.

Gehther and Jobst (2002) studied mathematical modeling of a continuous aerobic MBR for the treatment of different kinds of wastewater. As a first step, the process was balanced by developing a black box model. As a second step, two shortcut models of different complexity were successively developed. The basic shortcut model predicts TOC degradation as well sludge production by applying Monod kinetics for biological growth. The next shortcut model additionally considered an inhibition of biological growth due to insufficient oxygen supply. Practically, the enhancement resulted in an additional inhibition term in the growth kinetics as well as transport expression for oxygen passed from gas into liquid. Both models showed a reasonable agreement to data obtained from experiments. With insufficient oxygen supply, the agreement of the enhanced model with data was better than with the basic shortcut model.

Lee et al. (2002) have developed a mathematical model for (SMBR) combining ASM1 with a membrane fouling model. The ASM1 was modified to take into account biological characteristics of the SMBR process and the resistance-in-series model was integrated into the modified ASM1 to describe membrane fouling. They found that the non-biodegradable soluble microbial products (SMP) from cell lysis become a portion of the inert COD in the effluent. The SMP plays an important role with respect to effluent quality as well as membrane fouling.

Lu et al. (2002) used an approach similar to Lee et al. (2002) but they used ASM3 instead of ASM1. By incorporating the SMP concept into ASM3, the model could provide a more comprehensive image for the biological wastewater treatment process and therefore make it a more reasonable tool for practical engineering.

2.6 Summary

In this chapter, some of the mathematical models for activated sludge systems were studied. Early models included gross organic removal. Through the years, substrate and biomass were classified in more detail. Nitrogen removal in the '80s and phosphorus removal in the '90s were added to the models. All mathematical models are based on writing mass balances for different components. They have different substrate removal rate expressions and different classification of division of substrate and biomass.

In developing models, it must be realized that they are evolutionary in nature and subject to change as more knowledge is gained about the process. A model that is quite adequate as a first approximation might be replaced later by a more exact model with better estimates of the coefficients, fewer empirical relationships, and inclusion of more variables.

Chapter 3

Experimental Approach

3.1 General

To carry out the objectives of this study, laboratory scale experiments were designed to treat a synthetic wastewater in a completely mixed reactor using the activated sludge process. This chapter describes the material and the test methods used in this experimental work.

3.2 Experimental Set Up

The experimental set up is shown in Fig. 3.1. The heart of the system is a porous pot membrane reactor where the biological treatment is accomplished. Air is supplied to the porous pot by a diffuser placed at the bottom of the reactor, a second diffuser was sometimes added if necessary to keep solids in suspension and provide additional air. Synthetic waste was pumped from a storage container equipped with a mixer to the porous pot through suitable tubing; the effluent passes through a tube into a container for collection. Flow through the system was by gravity.

The porous pot is shown in Fig. 3.2 in detail. Some photos of this pot and its outer shell are presented in Fig. 3.3. The pot is constructed from sheets of porous polythene with 2 mm thickness and maximum pore size of 96 μm, which is made into 14 cm diameter cylinders with a conical base, sloped at an angle of 45°. The porous pot is contained in an impervious PVC vessel 15 cm in diameter with an outlet at a height of 17.2 cm on the cylindrical part, which determines the working volume of 3 L in the porous pot. There is a PVC supporting ring around the top of the porous pot, so that there is an effluent space of 0.5 cm between the inner and outer vessels. This apparatus is made by Bird and Tole Ltd.

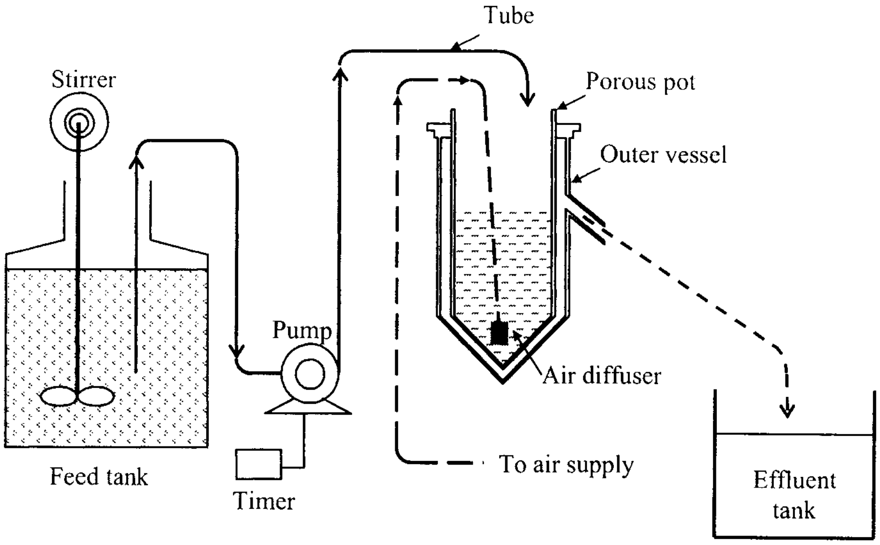


Fig. 3.1 Experimental Set up

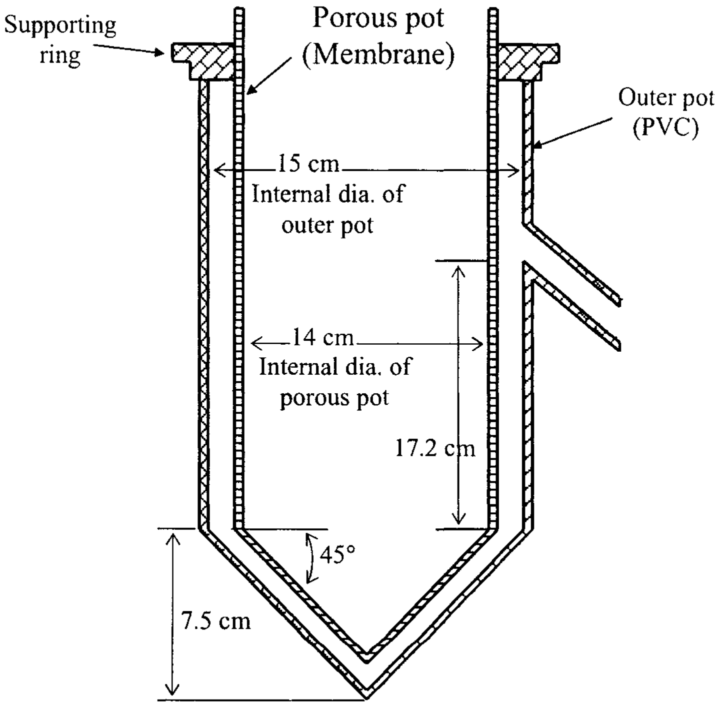
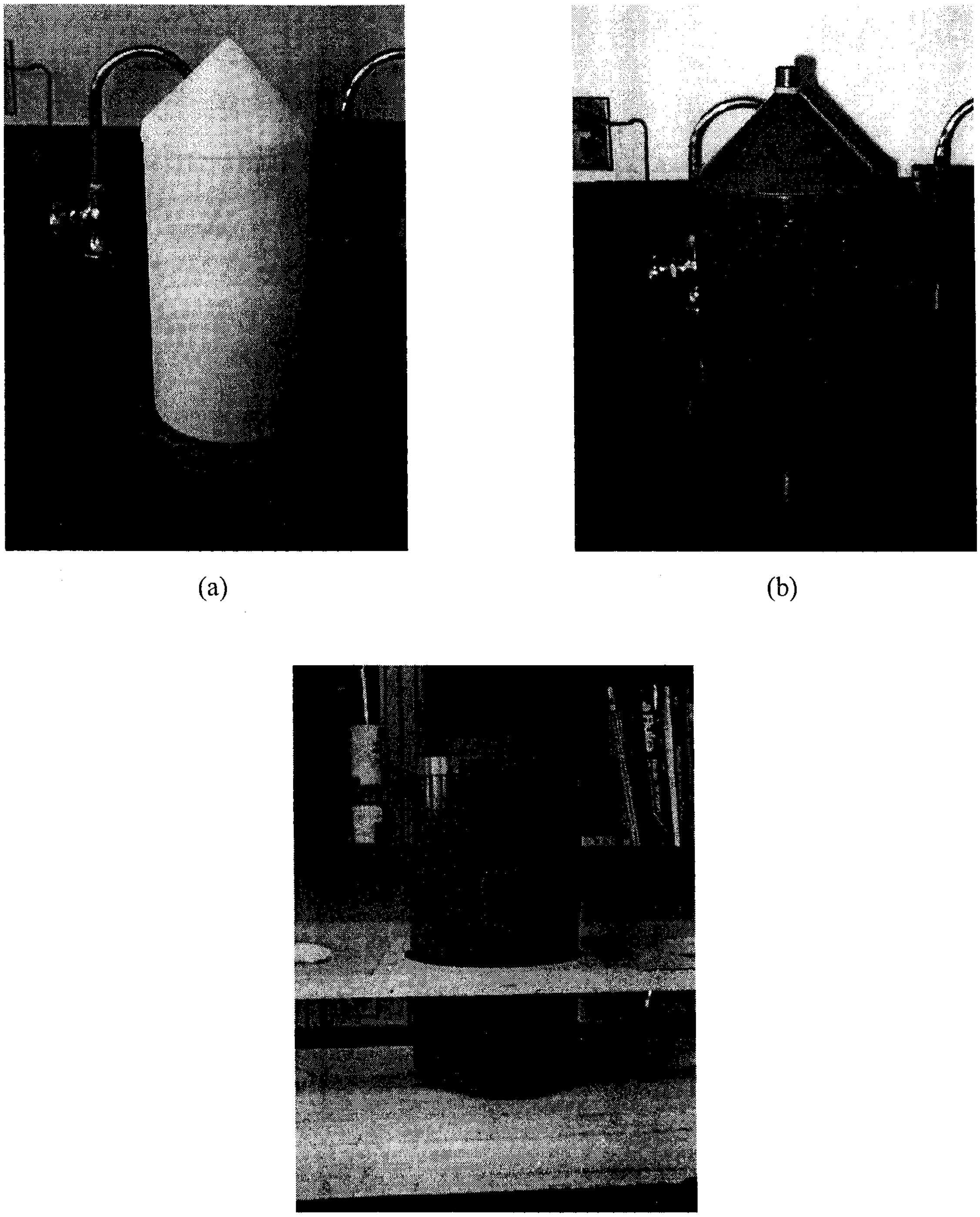


Fig. 3.2 Details of a 3 Litre Porous-Pot Aeration Vessel



(a)

(b)

(c)

Fig. 3.3 (a) Porous Pot, (b) Outer Shell, (c) Assembly of the Reactor

3.3 General Conditions

The standard approach to biological treatment kinetic studies, commonly evaluates system performance at three sludge ages and three detention times for each sludge age, with an identical feed concentration. The planned operational conditions are summarized in Table 3.1.

Table 3.1 Planned Operational Conditions

Condition	Units	1	2	3	4	5	6	7	8	9
HRT	Hours	6	6	6	12	12	12	1	1	1
SRT	Days	1	6	15	1	6	15	1	6	15

The systems could not work under HRT of 1 hour because the character of the sludge caused clogging and overflow of the porous pot. Different operating conditions including HRTs of 2 and 3 hours were used but these HRTs also resulted in reactor failure because of clogging and foaming problems. Aluminium sulphate was added to the system but it failed to improve the settling and resolving the clogging problem. The minimum HRT that the system could tolerate was 4 hours. A CAS system (Fig. 3.4) with separate aeration basin and clarifier was set up for low HRT conditions. This system also failed because of poor settling of the sludge. The biomass washed out of the system and there was little biomass in the system after two days. Therefore, again the original system setup was used and HRT of 4 hours and SRT of 2 days were selected for all originally planned runs with an HRT of 1 hour. The system with HRT of 12 hours and SRT of 15 days failed also, because of clogging and washout of biomass from the reactor. The biomass in the effluent was more than the amount that the system could tolerate to maintain an SRT of 15 days (Fig. 3.5c). In this figure, the turbid portion on top of the sludge is due to the biomass particles that were small. It was found that in this case, the operational SRT was about 7 days instead of 15 days. This operational condition did not reach steady state even after a few weeks. Finally, six runs were able to be performed as presented in Table 3.2.

Table 3.2 Experimental Operational Conditions

Condition	Units	Run					
		1	2	3	4	5	6
HRT	Hours	6	6	6	12	12	4
SRT	Days	1	6	15	1	6	2

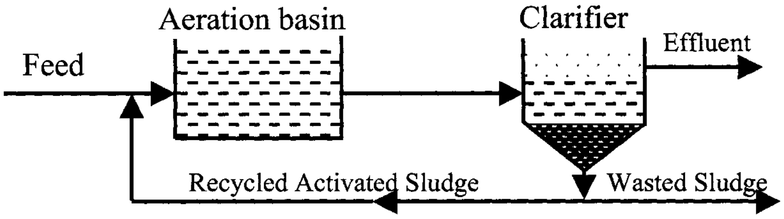
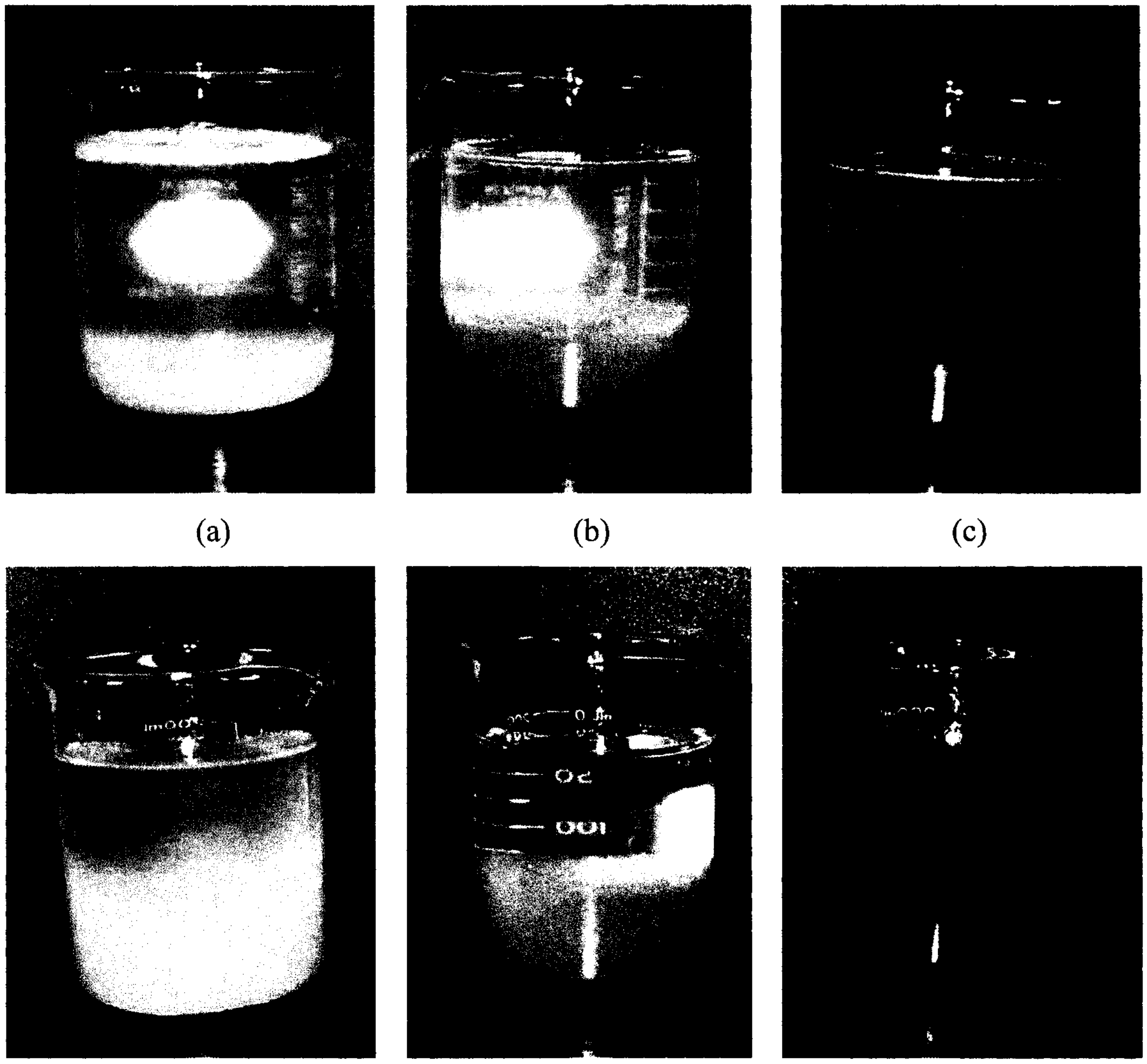


Fig.3.4 CAS System


(a) (b) (c)

(d) (e) (f)

Fig.3.5 Biomass Appearance

(a) HRT = 12 h, SRT = 1 d; (b) HRT = 12 h, SRT = 6 d;

(c) HRT = 12 h, SRT = 15 d; (d) HRT = 6 h, SRT = 1 d;

(e) HRT = 6 h, SRT = 6 d and (f) HRT = 6 h, SRT = 15 d

The sludge ages of the system were maintained at 1, 2, 6, and 15 days by daily withdrawal of a predetermined volume of mixed liquor from each reactor. The volume to be removed was calculated according to Eq. 2.15. The flow rate was calculated from Eq. 2.16 for different HRTs. Sludge was removed from the system every day between 8:00 A.M. and 10:00 A.M. At sludge withdrawal time, VSS analysis results were not available, thus sludge was removed based on the last day's data; this results in the SRT not being exactly 1, 2, 6, or 15 days.

A sample calculation of the amount of sludge wastage from the system is as follows. The following values were taken for December 5, 2001: $X_V = 4680$ mg/L, $X_{Ve} = 8$ mg/L, $Q = 11.77$ L/d and $\theta_X = 6.0$ d. It was required to calculate the amount of sludge to be removed from the system to obtain an SRT of 6 days on the following day. At the beginning of the day, the only known parameter is the flow rate $Q = 11.75$ L/d. Based on data from last day one can obtain the sludge volume to be wasted on December 6, 2001 as

$$Q_W = \frac{X_V V - Q X_{Ve} \theta_X}{X_V \theta_X} = \frac{4680 \times 3 - 11.77 \times 8 \times 6.0}{4680 \times 6.0} = 0.479 \text{ L}$$

By the end of the day the reactor and effluent VSS concentrations were measured as $X_V = 4540$ mg/L and $X_{Ve} = 4$ mg/L, respectively, therefore the SRT on Dec 6 is calculated as follows. Note that this value is slightly different from the theoretical value of 6.0.

$$\theta_X = \frac{X_V V}{X_{Ve} Q + X_V Q_W} = \frac{4540 \times 3.0}{4 \times 11.75 + 4540 \times 0.479} = 6.13 \text{ d}$$

The pump that was available in the lab is designed for higher flow rates; thus, a timer was used to control the flow rate for low HRTs.

3.4 Feed Solution

The feed solution was a synthetic wastewater. It was made of Enfalac^{TM} (infant formula) and tap water. Table 3.3 shows the composition of the formula and Table 3.4 includes some characteristics of the feed.

Table 3.3 Composition of the Iron Fortified Infant Formula

*Iron Fortified Enfalac™	Units	Per 100 g	Normal Dilution (100 mL)**
Protein	g	11.2	1.43
Carbohydrate	g	54	6.9
Fat	g	29.4	3.8
Linoleic Acid	g	4.76	0.61
Linolenic Acid	g	0.5	0.06
Ash	g	2.3	0.3
Energy	Kcal	525	67
	KJ	2194	281
Vitamin A	I.U.	1560	200
Vitamin D	I.U.	312	40
Vitamin E	I.U.	7.8	1.0
Vitamin C	mg	43	5.5
Vitamin B_1	mg	0.39	0.05
Vitamin B_2	mg	0.47	0.06
Niacin	mg	6.2	0.8
Vitamin B_6	mg	0.31	0.04
Folic Acid	mg	0.039	0.005
d-Pantothenic acid	mg	2.3	0.3
Vitamin B_{12}	mcg	1.2	0.15
Vitamin K	mg	0.055	0.007
Biotin	mg	0.012	0.002
Sodium	mg	125	16
Potassium	mg	540	69
Chloride	mg	330	42
Calcium	mg	350	45
Phosphorus	mg	233	30
Magnesium	mg	35	4.5
Iron	mg	5.5	0.7
Iodine	mg	0.035	0.004
Copper	mg	0.32	0.04
Zinc	mg	3	0.4
Manganese	mg	0.027	0.003
Choline	mg	63	8.1
Taurine	mg	31	4.0
Nucleotides	mg	22	2.8

*) Mead Johnson Nutritionals™
**) 17 g formula in 120 mL water

Ingredients: lactose, skim milk powder, palm olein oil, whey protein concentrate, soy oil, coconut oil, sunflower oil, corn syrup solids, maltodextrin, taurine, choline chloride, ascorbyl palmitate, cytidine-5'-monophosphate, disodium guanosine 5'monophosphate, disodium uridine 5'-monophosphate, adenosine 5'-monophosphate,

Minerals: calcium chloride, calcium hydroxide, cupric sulfate, ferrous sulfate, magnesium chloride, manganese sulfate, potassium bicarbonate, potassium citrate, sodium iodide, sodium citrate and zinc sulfate

Table 3.4 Feed Characteristics (Duguay, 2003)

(Average Un-supplemented 1000 mg CODt /L Fortified Iron Enfalac™)

Parameter	Units	Average	STD (±)	Range	V (mL)
COD Total	mg/L	‡ 1 059	‡ 65	‡ (994 & 1 125)	5
Soluble (centrifuged)	mg/L	‡ 756	‡ 13	‡ (743 & 769)	5
BOD_5	mg/L	‡ 665	‡ 5	‡ (660 & 670)	0.5, 1, 2; 3, 6, 10
pH	-	6.2	0.2	(6.0 – 6.4)	50
Total Alkalinity, as $CaCO_3$	mg/L	29.5	1.5	(28.0 & 31.0)	50
Total VFA (0.6g $NaHCO_3$/L)	mg/L	0.937 (AA) + 1.522 (Pr) = 2.459	NA	NA	0.5
TSS	mg/L	123	3	(120 & 126)	100
VSS	mg/L	112	9	(104 & 121)	100
FSS	mg/L	11	5	(16 & 5)	100
TDS (filtered sample)	mg/L	391	7	(384 & 398)	50
VDS	mg/L	325	5	(320 & 330)	50
FDS	mg/L	66	12	(54 & 78)	50
TS (liquid sample)	mg/L	759	2	(757 & 761)	100
VS	mg/L	684	3	(682 & 687)	100
FS	mg/L	75	0.5	(74 & 75)	100
TS (powder sample)	%	97.83	0.07	(97.7 & 97.9)	25 (g)
VS	%	97.41	0.01	(97.42 & 97.40)	25 (g)
FS	%	2.59	0.01	(2.58 & 2.60)	25 (g)
PO_4^{3-}–P Total	mg/L	2.74	0.68	(2.02 – 3.46)	50
Dissolved	mg/L	0.73	0.22	(0.51 & 0.94)	50
TKN–N	mg/L	~18.5 if 100% recovery (13.91 @75%)	0.41	(13.5 & 14.31)	50
org. N	mg/L	~14.7 if 100% recovery (10.31 @70%)	0.30	(10.00 & 10.61)	50
NH_3–N (4500-NH_3 B. & C.)	mg/L	~3.2 if 100% recovery (2.69 @82%)	0.60	(2.09 & 3.28)	25
Electrodes:		(Direct); Low-Level Method			
***NH_3** (feed sample)	mg/L	(0.045); < 0.017 or < 9.8×10^{-7} M	□NA	(NA)	50
***NH_3–N**	mg/L	(0.037); < 0.014 or < 9.8×10^{-7} M	□NA	(NA)	50
***NH_3** (*tap water*)	mg/L	(«10^{-8} M); « 0.017 or « 9.8×10^{-7} M	□NA	(NA)	50
***NH_3–N**	mg/L	(«10^{-8} M); « 0.014 or « 9.8×10^{-7} M	□NA	(NA)	50
***NH_3** (*distilled water*)	mg/L	(« 10^{-8} M); « 0.017 or « 9.8×10^{-7} M	□NA	(NA)	50
***NH_3–N**	mg/L	(< 10^{-8} M); < 0.014 or < 9.8×10^{-7} M	□NA	(NA)	50
§*NO_3 (feed sample)	mg/L	(3.85), 2.37	□0.06	(2.31; 2.43)	25 & 50
***NO_3–N**	mg/L	(0.87), 0.54	□0.02	(0.52; 0.55)	25 & 50
§*NO_3 (*tap water*)	mg/L	(2.44), 1.96	□0.07	(2.03; 1.88)	25 & 50
***NO_3–N**	mg/L	(0.55), 0.44	□0.02	(0.46; 0.42)	25 & 50
§*NO_3 (*distilled water*)	mg/L	(1.54), < 0.062 (< 10^{-6} M)	□(NA)	(NA)	25 & 50
***NO_3–N**	mg/L	(0.35), < 0.014 (< 10^{-6} M)	□(NA)	(NA)	25 & 50
COD: N: P Ratio		1 059: 19.1: 2.74 or ~106: ~2: ~0.3			

§ Boric Acid Preservation Solution added (no Interference Suppressor); ‡Dilution duplicates; NA – Not Applicable;

□ Ranges and STDs between *Excel* and *MATLAB* results (for Low-Level trials only); AA-Acetic acid; Pr-Propionic acid

* Test Limits for Direct Measurement Method:

For NH_3 (1 M to 5 x 10^{-7} M or 0.01 - 17 000 ppm NH_3 (0.01 - 14 000 ppm NH_3-N));

For NO_3 (1 M to 7 x 10^{-6} M or 0.4 - 62 000 ppm NO_3 (0.1 - 14 000 ppm NO_3-N));

* Low-Level Method:

For NH_3 (for < 4 x 10^{-6} M or 0.07 ppm NH_3 (0.06 ppm as NH_3-N));

For NO_3 (for < 10^{-4} M or 6.2 ppm NO_3 (1.4 ppm as NO_3-N))

The goal was to use wastewater with a total COD of about 700 mg/L. It was found that 500 mg of Enfalac™ powder per litre of tap water yields an average total COD of 700 mg/L. This feed strength can be categorized between medium and strong untreated domestic wastewater (Metcalf and Eddy, 2003). The feed mixture was always prepared with this amount of Enfalac™ powder per litre of tap water.

The major nutrient requirements are nitrogen and phosphorus. A typical formula for sludge is $C_5H_7NO_2P_{0.074}$. Based on that composition a suitable ratio of COD: N: P is 98.78: 5: 0.82 that usually is taken as 100:5:1.

Nitrogen is the sum of organic-N, NH_3-N, NO_3^--N and NO_2^--N. NO_2^--N was found to be negligible for the feed. TKN is approximately equal to organic-N plus NH_3-N (APHA, 1992). They were measured in the lab and total N of feed was found to be 13.1 mg N/L. The total phosphorus was found to be 1.7 mg P/L. Thus preliminary Enfalac ™ feed characterization results in the experimental ratio of COD: N: P of 700:13.1:1.7 or 100:1.87:0.24. Nutrients were added to the feed solution, ammonium chloride as the nitrogen source and di-potassium hydrogen orthophosphate as the phosphorus source to meet the optimal ratio of 100:5:1 (Droste, 1997).

Nitrogen supplement

$$N = 7 \times (5 - 1.87) = 21.91 \text{ mg N/L}$$

$$NH_4Cl = \frac{21.91 \text{ mg N/L} \times 53.49 \text{ g } NH_4Cl\text{/mol}}{14.007 \text{ g N/mol}} = 83.7 \text{ mg/L}$$

Phosphorus supplement

$$P = 7 \times (1 - 0.24) = 5.32 \text{ mg P/L}$$

$$K_2HPO_4 = \frac{5.32 \text{ mg P/L} \times 174.18 \text{ g } K_2HPO_4\text{/mol}}{30.974 \text{ g P/mol}} = 29.9 \text{ mg/L}$$

Thus, 100 mg N/L and 30 mg P/L were added to the feed solution. Approximately 250 mg/L of sodium hydroxide was also added to the feed to neutralize the pH of the system. Feed was prepared every day and it was stored in the lab at room temperature (20 ± 2 °C).

3.5 *Activated Sludge*

Biomass was obtained from the Robert O. Pickard Environmental Centre (ROPEC) wastewater treatment facility in Ottawa. This sludge was recycled activated sludge (RAS) that was ready to send to the aeration basin. Its concentration of TSS and VSS were 1550 mg/L and 1230 mg/L, respectively.

3.6 Cleaning the Porous Pot

The recommended method by Bird & Tole (2001) for cleaning the porous pot is:

- Transfer the activated sludge to a new porous pot
- Wash the fouled pot with water
- Immerse the pot in 50% sodium hypochlorite solution for 24 hours
- Soak the pot in water to remove all traces of hypochlorite

Instead of 50% sodium hypochlorite solution, commercial bleach with 3-5% sodium hypochlorite was used; therefore, the pot was immersed in it for a few days.

At the beginning of each run (acclimation phase) the pot was cleaned usually twice a day but after a few days operation, cleaning was not needed. Under normal condition, the pot could work two or three weeks without clogging.

3.7 Analytical Methods

A summary of all parameters monitored for influent feed, effluent, and contents of reactor during operation is illustrated in Table 3.5. The volumes of all samples taken were kept to a minimum to cause as little disturbance as possible to the reactor contents.

Dissolved Oxygen (DO) and pH were measured and controlled every day. Total COD, soluble COD, TSS and VSS were measured 3 or 4 times a week, until steady state occurred. When soluble COD and VSS were constant within 10% fluctuation for a few days the system was considered in steady state and in this situation, all of the parameters were measured three times.

For measuring total Kjeldahl nitrogen (TKN), samples were kept in a refrigerator and after five samples were collected, they were sent for analysis to the outside firm of ACCUTEST Lab. A few drops of sulphuric acid were added to each bottle for preservation immediately after a sample was taken.

Table 3.5 Analytical Techniques

Parameter	Method*	Specific Apparatus	V (mL)
pH	4500-H^+ B. Electrometric	Fisher Accument ® Model925 pH-ion Meter and Fisher Scientific Flexa-Mix magnetic stirrer	20-50
DO &Temp.	4500-OG. Membrane Electrode	ORION Model 860 DO meter and probe	NA
Temp.	2550 B.2.laboratory	Mercury-filled Celsius thermometer	NA
COD_t	5220C.Titrimetric Closed Reflux	Blue M Electric Company Stable-Therm Gravity 150°C oven, COD digestion tubes	5 (diluted)
COD_S	5220 B. 4.b.low-Level	Same as COD total plus 1.2μm GF/C glass filters and filtration apparatus	5 (diluted)
ALK	2320 B. Titration	Fisher Accument ® Model925 pH/ion Meter and Fisher Scientific Flexa-Mix magnetic stirrer	20
BOD_5	5210 B. 5-Day BOD Test and 4500-O G. Membrane Electrode	Drummond Scientific pipet-aid®, 300ml BOD bottles, VWR Scientific Model 2020 incubator, ORION Model 860 DO Meter and Electrode (overflow funnel, fixing ring, rotor stirring accessory), Fisher Scientific Flexa-Mix magnetic stirrer	3,5,...
TSS	2540 D. Total Suspended Solids Dried at (103-105°C)	1.2μm GF/C glass filters, filtration apparatus, aluminium dishes,103°C Fisher Isotemp® drying oven desiccators, Saturation analytical scale (0.1mg)	5-400
VSS	2540 E. Fixed and Volatile Solids Ignited at (500°C)	Same as TSS except Model 186A 550°C Fisher Scientific Isotemp® muffle furnace	5-400
TKN		ACCUTEST Lab.	
NH_3	4500-NH_3 F. Ammonia-Selective Electrode by Direct Calibration and Low-Level	ORION Model 95-12 Ammonia Electrode, Fisher Accument Model 750 pH/Ion Meter, American Dade Tek-pro® Tek-Stir® magnetic Stirrer	100
NO_3^-	4500-NO_3 D.Nitrate Electrode by Direct Measurement and Low-Level	Same as NH_3, except for ORION Model 93-07 Nitrate Electrode, ORION Model 90-02 Double Junction Reference Electrode	100
Org. P	4500-P	Bausch & Lomb, Spectronic-70, Market Forge, autoclave	50 (diluted)
PO_4^{3-}	4500-P	Bausch & Lomb, Spectronic-70	
Flow Rates	Volumetric Graduation	Graduated cylinders	

* Method numbers are those in *APHA (1992)*

Chapter 4

Modeling: Part I

4.1 General

In this chapter, a few models are applied to the system. These are the Lawrence and McCarty model (1970), the Goodman and Englande model (1974) and the ASM1 (1986).

4.2 The Idealized System

A schematic of the system under investigation is shown in Fig. 4.1.

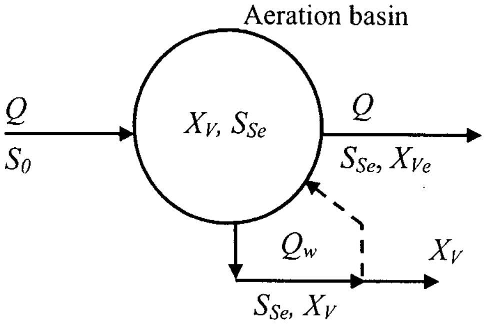


Fig. 4.1 The System under Investigation

In this system, the biomass is wasted with the flow rate Q_w. Solids were removed from the reactor by drawing a set volume each day. The volume of liquid removed was replaced in the reactor with clarified effluent. Therefore, the amount of soluble substrate remains unchanged during biomass wastage.

4.3 Data Fitting

4.3.1 Raw Data

The raw data of all experiments related to different working conditions are presented in Appendix A. The average steady state data from six experimental runs are summarized in

Table 4.1. This table includes total and soluble influent and effluent COD in addition to biomass concentration in the reactor, necessary for modeling the carbon cycle in the system. The value of X_V based on COD is 1.42 times of X_V based on VSS (Grady et. al., 1992).

Table 4.1 Summary of Experimental Runs (Carbon)

RUN	θ_X	θ_d	S_0	S_{S0}	X_{S0}	S_e	S_{Se}	X_V	X_{Ve}	X_V
	Day	Hour	mg /L*	mg/L*	mg/L*	mg/L*	mg/L*	mg/L**	mg/L**	mg/L*
1	1.0	6.2	653	390	263	105	48	1107	13.0	1571
2	6.1	6.1	711	413	298	47	39	4270	6.0	6063
3	15.6	6.2	653	390	263	31	22	8250	0.7	11715
4	1.0	12.8	733	418	315	65	44	573	16.0	814
5	5.9	12.5	733	418	315	36	31	2190	10.3	3110
6	2.2	4.0	702	464	238	127	46	2702	54.7	3836

* mg COD/L ** mg VSS/L

Other data needed for modeling nitrogen cycle are presented in Table 4.2. This table includes values of nitrate and nitrite S_{NO}, ammonia and ammonium S_{NH}, and organic nitrogen (ON) in the influent and the effluent. Standard deviations of data in Table 4.1 and Table 4.2 are presented in appendix A. SRT was based on the solids removed in the waste flow Q_W and solids in the effluent.

Table 4.2 Summary of Experimental Runs (Nitrogen)

RUN	S_{NH0}	S_{NH}	S_{NO0}	S_{NO}	ON_0	ON
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	29.5	0.7	11.3	3.8	0.3	1.5
2	25.0	0.3	9.8	63.9	0.4	1.8
3	29.5	2.5	11.3	93.0	0.3	1.9
4	27.5	2.9	16.7	6.0	4.2	4.8
5	27.5	1.8	16.7	52.3	4.2	2.3
6	28.8	3.9	19.7	37.7	2.6	6.0

4.3.2 Grid Search

All the models include parameters that must be evaluated simultaneously to obtain a suitable model. A statistical regression is required to find these parameters. If the number of parameters is two, a linear regression will be sufficient, but in most of the models there are more than two parameters involved. This indicates the necessity of multi-variable regression or a method such as a grid search. The grid search method was chosen because of its relative simplicity.

The grid search method is very sensitive to initial boundaries, so the boundaries have usually been chosen according to the literature.

4.3.3 Numerical Criteria

It is necessary to define reliable statistical criteria for comparing competing models. One criterion that commonly is used to illustrate the adequacy of a fitted regression model is the coefficient of determination or R^2. It is

$$R^2 = 1 - \frac{\mathrm{SSE}}{\mathrm{SST}} = 1 - \frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \tag{4.1}$$

Where, SSE and SST are the sum of squares of errors and data, respectively. y_i, $\bar{y}$ and $\hat{y}_i$ are data, data mean and the predicted value, respectively.

The coefficient of determination can be used to give an indication whether or not the model is an adequate explanation of the true situation. The value of unity indicates an exact model and a zero value is an indication of an inadequate model. Negative values show that the behaviour of data and model or the variation ranges of them are different. This may easily happen when the data range is very small.

Another good numerical criterion is the square root of sum of squares of residual errors or ε criterion. It is

$$\varepsilon = \sqrt{\sum_{i=1}^{n}\left(\frac{y_i - \hat{y}_i}{y_i}\right)^2} \tag{4.2}$$

In this research, the R^2 criterion has been widely used because its values for different components can be compared together. However when data values are very small, finding a model with positive R^2 can be difficult or even impossible. In these cases the ε criterion has been used instead.

4.4 Lawrence and McCarty Model

To model the system, either total or soluble COD must be chosen. Since the Lawrence and McCarty model (1974) does not distinguish between different kinds of substrates, total influent COD is used, because all COD entering the system must be treated whether it is soluble or not. All particulate matter was based on mg VSS/L and substrate on mg COD/L in this model.

4.4.1 Biomass Growth (X_V)

The feed was prepared from dehydrated media; therefore, it is assumed that no biomass exists in the influent. Therefore the mass balance relationship for the system biomass is

$$-QX_{Ve} - Q_w X_V + r_X V = V\frac{dX_V}{dt} \tag{4.3}$$

The biomass growth rate and the substrate removal rate are defined as $r_X = -Yr_S - k_e X_V$ and $r_S = (S_0 - S_{Se})/\theta_d$, respectively. The substrate removal rate is derived from the physical condition of the process not the mathematical definition of the model. Under steady state condition $dX_V/dt = 0$ therefore Eq. 4.3 results in

$$X_V = \frac{Y\ (S_0 - S_{Se})}{1 + k_e\theta_X}.\frac{\theta_X}{\theta_d} \tag{4.4}$$

Equation 4.4 includes only two parameters k_e and Y, thus a linear regression is performed to estimate them. By rearranging Eq. 4.4 one can obtain $\theta_X^{-1} = UY - k_e$ where $U = (S_0 - S_{Se})/(X_V\theta_d)$. Interchanging θ_X^{-1} with y and U with x, transforms the equation into a linear relation, $y = ax + b$. In this relation a and b indicate the values of Y and $-k_e$, respectively.

Linear regression for biomass growth according to the Lawrence and McCarty model based on total influent substrate is shown in Fig. 4.2.

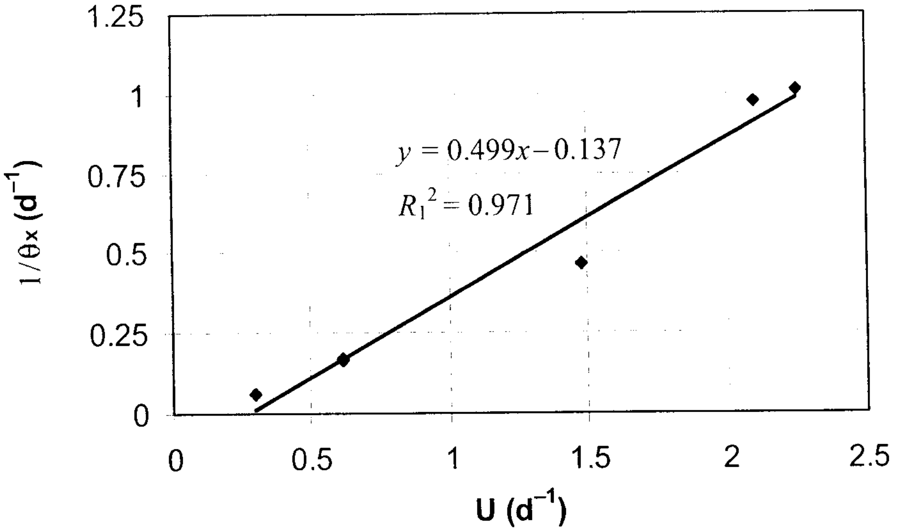


Fig. 4.2 Linear Regression for the Lawrence and McCarty Model, Biomass Growth

This figure shows that parameters of the model are Y= 0.499 mg VSS/mg COD and $k_e = 0.137$ d^{-1}. By substituting these two parameters in Eq. 4.4, the model yields X_V equal to 1045, 4343, 6076, 562, 2202 and 3310 mg VSS/L for the runs, respectively. In this model, R^2 is 0.879 from Eq. 4.1, which is less than the value in Fig. 4.2 (R_1^2) from the Excel program calculation. This is because U is a composite number that imposes additional errors into the calculation. For this reason and the relative simplicity of this particular model, the grid search was performed in detail. The concept of a grid search is the same when more than two parameters are involved, but it is not easily illustrated in table format.

According to the literature, Y is assumed to be between 0.20 and 0.70 mg VSS/mg COD and k_e were assumed between 0 and 0.30 d^{-1}, in the first step. These two intervals are sub-divided into ten divisions. The coefficient of determination for each pair of parameters is calculated. All calculated values are shown in Table 4.3.

The next step is to find which pair gives the highest R^2. The highest R^2 corresponded to $Y = 0.40$ mg VSS/mg COD and $k_e = 0.06$ d^{-1}, although each shaded values can also be a good choice for continuation. Now the grid search technique was applied again around greyed values in Table 4.4 and the results are presented in Table 4.4.

Table 4.3 R^2 Value for Various k_e and Y (Step 1)

K_e Y	0.00	0.03	0.06	0.09	0.12	0.15	0.18	0.21	0.24	0.27	0.30
0.20	0.90	0.62	0.34	0.12	-	-	-	-	-	-	-
0.25	0.94	0.86	0.62	0.39	0.21	0.05	-	-	-	-	-
0.30	0.76	0.98	0.82	0.62	0.43	0.27	0.13	0.02	-	-	-
0.35	0.35	0.97	0.94	0.78	0.62	0.46	0.32	0.20	0.09	-	-
0.40	-	0.85	0.98	0.89	0.76	0.61	0.48	0.36	0.25	0.15	0.06
0.45	-	0.61	0.95	0.95	0.86	0.73	0.61	0.49	0.38	0.28	0.19
0.50	-	0.24	0.84	0.95	0.91	0.82	0.71	0.60	0.50	0.40	0.31
0.65	-	-	0.65	0.90	0.93	0.87	0.79	0.70	0.60	0.51	0.42
0.60	-	-	0.38	0.79	0.90	0.90	0.84	0.76	0.68	0.59	0.51
0.65	-	-	0.04	0.62	0.83	0.88	0.86	0.81	0.74	0.66	0.59
0.70	-	-	-	0.40	0.72	0.84	0.86	0.83	0.78	0.72	0.65

Table 4.4 R^2 for Various k_e and Y (Step 2)

K_e Y	0.030	0.036	0.042	0.048	0.054	0.060	0.066	0.072	0.078	0.084	0.090
0.35	0.978	0.993	0.994	0.984	0.966	0.942	0.915	0.885	0.854	0.821	0.787
0.36	0.963	0.987	0.994	0.990	0.977	0.958	0.934	0.906	0.877	0.846	0.814
0.37	0.943	0.976	0.991	0.993	0.985	0.970	0.949	0.925	0.898	0.869	0.839
0.38	0.919	0.961	0.984	0.992	0.989	0.978	0.962	0.940	0.916	0.889	0.861
0.39	0.889	0.942	0.973	0.988	0.990	0.984	0.971	0.953	0.932	0.907	0.881
0.40	0.855	0.918	0.958	0.979	0.988	0.987	0.978	0.964	0.945	0.923	0.899
0.41	0.816	0.890	0.938	0.968	0.982	0.986	0.982	0.971	0.956	0.937	0.915
0.42	0.772	0.857	0.915	0.952	0.974	0.983	0.983	0.976	0.964	0.948	0.928
0.43	0.723	0.820	0.888	0.933	0.961	0.976	0.981	0.978	0.970	0.956	0.939
0.44	0.669	0.779	0.857	0.910	0.946	0.966	0.976	0.978	0.973	0.963	0.948
0.45	0.611	0.734	0.822	0.884	0.926	0.954	0.969	0.975	0.974	0.967	0.955

The values $Y = 0.36$ mg VSS/mg COD and $K_e = 0.042\ \mathrm{d}^{-1}$ are the result of a grid search with $R^2 = 0.9944$, indicating a good fit between model and data. This result can be slightly improved by performing the grid search once more.

The comparison of models based on linear regression and the grid search is presented in Fig. 4.3. This figure obviously shows the superiority of the model based on a grid search to the model based on linear regression.

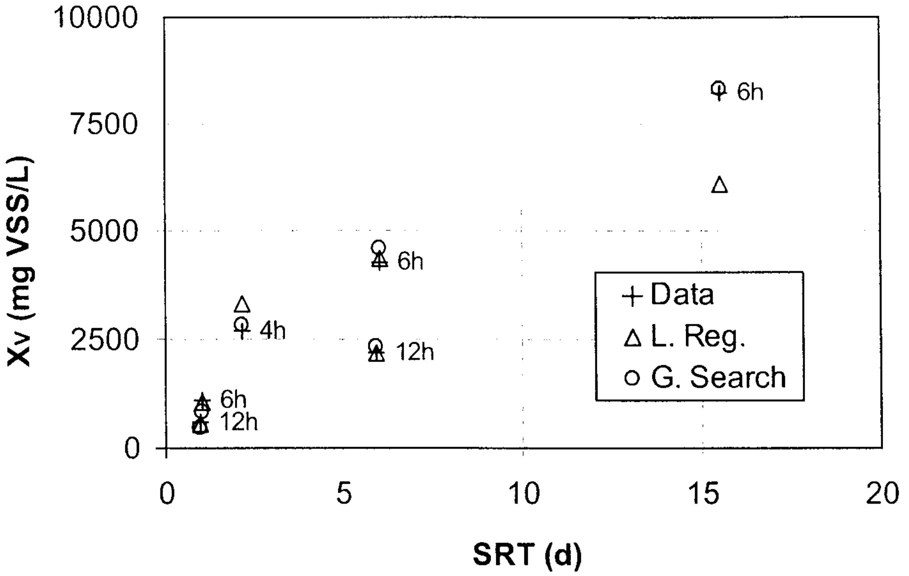


Fig. 4.3 Lawrence and McCarty Model for Biomass Growth

4.4.2 Substrate Removal (S_{Se})

The mass balance relation for substrate in the system is

$$QS_0 - QS_{Se} + r_S V = \frac{dS_{Se}}{dt} V \tag{4.5}$$

In the model, substrate removal rate is defined as $r_S = dS_S/dt = -kS_{Se}X_V/(K_S + S_{Se})$ (Monod, 1949). Substituting this rate into Eq. 4.5 and for a steady state condition $dS_S/dt = 0$ yields

$$S_{Se}^2 + \left(-S_0 + K_S + k\theta_d X_V\right)S_{Se} - K_S S_0 = 0 \tag{4.6}$$

By solving Eq. 4.6, substrate in effluent is found as

$$S_{Se} = \frac{1}{2}\left[-(-S_0 + K_S + k\theta_d X_V) + \sqrt{(-S_0 + K_S + k\theta_d X_V)^2 + 4K_S S_0}\right] \tag{4.7}$$

From the literature the limits for *k* and K_S were selected as 5 to 15 (mg COD/mg VSS) d^{-1}and 50 to 150 mg COD/L, respectively. The result of the grid search is shown in

Table 4.5. Values less than –5.0 are removed. Even the best pair of parameters is far away from a good model. The best R^2 was –2.3.

Table 4.5 R^2 for Various K_S and k (Initial Attempt)

k \ K_S	50	60	70	80	90	100	110	120	130	140	150
5	–4.1	–3.3	–3.0	–3.1	–3.6	–4.5	-	-	-	-	-
6	-	–4.5	–3.6	–3.0	–2.7	–2.6	–2.8	–3.2	–3.8	–4.6	-
7	-	-	–4.9	–4.0	–3.4	–2.9	–2.6	–2.4	–2.4	–2.6	–3.0
8	-	-	-	-	–4.4	–3.7	–3.2	–2.7	–2.5	–2.3	–2.3
9	-	-	-	-	-	–4.6	–4.0	–3.4	–3.0	–2.7	–2.4
10	-	-	-	-	-	-	–4.8	–4.2	–3.7	–3.3	–2.9
11	-	-	-	-	-	-	-	-	–4.5	–4.0	–3.5
12	-	-	-	-	-	-	-	-	-	–4.7	–4.2
13	-	-	-	-	-	-	-	-	-	-	–4.8
14	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-	-

One remedy for this problem is to include a non-biodegradable portion of influent substrate in the formulation. This may solve the problem because Lawrence and McCarty in the derivation of their model assumed that the all influent substrate is involved in the process of biodegradation. This assumption does not cause a large error when there is no inert substrate or effluent COD is relatively high. In the runs conducted in this research, the effluent COD is low and even a small percentage of inert influent organic can cause a large error. Therefore, the substrate removal rate was modified to include a non-biodegradable portion as

$$r_S = \frac{dS_S}{dt} = -\frac{k\left(S_{Se}-S_I\right)X_V}{K_S+\left(S_{Se}-S_I\right)} \tag{4.8}$$

in which:

$S_I = np \times S_0$ = non-biodegradable (inert) organics

np = the inert fraction of influent

Substituting Eq. 4.8 into Eq. 4.5 results in

$$S_{Se}^2 + \left(-S_0 + K_S - S_I + k\theta_d X_V\right)S_{Se} - K_S S_0 + S_0 S_I - kS_I\theta_d = 0 \tag{4.9}$$

By solving Eq. 4.9 effluent substrate is found as

$$S_{Se} = \left(-b + \sqrt{b^2 - 4c}\right)\Big/2 \qquad (4.10)$$

where, $b = -S_0 + K_S - S_I + k\,\theta_d X_V$ and $c = -K_S S_0 + S_0 S_I - kS_I\theta_d$

The fraction of inert substrate must be a small number. As the first trial, this number is assumed to be the lowest ratio of soluble effluent COD to total influent substrate COD. This means that $np = 22/653 = 0.034$. Performing a grid search technique with the same parameter intervals as Table 4.5 yields results shown in Table 4.6. Negative values are not shown.

Table 4.6 R^2 for Various K_S and k (Step 1: np = 3.4%)

K_S / k	50	60	70	80	90	100	110	120	130	140	150
5.0	-	-	-	-	-	-	-	-	-	-	-
6.0	0.47	0.16	-	-	-	-	-	-	-	-	-
7.0	0.54	0.54	0.36	0.01	-	-	-	-	-	-	-
8.0	0.41	0.56	0.58	0.47	0.23	-	-	-	-	-	-
9.0	0.23	0.45	0.57	0.60	0.53	0.37	0.12	-	-	-	-
10.0	0.04	0.30	0.48	0.58	0.61	0.57	0.45	0.27	0.02	-	-
11.0	-	0.14	0.35	0.50	0.59	0.62	0.59	0.51	0.37	0.18	-
12.0	-	-	0.22	0.39	0.52	0.60	0.63	0.61	0.55	0.44	0.29
13.0	-	-	0.08	0.27	0.42	0.53	0.60	0.63	0.62	0.58	0.49
14.0	-	-	-	0.15	0.32	0.45	0.54	0.61	0.64	0.63	0.60
15.0	-	-	-	0.03	0.21	0.35	0.47	0.55	0.61	0.64	0.64

All shaded cells can be selected as good parameter estimations for a more limited grid search. After performing a grid search on all three parameters, the best model that could be found is $np = 0.0391$, $K_S = 85.6$ mg COD/L and $k = 11.35$ (mg COD/mg VSS) d^{-1} that yields R^2 = 0.709. This model predicts effluent substrate values as 45.1, 32.7, 27.8, 49.6, 33.5, and 40.3 mg COD/L for runs 1-6, respectively. The relation is shown in Fig. 4.4. Including a nonbiodegradable component in influent total COD made a significant improvement in estimation of effluent soluble COD.

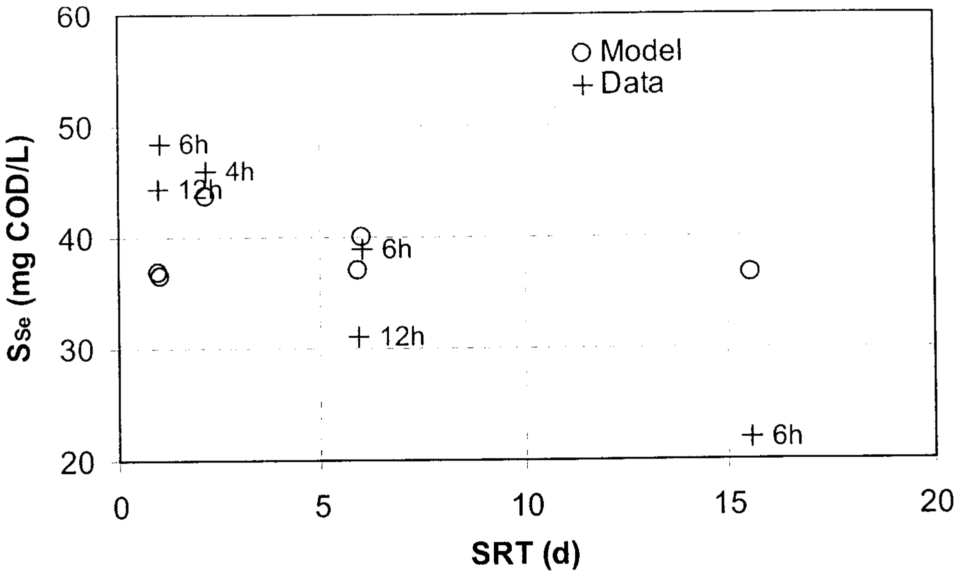


Fig. 4.4 Lawrence and McCarty Model for Substrate Removal

4.5 Goodman and Englande Model

The major difference between this model and Lawrence and McCarty model is the incorporation of an endogenous biomass term. In the Goodman and Englande model, it is assumed that just one portion of biomass is performing biodegradation, which is called active biomass. X_a, X_e and X_V are in mg VSS/L. Substrate terms are in mg COD/L.

4.5.1 Biomass Growth (X_V)

It is assumed that no biomass exists in the influent. Therefore the mass balance relationship for the system biomass is

$$-QX_{ae} - Q_w X_a + r_X V = V\frac{dX_a}{dt} \tag{4.11}$$

in which X_a is the active biomass.

Substituting biomass growth rate $r_X = -Yr_S - k_d X_V$ and substrate removal rate $r_S = (S_0 - S_{Se})/\theta_d$ into Eq. 4.11 and using the steady state condition $dX_a/dt = 0$ results in

$$X_a = \frac{Y\,(S_0 - S_{Se})}{1 + k_d\theta_X}\cdot\frac{\theta_X}{\theta_d} \tag{4.12}$$

This equation is similar to that for total biomass concentration in the Lawrence and McCarty model (Eq. 4.4). Total biomass in the reactor is determined as

$$X_V = \left(1 + f_{nd} k_d \theta_X\right) X_a \tag{4.13}$$

Since there are three parameters in this model, a three-dimensional grid search is required. It is known from the literature that typical values of these parameters are $0.30 \le Y \le 0.60$ mg VSS/mg COD, $0.10 \le k_d \le 0.50$ d^{-1} and f_{nd} is about 0.24. It was decided to perform a grid search with f_{nd} taken as 0.2, 0.25 and 0.30 (Table 4.7 through Table 4.9). Then the results were compared together and the best set was chosen.

Table 4.7 R^2 for Various k_d and Y (f_{nd} = 0.20)

K_d Y	0.10	0.14	0.18	0.22	0.26	0.30	0.34	0.38	0.42	0.46	0.50
0.30	0.802	0.67	0.57	0.48	0.41	0.35	0.29	0.24	0.20	0.17	0.14
0.33	0.89	0.78	0.68	0.60	0.53	0.47	0.41	0.36	0.32	0.29	0.25
0.36	0.95	0.86	0.77	0.70	0.63	0.57	0.52	0.47	0.43	0.40	0.36
0.39	0.98	0.92	0.85	0.78	0.72	0.67	0.62	0.57	0.53	0.50	0.46
0.42	0.99	0.96	0.91	0.85	0.80	0.75	0.70	0.66	0.62	0.59	0.56
0.45	0.97	0.98	0.95	0.91	0.86	0.82	0.78	0.74	0.70	0.67	0.64
0.48	0.92	0.98	0.97	0.94	0.91	0.87	0.84	0.80	0.77	0.74	0.71
0.51	0.85	0.95	0.98	0.97	0.94	0.92	0.89	0.86	0.83	0.80	0.78
0.54	0.75	0.91	0.96	0.97	0.96	0.95	0.93	0.90	0.88	0.85	0.83
0.57	0.62	0.84	0.93	0.96	0.97	0.96	0.95	0.93	0.92	0.90	0.88
0.60	0.47	0.75	0.88	0.94	0.96	0.97	0.97	0.96	0.94	0.93	0.91

Table 4.8 R^2 for Various k_d and Y (f_{nd} = 0.25)

K_d Y	0.10	0.14	0.18	0.22	0.26	0.30	0.34	0.38	0.42	0.46	0.50
0.30	0.84	0.74	0.65	0.58	0.52	0.46	0.42	0.38	0.34	0.31	0.29
0.33	0.92	0.84	0.76	0.69	0.63	0.58	0.54	0.50	0.46	0.43	0.41
0.36	0.97	0.91	0.85	0.79	0.73	0.68	0.64	0.60	0.57	0.54	0.52
0.39	0.99	0.96	0.91	0.86	0.81	0.77	0.73	0.70	0.67	0.64	0.61
0.42	0.98	0.98	0.96	0.92	0.88	0.84	0.81	0.78	0.75	0.72	0.70
0.45	0.94	0.99	0.98	0.96	0.93	0.90	0.87	0.85	0.82	0.80	0.77
0.48	0.87	0.96	0.98	0.98	0.96	0.94	0.92	0.90	0.88	0.86	0.84
0.51	0.78	0.92	0.97	0.98	0.98	0.97	0.96	0.94	0.92	0.91	0.89
0.54	0.65	0.85	0.93	0.97	0.98	0.98	0.98	0.97	0.96	0.94	0.93
0.57	0.50	0.75	0.87	0.94	0.97	0.98	0.98	0.98	0.98	0.97	0.96
0.60	0.31	0.63	0.80	0.88	0.93	0.96	0.98	0.98	0.98	0.98	0.98

Table 4.9 R^2 for Various k_d and Y (f_{nd} = 0.30)

K_d / Y	0.10	0.14	0.18	0.22	0.26	0.30	0.34	0.38	0.42	0.46	0.50
0.30	0.88	0.80	0.73	0.67	0.61	0.57	0.53	0.50	0.47	0.44	0.42
0.33	0.95	0.89	0.83	0.77	0.72	0.68	0.65	0.62	0.59	0.56	0.54
0.36	0.99	0.95	0.90	0.86	0.82	0.78	0.75	0.72	0.69	0.67	0.65
0.39	0.99	0.98	0.95	0.92	0.89	0.86	0.83	0.80	0.78	0.76	0.74
0.42	0.96	0.99	0.98	0.96	0.94	0.92	0.89	0.87	0.85	0.83	0.81
0.45	0.90	0.97	0.99	0.99	0.97	0.96	0.94	0.93	0.91	0.89	0.88
0.48	0.81	0.93	0.97	0.99	0.99	0.98	0.97	0.96	0.95	0.94	0.93
0.51	0.69	0.86	0.93	0.97	0.99	0.99	0.99	0.98	0.98	0.97	0.96
0.54	0.53	0.76	0.87	0.93	0.96	0.98	0.99	0.99	0.99	0.99	0.98
0.57	0.35	0.63	0.78	0.87	0.92	0.95	0.97	0.98	0.99	0.99	0.99
0.60	0.13	0.48	0.67	0.78	0.86	0.90	0.93	0.96	0.97	0.98	0.99

The preceding tables clearly show that 0.30 is the best value of f_{nd} among those that were evaluated. The value of 0.35 was not found to improve the model noticeably. All shaded cells can be selected as a good parameter set. The two underlined values yield the best coefficient of determination and are selected for a more limited grid search. The first set of parameters is $Y = 0.390$ mg VSS/mg COD, $k_d = 0.111$ d^{-1} and $f_{nd} = 0.30$ with $R^2 = 0.9961$. The second set is $Y = 0.561$ mg VSS/mg COD, $k_d = 0.498$ d^{-1} and $f_{nd} = 0.30$ with $R^2 = 0.9963$. The values of R^2 show an improvement, although small, in modeling biomass growth compared to the Lawrence and McCarty model. The predicted value for total biomass and active biomass concentrations are depicted in Fig. 4.5.

A residual error comparison between the Lawrence and McCarty and Goodman and Englande models is shown in Fig. 4.6. Percentage of residuals is calculated by

$$\text{Residual Error (\%)} = \frac{y - \hat{y}}{y} \times 100 \tag{4.14}$$

A specific pattern for residual error indicates that something in the model is missing and model can be improved, while a random pattern shows that model is a good fit. Therefore the random pattern in Fig. 4.6 shows that models are acceptable.

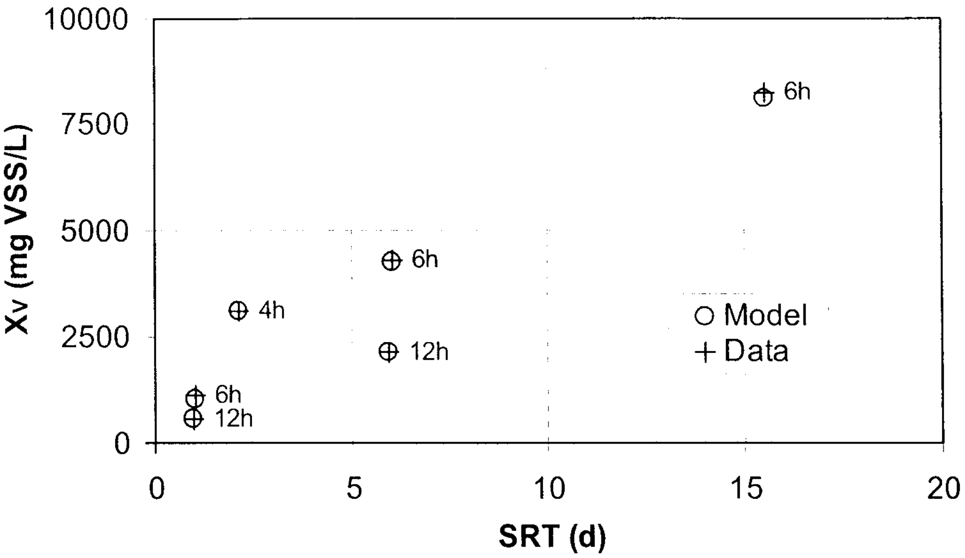


Fig. 4.5 Goodman and England Model for Biomass Growth

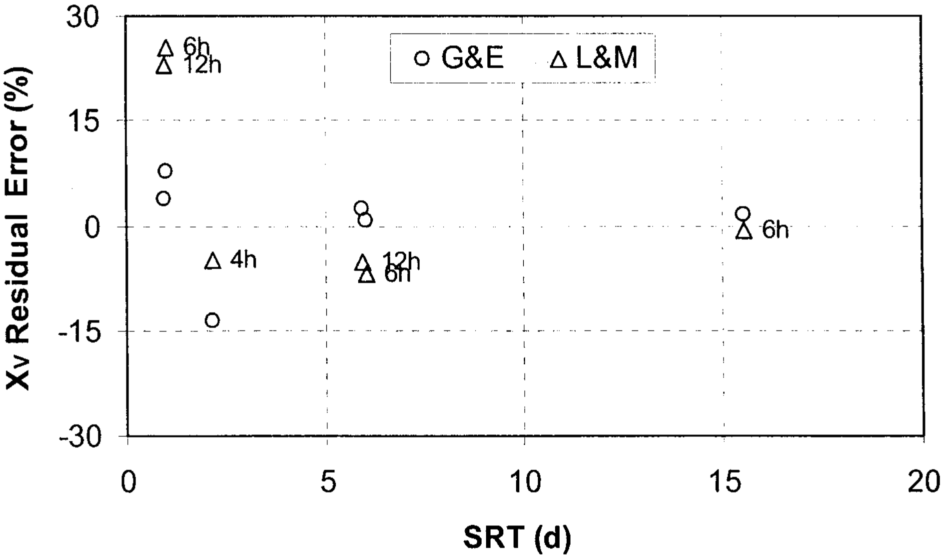


Fig. 4.6 Residual Errors of Biomass Growth Modeling

4.5.2 Substrate Removal (S_{Se})

Goodman and Englande (1974) compared two different substrate removal rate expressions: McKinney's (1962) and Eckenfelder's (1966) equations and they built their model based on the former. McKinney assumed that the substrate removal rate is a first-order function of existing substrate in the system that is $r_S = -K_m S_{Se}$. Eckenfelder proposed a different substrate removal expression by taking into account the existing amount of biomass in the system as well, which is $r_S = -kX_I S_{Se}$. Both expressions will be utilized to find the best model.

It is known that a part of influent substrate is inert; therefore, the substrate removal rate according to the McKinney relation is modified to incorporate an inert fraction.

$$r_S = \frac{dS_S}{dt} = -K_m (S_{Se} - S_I) \tag{4.15}$$

Substituting this into the substrate mass balance (Eq. 4.5) and using the steady state condition $dS_{Se}/dt = 0$ results in the following equation for predicting substrate in the effluent as

$$S_{Se} = \frac{S_0 + K_m \theta_d S_I}{1 + K_m \theta_d} \tag{4.16}$$

Equation 4.16 includes only two parameters, therefore a two-dimensional grid search or a linear regression is sufficient for parameter estimation. According to the literature $50 \le K_m \le 1500$ d^{-1} and $0 \le np \le 0.05$. The best possible parameters are $np = 0.045$ and $K_m = 331$ d^{-1} that yields R^2 = 0.13 (Fig. 4.7). This indicates that this formula is not suitable for the system under investigation.

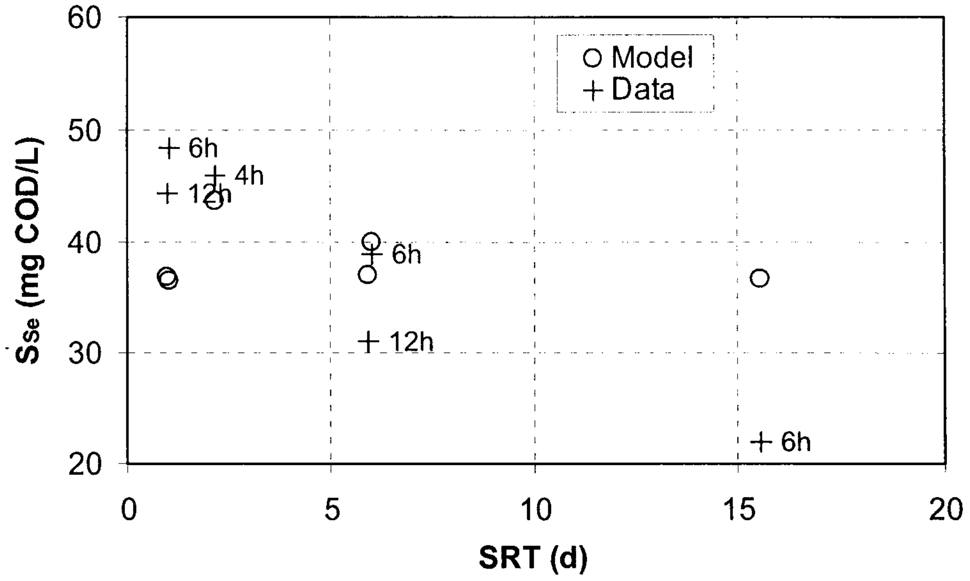


Fig. 4.7 Goodman and Englande Model for Substrate Removal (McKinney, 1962)

By following the same method in deriving the McKinney relation for predicting substrate in the effluent, a similar formula according to the Eckenfelder removal rate is found as

$$S_{Se} = \frac{S_0 + k\,\theta_d X_V S_I}{1 + k\,\theta_d X_V} \tag{4.17}$$

By performing a two dimensional grid search and assuming $0 \le np \le 0.05$ and $0.01 \le k \le 0.50$ (L/mg VSS) d^{-1}, the best possible parameters are found as $np = 0.037$ and $k = 0.1005$ (L/mg VSS) d^{-1} with R^2 = 0.736 (Fig. 4.8). This coefficient of determination indicates a better prediction of substrate removal compared to the Lawrence and McCarty model.

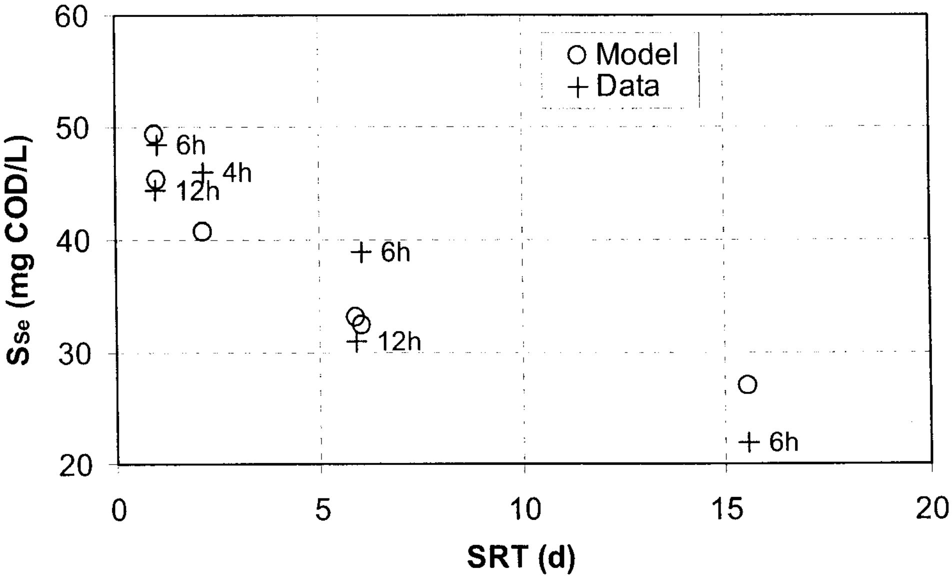


Fig. 4.8 Goodman and Englande Model for Substrate Removal (Eckenfelder, 1966)

Replacement of total biomass with active biomass in the Eckenfelder rate results another known function for substrate removal rate. The effluent substrate will be the same as Eq. 4.17 with replacement of X_V with X_a. A two dimensional grid search yields np = 0.031, K = 0.097 d^{-1} and R^2 = 0.654.

Another substrate removal rate is the Monod rate as a function of active biomass instead of total biomass. Equations are the same as Eqs. 4.8 through 4.10 with replacement of X_V with X_a. Predicted values for active biomass concentration from the Goodman and Englande model were used. A three dimensional grid search results in np = 0.0365, $K_S = 86.5$ mg COD/L and k =13.0 (mg COD/mg VSS) d^{-1} that yields $R^2 = 0.621$.

Comparison of residual errors in modeling of substrate removal in both the Lawrence and McCarty and the Goodman and Englande models based on total biomass (Fig. 4.9) shows that these two are essentially the same for the system under investigation. This is logical because the value of K_S in the Lawrence and McCarty model is high related to the value of effluent substrate; therefore, the effluent term in the denominator is negligible and k/K_S can be replaced by one coefficient.

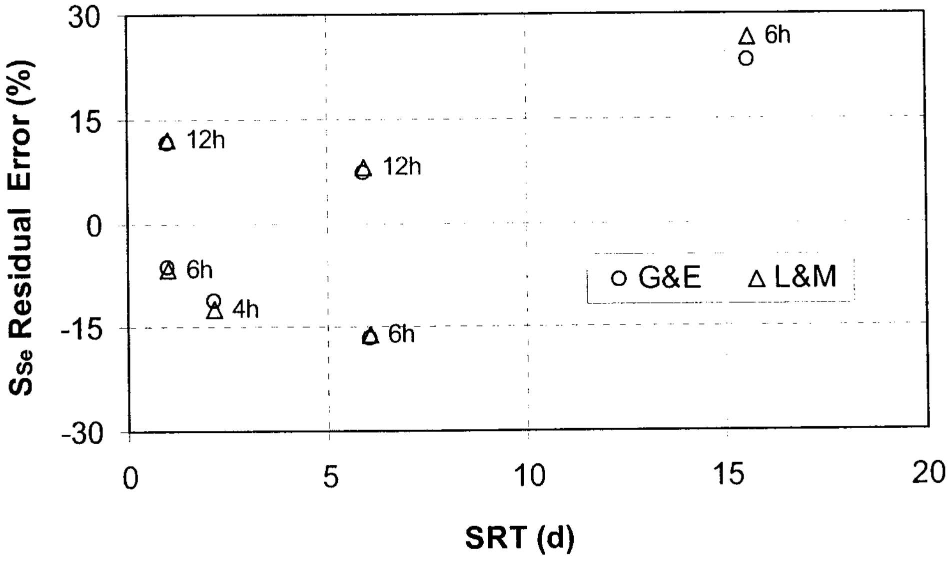


Fig. 4.9 Residual Errors of Substrate Removal Modeling

4.6 ASM1: Carbon Processes

4.6.1 Derivations

In order to have a perfect ASM, it is necessary to perform parameter estimation for all parameters simultaneously. This is possible if the number of equations is more than the number of parameters. In this case, there are just six steady state equations available, far less than the number of parameters involved. Therefore, it was decided to model the carbon processes of the system first, and then the nitrogen processes separately according to parameters estimated for carbon processes. Although this method does not yield the best model, it can provide a good footprint for future studies with more runs.

In this section, the equations that have been used for carbon processes of the ASM1 model are presented. Autotrophs, X_{BA} are ignored or lumped into heterotrophs, X_{BH}; therefore, Eqs. 4.18 through 4.22 are taken as the fundamental equations. All relations used in writing mass balances are extracted from the ASM1 components and processes matrix. In the system under investigation the concentration of DO was always kept above 4 mg/L; therefore, oxygen limitations in the system and anoxic growth of heterotrophs can be ignored. This means $S_O/(K_{OH}+S_O)=1$ and $\eta_h=0$.

Total biomass in the system is

$$X_V = X_{BH} + X_S + X_P \tag{4.18}$$

Readily biodegradable substrate S_S mass balance

$$\begin{gathered} QS_{S0} - QS_S - \left(\frac{\hat{\mu}_H}{Y_H}\right)\left(\frac{S_S}{K_S+S_S}\right)X_{BH}V + \\ k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)X_{BH}V = 0 \end{gathered} \tag{4.19}$$

Mass balance of X_{BH}

$$QX_{BH0} - Q_wX_{BH} - QX_{BHe} + \hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)X_{BH}V - b_HX_{BH}V = 0 \tag{4.20}$$

Mass balance of slowly biodegradable substrate X_S

$$\begin{gathered} QX_{S0} - Q_wX_S - QX_{Se} + (1-f_P)b_HX_{BH}V - \\ k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)X_{BH}V = 0 \end{gathered} \tag{4.21}$$

Mass balance of particulate product from biomass decay X_P

$$QX_{P0} - Q_wX_P - QX_{Pe} + f_Pb_HX_{BH}V = 0 \tag{4.22}$$

The following derivation is necessary to use the ASM1 model. At a steady state condition, dividing Eq. 4.20 by $X_{BH}V$ and assuming $X_{BH0} = 0$ results in

$$\frac{1}{\theta_X} + b_H = \hat{\mu}_H \left(\frac{S_S}{K_S + S_S} \right) \tag{4.23}$$

and rearranging this into

$$(K_S + S_S)\left(\frac{1}{\theta_X} + b_H \right) = \hat{\mu}_H S_S \tag{4.24}$$

Solving for S_S gives one of the basic equations of the model as

$$S_{Sm} = \frac{K_S\left(\frac{1}{\theta_X} + b_H \right)}{\hat{\mu}_H - \frac{1}{\theta_X} - b_H} = \frac{K_S\,(1 + b_H\theta_X)}{\hat{\mu}_H\theta_X - 1 - b_H\theta_X} \tag{4.25}$$

Subscript m stands for a model value. At steady state from Eq. 4.19

$$\hat{\mu}_H \left(\frac{S_S}{K_S + S_S} \right) X_{BH} = \frac{Y_H\,(S_{S0} - S_S)}{\theta_d} + Y_H k_h \left(\frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} \right) \tag{4.26}$$

If $\Psi = \dfrac{X_S/X_{BH}}{K_X + X_S/X_{BH}}$, substituting Eq. 4.23 into Eq. 4.26 yields

$$\frac{1}{\theta_X} = \frac{Y_H\,(S_{S0} - S_S)}{X_{BH}\theta_d} + Y_H k_h \Psi - b_H \tag{4.27}$$

Rearranging Eq. 4.27,

$$S_S = S_{S0} - \frac{X_{BH}\theta_d}{Y_H}\left(\frac{1}{\theta_X} + b_H - Y_H k_h \Psi \right) \tag{4.28}$$

Substituting Eq. 4.25 into Eq. 4.28 gives

$$\frac{K_S\left(\frac{1}{\theta_X}+b_H\right)}{\hat{\mu}_H-\frac{1}{\theta_X}-b_H}=S_{S0}-\frac{X_{BH}\theta_d}{Y_H}\left(\frac{1}{\theta_X}+b_H-Y_Hk_h\Psi\right) \tag{4.29}$$

Solving Eq. 4.29 for X_{BH} and using the identity in Eq. 4.25 results in another basic equation in the model as

$$X_{BH}=\frac{Y_H}{\theta_d}(S_{S0}-S_{Sm})\left(\frac{1}{\theta_X}+b_H-Y_Hk_h\Psi\right)^{-1} \tag{4.30}$$

Total COD higher than soluble COD for influent indicates that X_{S0} is not negligible in the system and assumed equal to the difference of total and soluble influent COD. Therefore from Eq. 4.21 by dividing with X_SV

$$\frac{X_{S0}}{X_S\theta_d}-\frac{1}{\theta_X}+(1-f_P)b_H\frac{X_{BH}}{X_S}-k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\frac{X_{BH}}{X_S}=0 \tag{4.31}$$

Equation 4.31 is rearranged to form a quadratic equation with respect to X_S as

$$\begin{aligned}&-\theta_dX_S^2+(X_{S0}\theta_X-\theta_dK_XX_{BH}+(1-f_p)b_H\theta_d\theta_XX_{BH}-k_h\theta_d\theta_XX_{BH})X_S+\\&K_XX_{S0}\theta_XX_{BH}+(1-f_p)\theta_d\theta_XK_Xb_HX_{BH}^2=0\end{aligned} \tag{4.32}$$

Equations 4.30 and 4.32 are circularly related. This causes some difficulties in the estimation of model parameters that will be explained later. Equation 4.32 can be solved using an Euler relationship.

$$X_S=\frac{-b+\sqrt{b^2-4ac}}{2a} \tag{4.33}$$

where $a=-\theta_d$, $b=X_{S0}\theta_X-\theta_dK_XX_{BH}+(1-f_p)b_H\theta_d\theta_XX_{BH}-k_h\theta_d\theta_XX_{BH}$ and $c=K_XX_{S0}\theta_XX_{BH}+(1-f_p)\theta_d\theta_XK_Xb_HX_{BH}^2$. When X_S is determined, the value of Ψ is known and X_{BH} can be calculated using Eq. 4.30.

From Eq. 4.22 dividing by $X_P V$ one finds

$$\frac{X_P}{X_{BH}} = f_P b_H \theta_X \tag{4.34}$$

Using Eqs. 4.18, 4.25, 4.30, 4.32 and 4.34 one can model carbon processes of ASM1 for an aerated reactor.

It is required to include the amount of inert soluble substrate in the model. This kind of substrate has two sources, first it is a fraction of soluble influent substrate and second it is produced by hydrolysis of the entrapped biomass. Therefore the function

$$S_I = f_{nS} S_{S0} \tag{4.35}$$

is used for taking into account the effect of inert soluble substrate. In this function f_{nS} is a parameter that should be estimated.

4.6.2 AQUASIM Program

The ASM1 model originally had nineteen parameters that must be estimated but with the simplifications made in the previous section, only eight parameters must be estimated. These are kinetic parameters $\hat{\mu}_H$, b_H, K_S, k_h, K_X and f_{nS} and stoichiometric parameters Y and f_P.

The grid search technique includes nested loops equal to the number of parameters needed to be estimated. This causes the time for performing a grid search to increase exponentially with the number of parameters. For this reason, in this case, the grid search is not sufficiently helpful and it is required to select a faster technique. AQUASIM 2.1 (Reichert, 1998) thus has been chosen for modeling the system.

The program AQUASIM was designed to identify and simulate aquatic systems. This program provides important tools for model comparison and parameter estimation. AQUASIM is capable of performing simulations, sensitivity analyses and parameter estimations. The last feature, which is used here, is to estimate parameters in a given model using measured variables.

AQUASIM can estimate model parameters represented by constant variables by minimizing the sum of the squares of the weighted derivatives χ^2 between measurements and the calculated model results. Chi Square is defined as $\chi^2 = \sum(\hat{y}_i - y_i)^2 / \sigma^2$ in which σ is the standard deviation of data. $\hat{y}_i$ is a function of $p = (p_1, p_2, ..., p_m)$ which are model parameters. The minimization of the sum of squares is done with the constraints $p_{i,\min} \leq p_i \leq p_{i,\max}$. Due to the possible nonlinearity of the model Chi Square should be minimized numerically.

4.6.3 Parameter Estimation

In order to use AQUASIM's parameter estimation procedure, it is required to have at least one datum more than parameters. For this reason, data collected for three days during steady state periods for each run were used instead of average steady state values. Another requirement of AQUASIM is to provide functions free of circular references. Although it is not a mathematical obligation, AQUASIM can perform parameter estimations only when all state functions are independent, unlike Eqs. 4.30 and 4.32. To solve this problem the following technique was used.

According to the literature (Henze et al., 2002), K_X is a very small number and X_S is greater than X_{BH}. This results in $\Psi \cong 1.0$. By approximating Ψ with unity in Eq. 4.30, it becomes independent of Eq. 4.32 and AQUASIM can be used to estimate the involved parameters. Then the MATHCAD™ program was used to calculated exact values of X_{BH} and X_S for the estimated parameters.

In order to estimate parameters, all variables including constant (model parameters), real list (data collected) and state variables (biomass and substrate concentration) are defined in AQUASIM. In the definition of model parameters, it is required to include upper and lower limits of them. These two bounds are chosen according to the literature and engineering judgment. All ranges in the literature are given for domestic waste. Therefore, the selected ranges are wider than reported values in the literature (Table 2.2) to be able to capture possible answers outside the given ranges (Table 4.10). Then processes of biomass growth, biomass decay, and biomass hydrolysis and substrate removal are defined according to Section 4.6.1. The next step is to define the reactor and to establish proper relations between processes and state variables.

Table 4.10 Range of ASM1 Parameters (Carbon Processes)

Parameter	b_H	f_{ns}	f_p	k_h	K_S	K_X	$\hat{\mu}_H$	Y_H
Unit	d^{-1}	-	-	mg/mg*	mg/L*	mg/mg*	d^{-1}	mg/mg*
L Bound	1	0	0	1	5	0	1	0.4
U Bound	5	0.2	0.2	10	200	0.1	20	0.8

*Based on COD

After defining all components of the system, it is required to introduce an initial value for each parameter. AQUASIM takes these initial values and attempts to improve them by minimizing the Chi square value. The parameter estimation technique is extremely sensitive to initial values and small changes in these values can cause convergence to a different set of parameters. In order to use ASM, VSS was converted to COD by a conversion factor of 1.42 (Grady et al., 1999). Most results are similar to each other and differences are negligible. Among tens of parameter sets found by using AQUASIM, the best (Set 1) was chosen and is reported in Table 4.11. Many other parameter sets that provide reasonable to good prediction can be found with parameter values outside the selected ranges or $\bar{\Psi}$ values not close to unity. It is of importance to note that R^2 in Table 4.11 is calculated by assuming Ψ =1.0. In this table the coefficient of determination is calculated using average values (Table 4.1).

Table 4.11 Parameter Estimation Results for ASM1 (Carbon Processes)

Parameter	b_H	f_{ns}	f_p	k_h	K_S	K_X	$\hat{\mu}_H$	Y_H	R^2 of S_S	R^2 of X_V	$\bar{\Psi}$
Set 1	2.91	0.007	0.099	3.26	56.5	0.020	8.79	0.665	0.602	0.993	0.989
Set 2	3.20	0.003	0.095	3.80	160	0.015	19.5	0.733	0.550	0.989	0.934
Set 3	2.78	0.013	0.118	3.78	53.9	0.012	8.54	0.635	0.609	0.979	0.870
Set 4	2.59	0.004	0.602	4.07	58.6	0.008	8.04	0.380	0.591	0.957	0.884

Among the four parameter sets in Table 4.11, set one is judged to be the best. This set was selected for further calculations because values of R^2 and $\bar{\Psi}$ are closer to unity. Table 4.12 shows application of the first parameter set to ASM1.

The components of biomass according to ASM1 with parameter set one is depicted in Fig. 4.10. The biomass and effluent substrate model based on ASM1 are shown in Fig. 4.11 and Fig. 4.12, respectively.

Table 4.12 Applying the First Parameter Set of Carbon Processes to ASM1

Variable	Unit (COD)	Run#						Explanation (Equation#)
		1	2	3	4	5	6	
Data:								
S_S	mg/L	48	39	22	44	31	46	-
X_V	mg/L	1571	6063	11715	814	3110	3836	-
Model:								
S_{Sm}	mg/L	44.7	30.4	28.9	45.5	30.5	35.2	(4.25)
S_I	mg/L	2.7	2.9	2.7	2.9	2.9	3.2	(4.35)
Model S_S	mg/L	47.5	33.3	31.6	48.4	33.4	38.4	$S_{Sm} + S_I$
Res. Err.	%	2	15	−44	−9	−8	16	(4.14)
X_{BH}	mg/L	498	1083	1140	263	534	1402	(4.30)MCAD
X_S	mg/L	716	3064	4826	433	1623	1380	(4.32)MCAD
X_p	mg/L	143	1904	5124	76	908	888	(4.34)
X_V	mg/L	1357	6051	11090	772	3065	3669	(4.18)
Ψ	–	0.986	0.993	0.995	0.988	0.993	0.979	(4.27)
Res. Err.	%	−13.6	−0.2	−5.3	−5.2	−0.14	−0.44	(4.14)

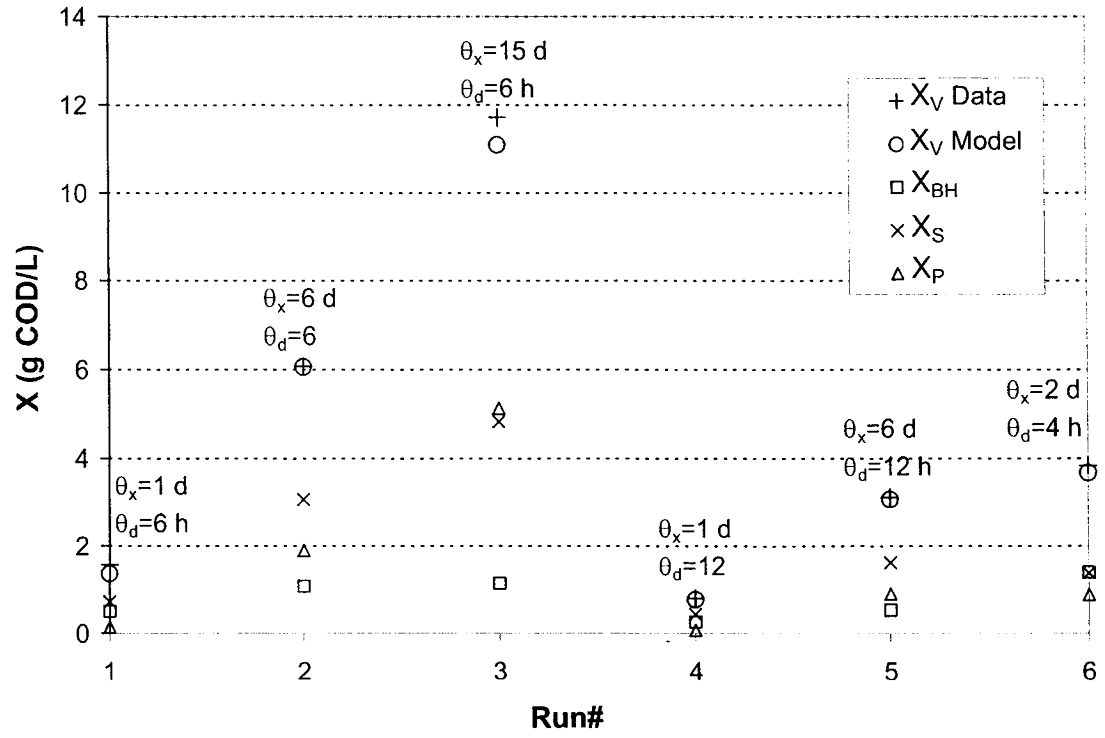


Fig. 4.10 Biomass Components According to ASM1

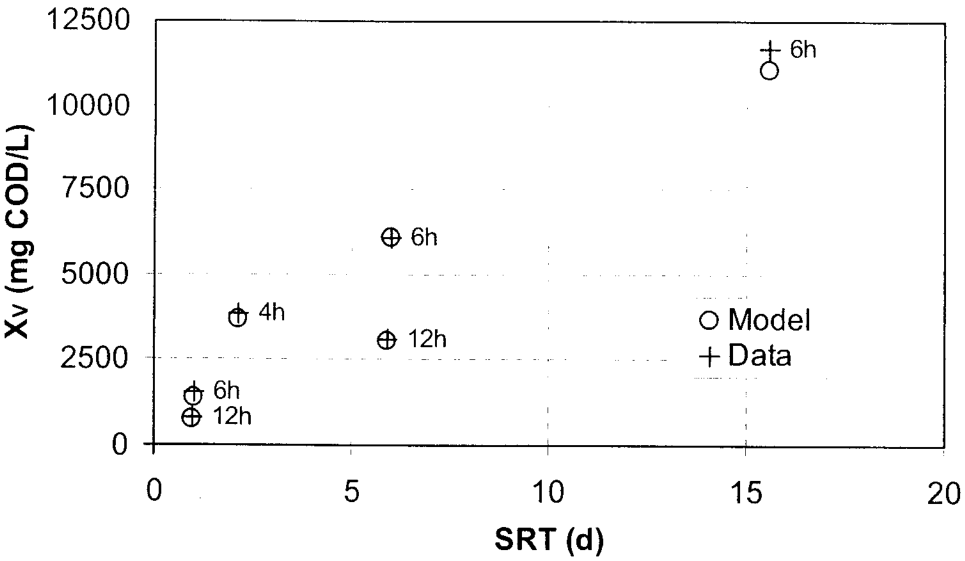


Fig. 4.11 ASM1 for Biomass Growth

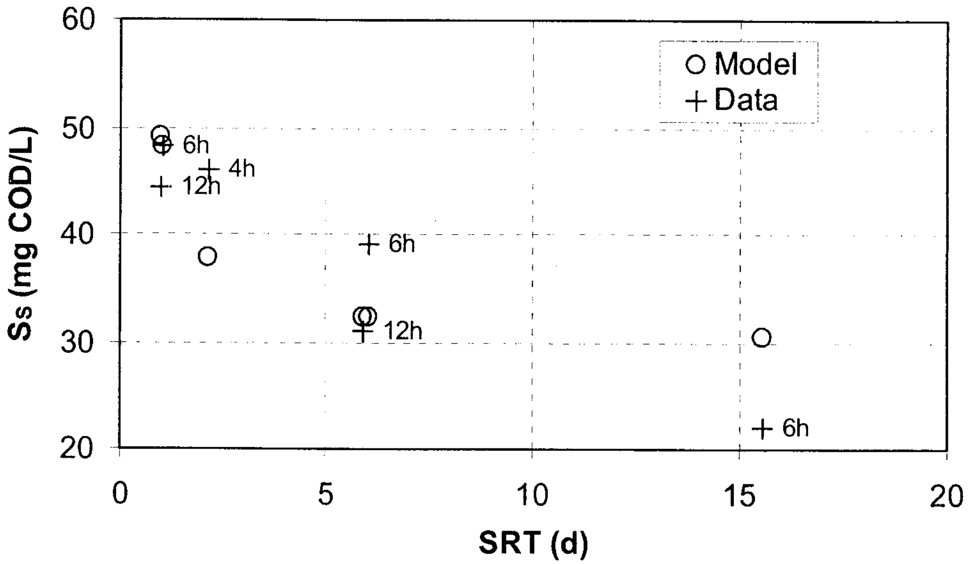


Fig. 4.12 ASM1 for Substrate Removal

4.7 ASM1: Nitrogen Processes

4.7.1 Derivations

In this section, the equations that have been used for nitrogen processes of ASM1 are presented. Nitrogen in the system is presented in the form of nitrate and nitrite, ammonia, soluble and particulate organic nitrogen.

Fundamental equations of the model in steady state are presented in Eqs. 4.36 through 4.40. Again because of a high amount of oxygen in the system, the limiting effects of oxygen are neglected.

Mass balance of autotrophic biomass X_{BA} .

$$QX_{BA0} - Q_w X_{BA} - QX_{BAe} + \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA} V - b_A X_{BA} V = 0 \tag{4.36}$$

Mass balance of nitrate and nitrite nitrogen S_{NO}

$$QS_{NO0} - QS_{NO} + \frac{1}{Y_A} \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA} V = 0 \tag{4.37}$$

Mass balance of ammonia nitrogen S_{NH}

$$\begin{gathered} QS_{NH0} - QS_{NH} - i_{XB} \hat{\mu}_H \frac{S_S}{K_S + S_S} X_{BH} V - \\ \left(i_{XB} + \frac{1}{Y_A} \right) \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA} V + k_a S_{ND} X_{BH} V = 0 \end{gathered} \tag{4.38}$$

Mass balance of soluble organic nitrogen S_{ND}

$$QS_{ND0} - QS_{ND} - k_a S_{ND} X_{BH} V + k_h \frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} X_{BH} \frac{X_{ND}}{X_S} V = 0 \tag{4.39}$$

Mass balance of particulate organic nitrogen X_{ND}

$$\begin{gathered} QX_{ND0} - Q_w X_{ND} - QX_{NDe} + \left(i_{XB} - f_P i_{XP} \right) \left(b_H X_{BH} + b_A X_{BA} \right) V - \\ k_h \frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} X_{BH} \frac{X_{ND}}{X_S} V = 0 \end{gathered} \tag{4.40}$$

Dividing Eq. 4.36 by $X_{BA} V$ and assuming $X_{BA0} = 0$

$$\frac{1}{\theta_X} + b_A = \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} \tag{4.41}$$

From Eq. 4.37

$$\frac{S_{NO0}-S_{NO}}{\theta_d}=-\frac{1}{Y_A}\hat{\mu}_A\frac{S_{NH}}{K_{NH}+S_{NH}}X_{BA} \tag{4.42}$$

Using the identity in Eq. 4.41 results in

$$S_{NO}=S_{NO0}+\frac{\theta_d}{Y_A}\left(\frac{1}{\theta_X}+b_A\right)X_{BA} \tag{4.43}$$

Dividing Eq. 4.40 by $X_{ND}V$, assuming $X_{ND0}=0$ and rearranging the equation gives the expression of particulate organic nitrogen as

$$X_{ND}=\frac{(i_{XB}-f_p i_{XP})(b_H X_{BH}+b_A X_{BA})}{\dfrac{1}{\theta_X}+\dfrac{k_h}{K_X+X_S/X_{BH}}} \tag{4.44}$$

Dividing Eq. 4.39 by V results in

$$\frac{S_{ND}-S_{ND0}}{\theta_d}=-k_a S_{ND}X_{BH}\theta_d+k_h\frac{X_{ND}}{K_X+X_S/X_{BH}}\theta_d \tag{4.45}$$

Rearranging Eq. 4.45 gives

$$S_{ND}=\frac{S_{ND0}+k_h\theta_d\dfrac{X_{ND}}{K_X+X_S/X_{BH}}}{1+k_a\theta_d X_{BH}} \tag{4.46}$$

From Eq. 4.38 one can obtain

$$\begin{aligned}S_{NH}&=S_{NH0}-i_{XB}\hat{\mu}_H\frac{S_S}{K_S+S_S}X_{BH}\theta_d-\\&\left(i_{XB}+\frac{1}{Y_A}\right)\hat{\mu}_A\frac{S_{NH}}{K_{NH}+S_{NH}}X_{BA}\theta_d+k_a S_{ND}X_{BH}\theta_d=0\end{aligned} \tag{4.47}$$

Substituting Eqs. 4.23 and 4.41 into 4.47 results in

$$S_{NH} = S_{NH0} - i_{XB}\left(\frac{1}{\theta_X} + b_H\right)X_{BH}\theta_d - \left(i_{XB} + \frac{1}{Y_A}\right)\left(\frac{1}{\theta_X} + b_A\right)X_{BA}\theta_d + k_a S_{ND} X_{BH}\theta_d = 0 \tag{4.48}$$

Equations 4.43, 4.44, 4.46 and 4.48 will be used to predict the behaviour of nitrogen in the system.

4.7.2 Parameter Estimation

In this section, parameters used in the derived formulas are estimated to fit the data. Those parameters that are in common with carbon processes are taken as they were estimated when only carbon processes were taken into consideration. Autotrophs were assumed to be a fraction of heterotrophs, f_{XBA}, which is a new parameter in the model. Although by using this method the best parameter set cannot be captured, it will be utilized for two reasons: Firstly, in order to obtain the optimum parameter set, it is required to perform parameter estimations simultaneously on both carbon and nitrogen processes. In such an analysis, more than fifteen parameters must be considered, while just six steady state runs are available. The results of this analysis will likely yield some fictitious numbers. Though they fit well with the data, they may not describe the true behaviour of the system. Secondly, this method is much simpler.

Particulate organic nitrogen in the effluent, X_{ND}, is assumed to be negligible; therefore, the S_{ND} value can be taken as effluent organic nitrogen, ON. Parameter estimation should be done simultaneously using Eqs. 4.43, 4.46 and 4.48 and the result of each equation compared with data for S_{NO}, ON and S_{NH} of effluent, respectively. For that reason and because the values of S_{NH} and ON are very small, and the corresponding functions for modeling them are based on different processes, it is unlikely to find many parameter sets that suit the model. Because of the small values and error involved in modeling and measurements in the lab, the R^2 criterion does not yield positive values; therefore the ε criterion will be used.

Table 4.13 shows ranges of ASM1 parameters that have been used in modeling. These ranges are set based on the literature (Henze et al., 2002 and Table 2.2).

Table 4.13 Ranges of ASM1 Parameters (Nitrogen Processes)

Parameter	f_{XBA}	Y_A	b_A	k_a	i_{XB}	i_{XP}
Unit	-	mg COD/mg N	d^{-1}	(L/mg COD) d^{-1}	mg N/mg COD	mg N/mg COD
L Bound	0.01	0.20	0	0.01	0.02	0.02
U Bound	0.06	0.30	0.20	0.20	0.20	0.20

Among several parameters sets found to fit the data, the best one is $Y_A = 0.22$, $b_A = 0.03$, $f_{XBA} = 0.01$, $k_a = 0.023$, $i_{XB} = 0.034$ and $i_{XP} = 0.045$. Other parameter sets either yield much poorer predictions of data or they are similar to this one. Some parameter sets may improve the prediction of one component but the overall prediction is poor. Application of the parameters is shown in Table 4.14.

Table 4.14 Applying Parameters of Nitrogen Processes to ASM1

Variable	Unit	Run#						Explanation (Equation#)
		1	2	3	4	5	6	
Data:								
S_{NO}	mg/L	3.8	63.9	93	6.0	52.3	37.7	
S_{NH}	mg/L	0.7	0.3	2.5	2.9	1.8	3.9	
ON	mg/L	1.5	1.8	1.9	4.8	2.3	6.0	
Model:								
X_{ND}	mg/L	3.9	50.2	134.8	2.1	24.1	22.1	(4.44)
S_{ND}	mg/L	2.9	3.4	3.5	3.6	3.6	3.2	(4.46)
ONp	mg/L	2.9	3.4	3.5	3.6	3.6	3.2	$= S_{ND}$
Res. Err.	%	−91	−89	−84	25	−57	46	(4.14)
S_{NOP}	mg/L	20.0	51.8	94.2	27.5	61.9	30.7	(4.43)
Res. Err.	%	−422	19	−1	−358	−18	19	(4.14)
S_{NHp}	mg/L	8.8	-1.6	-0.1	5.1	2.5	14.8	(4.48)
Res. Err.	%	1160	650	150	−80	−50	−280	(4.14)

The main reason that residual error for nitrogen components is large is that their values are very small. Equipment available in the laboratory is not capable of measuring low concentration of ammonia-N or nitrate and nitrite-N precisely; the measurements thus are erroneous also. On the other hand, the measurement of TKN has been done by another laboratory (ACCUTEST LTD), while the ammonia was measured in the university lab. Usually five samples together, each related to one steady state condition were sent to

ACCUTEST for economic reasons; therefore, some samples were kept in a refrigerator for over one week. This affected the reliability of values for organic nitrogen. There may have been some nitrogen loss during storage although storage times did not exceed recommendations of the analytical laboratories. In many cases the calculated value for organic nitrogen is negative, i.e., ammonia was higher than the TKN. In these cases ON was assumed to be zero in further calculations. This can be another source of error in the modeling of nitrogen.

The ASM1 model for organic nitrogen in the effluent based on estimated parameters is shown in Fig. 4.13. This model has $\varepsilon = 1.71$ and $R^2 = 0.0$.

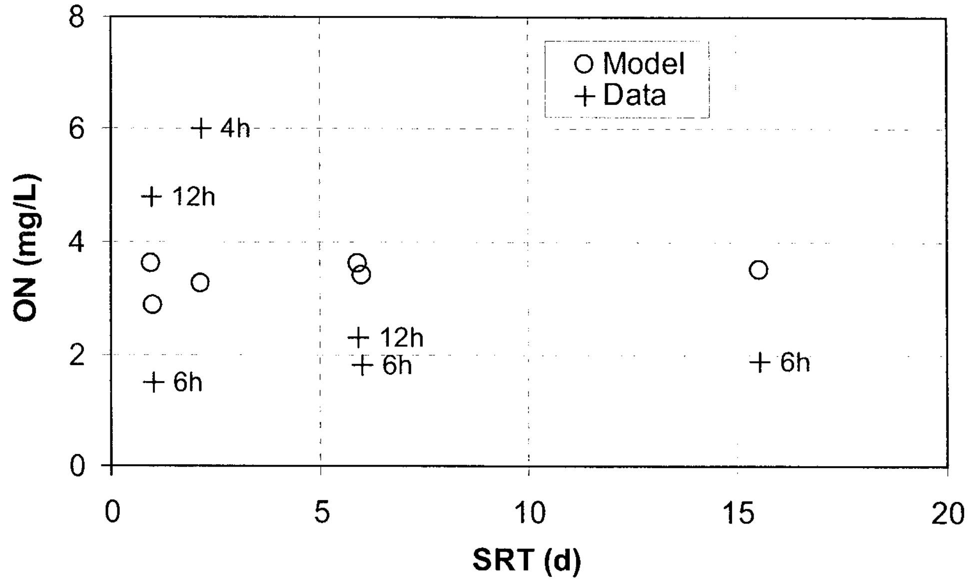


Fig. 4.13 Effluent Organic Nitrogen According to ASM1

Based on estimated parameters, ASM1 for S_{NO} is shown in Fig. 4.14. As this figure shows, the prediction is quite poor and the model cannot capture the behaviour of this component. But an observation can be made from this figure: the amount of S_{NO} in the effluent increases when sludge age increases. For this reason the following modified version of Eq. 4.43 is proposed.

$$S_{NOP} = S_{NO0} + \frac{\theta_d}{Y_A}\theta_X\left(\frac{1}{\theta_X} + b_A\right)X_{BA} \qquad (4.49)$$

This modification has no significant effect on the ε criterion. The modification decreases ε from 5.65 to 5.55, but R^2 is –0.60 before modification and it becomes 0.83 after that the correction. This equation does not affect the concentration of ammonia. The modified model is shown in Fig. 4.15.

The model for ammonia is shown in Fig. 4.16. Based on this model ε is 13.63 and R^2 is –20.5.

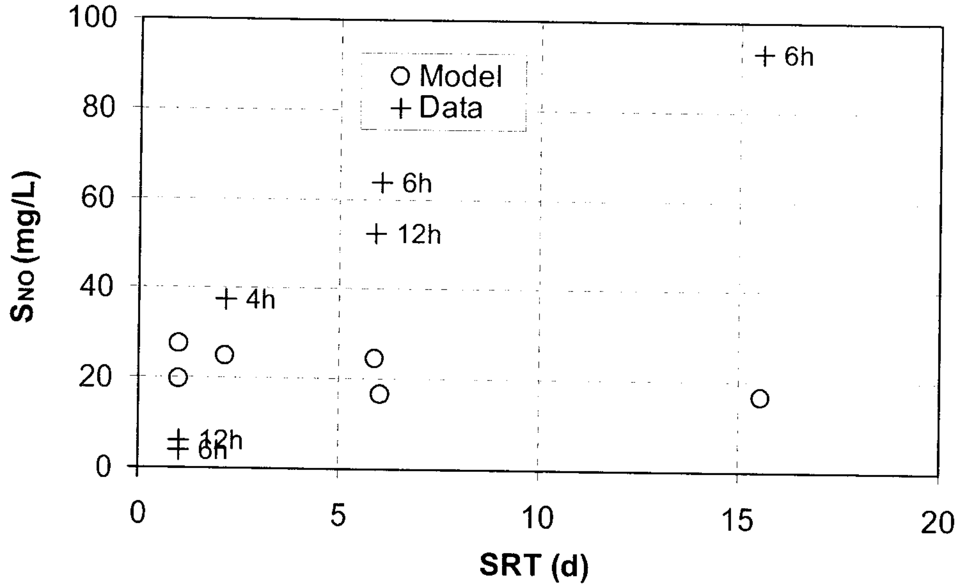


Fig. 4.14 Nitrate and Nitrite Nitrogen According to ASM1

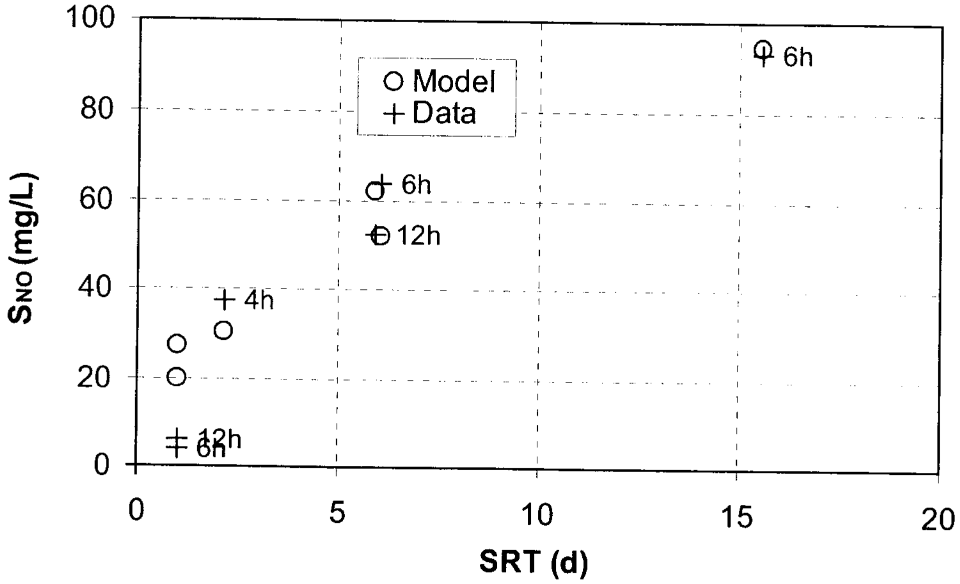


Fig. 4.15 Modified ASM1 for Nitrate and Nitrite Nitrogen

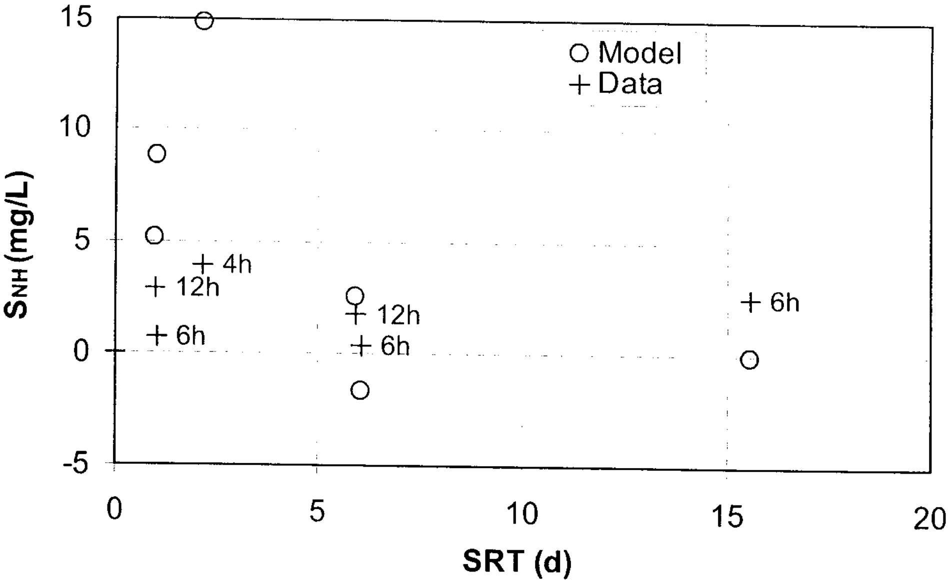


Fig. 4.16 Ammonia Nitrogen According to ASM1

Chapter 5

Modeling: Part II

5.1 General

In this chapter modeling of the system is continued. Modeling is extended to ASM2 excluding phosphorus processes and to ASM3. At the end an empirical model for total effluent substrate is presented.

5.2 ASM2: Carbon Processes

In this section the equations that have been used for carbon processes of ASM2 are presented. This model is adapted from Henze et al. (2002). In order to compare the results, the same notation as ASM1 was used as much as possible. Autotrophs X_{BA} are ignored or lumped into heterotrophs X_{BH}. In the system DO was always kept above 4 mg/L; therefore, all anoxic, anaerobic hydrolysis and fermentation processes can be safely ignored. For the same reason, the fermentation product S_A is zero. A brief version of the ASM2 stoichiometry and kinetics matrix adopted for the system under investigation is presented in Table 5.1.

Equations 5.1 through 5.6 are the fundamental relationships for the system. Total biomass in the system is

$$X_V = X_{BH} + X_S + X_I \tag{5.1}$$

Mass balance of fermentable readily biodegradable substrate S_F

$$\begin{aligned} &QS_{F0} - QS_F - \frac{\hat{\mu}_H}{Y_H}\frac{S_F}{K_F + S_F}X_{BH}V + \\ &(1 - f_{SI})k_h\frac{X_S/X_{BH}}{K_X + X_S/X_{BH}}X_{BH}V = 0 \end{aligned} \tag{5.2}$$

Mass balance of inert soluble organic material S_I

$$QS_{I0} - QS_I + f_{SI}k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH}V = 0 \tag{5.3}$$

Mass balance of X_{BH}

$$QX_{BH0} - Q_w X_{BH} - QX_{BHe} + \hat{\mu}_H \frac{S_F}{K_F + S_F} X_{BH}V - b_H X_{BH}V = 0 \tag{5.4}$$

Mass balance of slowly biodegradable substrate X_S

$$QX_{S0} - Q_w X_S - QX_{Se} + (1 - f_{XI})b_H X_{BH}V - k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH}V = 0 \tag{5.5}$$

Mass balance of inert particulate organics X_I

$$QX_{I0} - Q_w X_I - QX_{Ie} + f_{XI}b_H X_{BH}V = 0 \tag{5.6}$$

It is known from the literature (Henze et al., 2002) f_{SI} with zero in Eqs. 5.2 and 5.3 the fundamental equations for carbon processes based on ASM2 are the same as ASM1. Therefore all derivations and methods used in ASM1 hold true for ASM2. Estimated parameters are applicable to this model as well but three points should be considered. a) Due to simplifications made, f_{XI} in ASM2 is equivalent to f_p in ASM1; b) Because fermentation processes do not exist in the system, S_F in ASM2 is equivalent to S_S in ASM1; c) X_I is ASM2 is equivalent to the summation of X_P and X_I in ASM1. In the derivation of ASM1 formulas X_I was assumed to be negligible, thus X_I in ASM2 can be taken the same as X_P in ASM1.

It is important to note that these two models will not be identical if anoxic processes are included in the formulations.

Table 5.1 ASM2: Kinetics and Stoichiometry for Aerobic Processes

Component →	i	1	2	3	4	5	6	7	8	9
j	Process ↓	S_F	S_{NH}	S_{NO}	S_I	X_I	X_S	X_{BH}	X_{BA}	Process Rate, $\rho_j[ML^{-3}T^{-1}]$
Hydrolysis Processes										
1	Aerobic hydrolysis	$1-f_{SI}$	ν_1		f_{SI}		-1			ρ_1
Facultative Heterotrophic Organisms										
2	Aerobic growth on S_S	$-\frac{1}{Y_H}$	ν_2					1		ρ_2
3	Lysis		ν_3			f_{XI}	$1-f_{XI}$	-1		ρ_3
Growth and Decay of Nitrifying Organisms										
4	Aerobic growth of X_{BA}		ν_4	$\frac{1}{Y_A}$					1	ρ_4
5	Lysis of X_{BA}		ν_5			f_{XI}	$1-f_{XI}$		-1	ρ_5

in which

$$\rho_1 = k_h \frac{X_S/X_{BH}}{K_X + (X_S/X_{BH})} X_{BH},\ \rho_2 = \hat{\mu}_H \frac{S_F}{K_F + S_F} \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BH},\ \rho_3 = b_H X_{BH},$$

$$\rho_4 = \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA},\ \rho_5 = b_A X_{BA},\ \nu_1 = i_{NXS} - f_{SI} i_{NSI} - (1 - f_{SI}) i_{NSF},\ \nu_2 = \frac{i_{NSF}}{Y_H} - i_{NBM},$$

$$\nu_3 = i_{NBM} - f_{XI} \cdot i_{NXI} - (1 - f_{XI}) i_{NXS},\ \nu_4 = -i_{NBM} - \frac{1}{Y_H},\ \nu_5 = \nu_3$$

f_{SI} = fraction of inert COD in particulate substrate

f_{XI} = fraction of inert COD generated in biomass lysis

i_{NXS} = nitrogen content of inert particulate substrate X_S

i_{NSI} = nitrogen content of inert soluble COD S_I

i_{NSF} = nitrogen content of soluble substrate S_F

i_{NBM} = nitrogen content of biomass X_{BA}, X_{BH}

5.3 ASM2: Nitrogen Processes

5.3.1 Derivations

In this section the equations that have been used for nitrogen processes of ASM2 are presented. Nitrogen in the system is presented in the form of nitrate and nitrite, ammonia and gaseous nitrogen. Nitrogen as a gas is produced in the anoxic processes, thus it can be neglected in the system under discussion.

Fundamental equations of the model in steady state are presented in Eqs. 5.7 to 5.9.

Mass balance of X_{BA}

$$QX_{BA0} - Q_w X_{BA} - QX_{BAe} + \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA}V - b_A X_{BA}V = 0 \tag{5.7}$$

Mass balance of S_{NO}

$$QS_{NO0} - QS_{NO} + \frac{1}{Y_A}\hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA}V = 0 \tag{5.8}$$

Mass balance of S_{NH}

$$\begin{aligned}
&QS_{NH0} - QS_{NH} + \\
&\left[i_{NXS} - f_{SI} i_{NSI} - (1 - f_{SI}) i_{NSF}\right] k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH}V + \\
&\left(\frac{i_{NSF}}{Y_H} - i_{NBM}\right) \hat{\mu}_H \frac{S_F}{K_F + S_F} \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BH}V + \\
&\left[i_{NBM} - f_{XI} i_{NXI} - (1 - f_{XI}) i_{NXS}\right] \left(b_A X_{BA} + b_H X_{BH}\right) V + \\
&\left(-i_{NBM} - \frac{1}{Y_A}\right) \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA}V = 0
\end{aligned} \tag{5.9}$$

From Eq. 5.7, assuming $X_{BA0} = 0$ and dividing by VX_B

$$\hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} = \frac{1}{\theta_X} + b_A \tag{5.10}$$

Equation 5.8 and using the identity in Eq. 5.10 results in

$$S_{NO} = S_{NO0} + \frac{\theta_d}{Y_A}\left(\frac{1}{\theta_X} + b_A\right) X_{BA} \tag{5.11}$$

which is identical to the equation of nitrate and nitrite nitrogen component of ASM1.

Substituting Eq. 5.10 and its equivalent for heterotrophs into Eq. 5.9 results in

$$\begin{aligned}
S_{NH} &= S_{NH0} + \left[i_{NXS} - f_{SI} i_{NSI} - (1-f_{SI}) i_{NSF}\right] k_h \theta_d \frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} X_{BH} \\
&\left(\frac{i_{NSF}}{Y_H} - i_{NBM}\right)\left(\frac{1}{\theta_X} + b_H\right)\left(\frac{1}{\theta_X} + b_A\right)\theta_d \frac{X_{BH}}{\hat{\mu}_A} + \\
&\left[i_{NBM} - f_{XI} i_{NXI} - (1-f_{XI}) i_{NXS}\right]\left(b_A X_{BA} + b_H X_{BH}\right)\theta_d - \\
&\left(i_{NBM} + \frac{1}{Y_A}\right)\left(\frac{1}{\theta_X} + b_A\right)\theta_d X_{BA}
\end{aligned} \tag{5.12}$$

The last two equations are used to predict the behaviour of nitrogen in the system.

5.3.2 Parameter Estimation

During the literature study made for this research, no reliable ranges were found for parameters in ASM2. The best range available is typical values for these parameters which are proposed by Henze et al. (2002). Again for the same reasons as ASM1, nitrogen processes modeling based on ASM2 do not yield good predictions. Table 5.2 shows the selected ranges for nitrogen modeling. Table 5.3 shows three of the best parameter sets found.

Table 5.2 Range of ASM2 Parameters (Nitrogen Processes)

Parameter	f_{XBA}	Y_A	b_A	i_{NSI}	i_{NSF}	i_{NXI}	i_{NXS}	i_{NBM}	$\hat{\mu}_A$
U. Bound	0.01	0.15	0	0	0.01	0.01	0.01	0.01	0.5
L. Bound	0.05	0.25	0.2	0.02	0.05	0.05	0.05	0.30	30.0

Table 5.3 Parameters Estimation Results for Nitrogen Processes of ASM2

Parameter	f_{XBA}	Y_A	b_A	i_{NSI}	i_{NSF}	i_{NXI}	i_{NXS}	i_{NBM}	$\hat{\mu}_A$	ε of S_{NO}	ε of S_{NH}
Set 1	0.022	0.19	0.005	0	0.030	0.046	0.025	0.28	22.4	9.8	9.8
Set 2	0.012	0.19	0.010	0	0.038	0.036	0.044	0.03	71.2	6.8	19.0
Set 3	0.010	0.22	0.030	0	0.039	0.040	0.044	0.03	18.8	5.6	24.6

Set 1 is selected as the model, because it has the lowest value of ε for both S_{NO} and S_{NH}. Predicted values of S_{NH} based on parameters sets 1 are depicted on Fig. 5.1. The value of R^2 for S_{NO} and S_{NH} are –5.4 and –19.7, respectively.

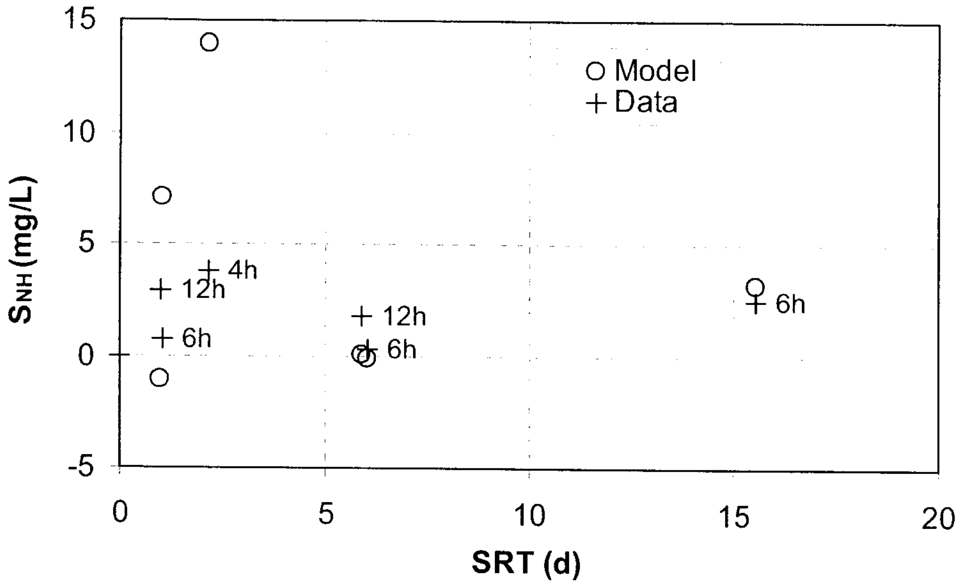


Fig. 5.1 Ammonia Nitrogen Based on ASM2

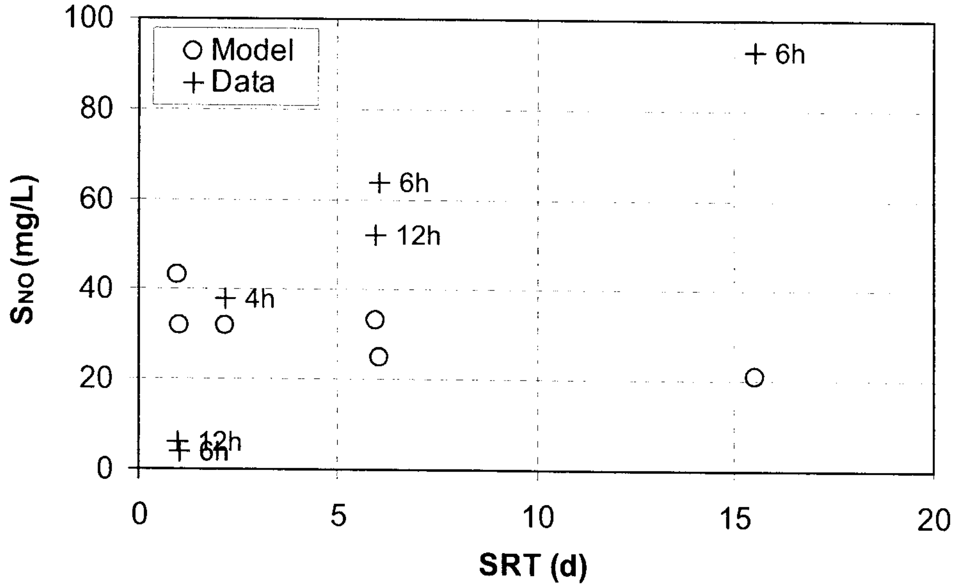


Fig. 5.2 Nitrate and Nitrite Nitrogen Based on the ASM2

5.4 ASM3: Carbon Processes

5.4.1 Derivations

In this section the appropriate equations are derived the system according to ASM3. This model is adapted from Gujer et al. (1999). Notation was kept consistent with ASM1 where possible. Autotrophs X_{BA} are ignored or lumped into heterotrophs, X_{BH}. In the system DO was always kept above 4 mg/L; therefore, all anoxic, processes can be safely ignored. A brief version of the ASM3 stoichiometry and kinetics matrix adopted for the system is presented in Table 5.4. Some simplifications are made to the naming of parameters, for example $Y_{STO,O2}$ is simply called Y_{STO} because $Y_{STO,N2}$ does not exist in the model therefore there is no need for distinction between these two.

Table 5.4 ASM3: Kinetics and Stoichiometry for Aerobic Processes

Component →	i	1	2	3	4	5	6	7	8	9	10
j	Process ↓	S_S	S_{NH}	S_{NO}	S_I	X_I	X_S	X_{BH}	X_{STO}	X_{BA}	Process Rate, $\rho_i[ML^{-3}T^{-1}]$
1	Hydrolysis	$1-f_{SI}$	ν_1		f_{SI}		-1				ρ_1
2	Aerobic storage of COD	-1	i_{NSS}						Y_{STO}		ρ_2
3	Aerobic growth of X_{BH}		$-i_{NBM}$					1	$-\frac{1}{Y_H}$		ρ_3
4	Aerobic end. resp. of X_{BH}		ν_4			f_{XI}		-1			ρ_4
5	Aerobic resp. of X_{STO}								-1		ρ_5
6	Aerobic growth of X_{BA}		ν_6	$-\frac{1}{Y_H}$						1	ρ_6
7	Aerobic end. resp. of X_{BA}		ν_7			f_{XI}				-1	ρ_7

in which

$$\rho_1 = k_h \frac{X_S/X_{BH}}{K_X + (X_S/X_{BH})} X_{BH},\ \rho_2 = K_{STO}\frac{S_S}{K_S + S_S} X_{BH},\ \rho_3 = \hat{\mu}_H \frac{X_{STO}/X_{BH}}{K_{STO} + (X_{STO}/X_{BH})} X_{BH},$$

$$\rho_4 = b_H X_{BH},\ \rho_5 = b_{STO} X_{STO},\ \rho_6 = \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA},\ \rho_7 = b_A X_{BA},$$

$$\nu_1 = i_{NXS} - f_{SI} i_{NSI} - (1 - f_{SI}) i_{NSS},\ \nu_4 = i_{NBM} - f_{XI} \cdot i_{NXI},\ \nu_6 = -i_{NBM} - \frac{1}{Y_H},\ \nu_7 = \nu_4$$

X_{STO} = oganics stored by heterotrophs

Y_{STO} = aerobic yield of stored product per S_S

K_{STO} = storage rate constant

b_{STO} = aerobic respiration rate for X_{STO}

i_{NSS} = nitrogen content of soluble substrate S_S

Mass balance relations for related substrates and biomass in steady state are presented in Eqs. 5.13 through 5.19. Total biomass in the system is

$$X_V = X_{BH} + X_S + X_{STO} + X_I \tag{5.13}$$

Mass balance of S_I

$$QS_{I0} - QS_I + f_{SI} k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH} V = 0 \tag{5.14}$$

Mass balance of S_S

$$\begin{aligned} &QS_{S0} - QS_S - k_{STO} \frac{S_S}{K_S + S_S} X_{BH} V + \\ &(1 - f_{SI}) k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH} V = 0 \end{aligned} \tag{5.15}$$

Mass balance of X_I

$$QX_{I0} - Q_w X_I - QX_{Ie} + f_{XI} b_H X_{BH} V = 0 \tag{5.16}$$

Mass balance of X_{BH}

$$QX_{BH0} - Q_w X_{BH} - QX_{BHe} + \hat{\mu}_H \frac{X_{STO}/X_H}{K_{STO} + X_{STO}/X_H} X_{BH} V - b_H X_{BH} V = 0 \tag{5.17}$$

Mass balance of X_{STO}

$$\begin{aligned} &QX_{STO0} - Q_w X_{STO} - QX_{STOe} + Y_{STO} k_{STO} \frac{S_S}{K_S + S_S} X_{BH} V - \\ &\frac{\hat{\mu}_H}{Y_H} \frac{X_{STO}/X_H}{K_{STO} + X_{STO}/X_H} X_{BH} V - b_{STO} X_{STO} V = 0 \end{aligned} \tag{5.18}$$

Mass balance of X_S

$$QX_{S0} - Q_w X_S - QX_{Se} - k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH} V = 0 \tag{5.19}$$

From Eq. 5.14

$$S_I = S_{I0} + f_{SI} k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH} \tag{5.20}$$

From Eq. 5.15

$$S_S = S_{S0} - k_{STO} \frac{S_S}{K_S + S_S} X_{BH} \theta_d + \left(1 - f_{SI}\right) k_h \frac{X_S/X_{BH}}{K_X + X_S/X_{BH}} X_{BH} \theta_d \tag{5.21}$$

Dividing Eq. 5.16 by $X_I V$ and assuming $X_{I0} = 0$ results in

$$X_I = f_{XI} b_H X_{BH} \theta_X \tag{5.22}$$

Dividing Eq. 5.17 by $X_{BH} V$ and assuming no biomass exists in the influent gives

$$\frac{1}{\theta_X} + b_H = \hat{\mu}_H \frac{X_{STO}/X_{BH}}{K_{STO} + X_{STO}/X_{BH}} \tag{5.23}$$

Rearranging Eq. 5.23 results in

$$\frac{X_{BH}}{X_{STO}} = \frac{\theta_X \left(\hat{\mu}_H - b_H\right) - 1}{K_{STO}\left(1 + b_H \theta_X\right)} \tag{5.24}$$

Dividing Eq. 5.18 by $X_{STO} V$, assuming X_{STO0} is negligible and using the identity in Eq. 5.23 yield

$$\frac{1}{\theta_X} = -Y_{STO} K_{STO} \frac{S_S}{K_S + S_S} \frac{X_{BH}}{X_{STO}} + \frac{1}{Y_H}\left(\frac{1}{\theta_X} + b_H\right) \frac{X_{BH}}{X_{STO}} + b_{STO} = 0 \tag{5.25}$$

Solving for X_{BH} / X_{STO} gives

$$\frac{X_{BH}}{X_{STO}} = \frac{\dfrac{1}{\theta_X} - b_{STO}}{\dfrac{1}{Y_H}\left(\dfrac{1}{\theta_X} + b_H\right) - Y_{STO} k_{STO} \dfrac{S_S}{K_S + S_S}} \tag{5.26}$$

Eliminating the X_{BH}/X_{STO} term from Eqs. 5.24 and 5.26 yields

$$A=\frac{B}{C-Y_{STO}D} \tag{5.27}$$

in which

$$A=\frac{\theta_X(\hat{\mu}_H-b_H)-1}{K_{STO}(1+b_H\theta_X)},\ B=\frac{1}{\theta_X}-b_{STO},\ C=\frac{1}{Y_H}\left(\frac{1}{\theta_X}+b_H\right)\text{ and }D=k_{STO}\frac{S_S}{K_S+S_S}$$

From Eq. 5.27

$$D=\frac{AC-B}{AY_{STO}} \tag{5.28}$$

By calculating D from Eq. 5.28 and using the definition of D one can obtain an equation for predicting soluble substrate in the system as

$$S_{Sm}=\frac{DK_S}{k_{STO}-D} \tag{5.29}$$

The next step is to calculate X_S and X_{BH}. Dividing Eq. 5.19 by X_SV and knowing that X_{S0} is not negligible, results in

$$\frac{X_{S0}}{X_S\theta_d}-\frac{1}{\theta_X}=k_h\frac{1}{K_X+X_S/X_{BH}} \tag{5.30}$$

Solving Eq. 5.30 with respect to X_{BH} yields

$$X_{BH}=\frac{X_S}{k_hX_S\dfrac{\theta_d\theta_X}{\theta_XX_{S0}-\theta_dX_S}-K_X} \tag{5.31}$$

From Eq. 5.15 and the definition of the variable D

$$\frac{S_{Sm}-S_{S0}}{\theta_d}=(1-f_{SI})k_h\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}X_{BH}-D\cdot X_{BH} \tag{5.32}$$

Substituting X_{BH} from Eq. 5.31 into Eq. 5.32 and using the identity in Eq. 5.30 results in a nonlinear equation with respect to X_S. It is

$$
\begin{aligned}
&S_{Sm} - S_{S0} - (1 - f_{SI})\left(\frac{X_{S0}}{X_S\theta_d} - \frac{1}{\theta_X}\right)\theta_d X_S + \\
&D \cdot \frac{X_S}{k_h X_S \dfrac{\theta_d\theta_X}{\theta_X X_{S0} - \theta_d X_S} - K_X}\theta_d = 0
\end{aligned}
\tag{5.33}
$$

Equation 5.33 is a quadratic function and it can be written in classical form as

$$aX_S^2 + bX_S + c = 0 \tag{5.34}$$

in which

$a = \theta_d^2\left[(1 - f_{SI})(k_h\theta_X + K_X) - D\theta_X\right]$;

$b = \theta_X\theta_d\left[-(1 - f_{SI})X_{S0}(\theta_X k_h + 2K_X) + \theta_X X_{S0} D + (S_{Sm} - S_{S0})(\theta_X k_h + K_X)\right]$ and

$c = \theta_X^2 K_X X_{S0}\left[(1 - f_{SI})X_{S0} - (S_{Sm} - S_{S0})\right]$

Based on ranges of parameters, typical values of ASM3 in the literature and the data, it was found that in this system $X_S = (-b - \sqrt{b^2 - 4ac})/(2a)$.

By knowing X_S, X_{BH} is calculated from Eq. 5.31, X_I and X_{STO} are calculated using Eqs. 5.22 and 5.24, respectively. Total biomass in the system is found by using Eq. 5.13 and its prediction is compared the data to calculate the error in the modeling.

5.4.2 Parameter Estimation

All parameters and their ranges and relations between them are defined in AQUASIM. Unfortunately the literature for ASM3 modeling is very limited and just a few investigations have been made on it and its sensitivity. Because of that, parameter ranges are not well established. Koch et al. (2000) and Gujer et al. (1999) are two references that have been used to find parameter initial values and their ranges. In order to capture the best parameter set, these ranges were made wider according to engineering judgements and physical meaning of them (Table 5.5).

Table 5.5 Range of ASM3 Parameters (Carbon Processes)*

Parameter	b_H	b_{STO}	f_{SI}	f_{XI}	k_h	K_S	K_{STO}	k_{STO}	K_X	$\hat{\mu}_H$	Y_H	Y_{STO}
Units	d^{-1}	d^{-1}	mg/mg	mg/mg	d^{-1}	mg/L	mg/mg	d^{-1}	mg/mg	d^{-1}	mg/mg	mg/mg
L Bound	0.1	0.1	0	0	0.1	1	0	1	0.5	1	0.55	0.6
U Bound	1.5	1.0	0.1	0.4	10	120	2.8	10	2	10	0.75	0.9

*Based on COD

Although tens of parameter sets providing acceptable predictions were found for the system, they are mostly similar and differences are negligible. As for ASM1 any other parameter sets with parameters outside the selected ranges that result in unrealistic physical characterization of the system, can be found to give reasonable to good predictions. The parameter set 5 is representative of them. Among the results, four of the best sets are shown in Table 5.6.

Table 5.6 Parameter Estimation Results for ASM3 (Carbon Processes)

Parameter	b_H	b_{STO}	f_{SI}	f_{XI}	k_h	K_S	K_{STO}
Set 1	0.699	0.633	0.0	0.380	2.21	63.5	1.51
Set 2	0.601	0.538	0.0	0.349	1.98	72.5	1.53
Set 3	0.643	0.497	0.0	0.338	5.79	59.3	1.93
Set 4	0.485	0.764	0.0	0.347	0.71	109.6	2.72
Set 5	0.735	0.536	0.0	0.779	3.68	51.2	1.90

Parameter (Cont')	k_{STO}	K_X	$\hat{\mu}_H$	Y_H	Y_{STO}	R^2 of S_S	R^2 of X_V
Set 1	5.34	1.019	3.18	0.66	0.860	0.830	0.961
Set 2	5.77	1.214	3.14	0.61	0.822	0.823	0.953
Set 3	4.67	0.516	3.75	0.64	0.876	0.827	0.947
Set 4	7.50	0.621	3.56	0.64	0.818	0.834	0.959
Set 5	6.66	0.368	3.65	0.56	0.711	0.817	0.998

Among the four parameter sets, set one was taken for further calculations. Because it has the highest R^2 while the parameter values are in the range typically found. Table 5.7 shows application of the first parameter set to ASM3. This table was filled row by row in the modeling because each row is dependent on the row before. Components of biomass removal according to ASM3 are shown in Fig. 5.3. The predicted behaviour of the system for substrate removal according to this model is shown in Fig. 5.5.

Comparison of models shows that ASM3 provides the best prediction for substrate removal of the system under investigation among all models.

Table 5.7 Applying the First Parameter Set of Carbon Processes to ASM3

Variable	Unit	Run#						Explanation (Equation#)
		1	2	3	4	5	6	
Data:								
S_S	mg/L	48	39	22	44	31	46	–
X_V	mg/L	1571	6063	11715	814	3110	3836	–
Model:								
S_{Sm}	mg/L	47.2	32.8	28.4	45.8	32.9	44.8	(5.29)
Res. Err.	%	2	16	–29	–3	–6	3	(4.14)
X_S	mg/L	373	652	583	217	342	656	(5.34)
X_{BH}	mg/L	820	1336	1385	452	672	1602	(5.31)
X_{STO}	mg/L	492	2387	2923	259	1195	1854	(5.26)
X_I	mg/L	224	2147	5725	119	1059	918	(5.22)
X_V	mg/L	1908	6523	10615	1047	3269	5039	(5.13)
Res. Err.	%	–21	–7	9	–28	–5	–31	(4.14)

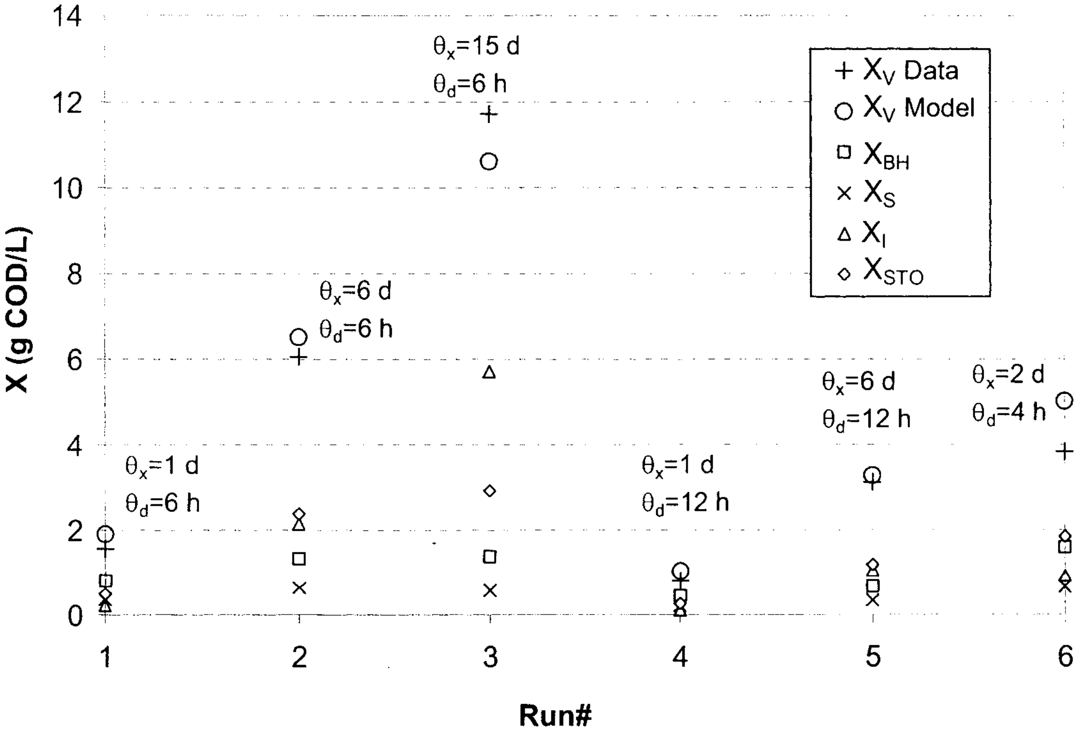


Fig. 5.3 Biomass Components According to ASM3

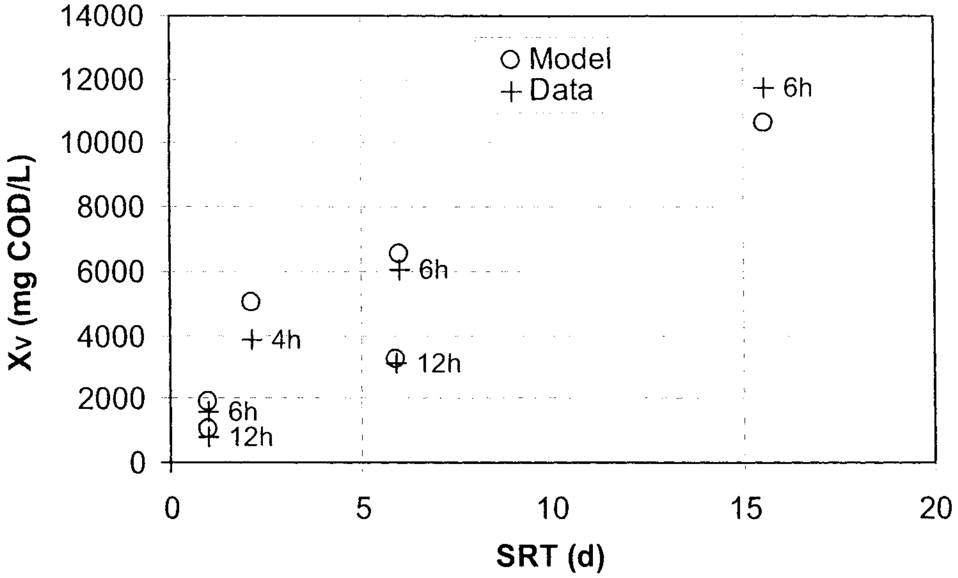


Fig. 5.4 Biomass Growth According to ASM3

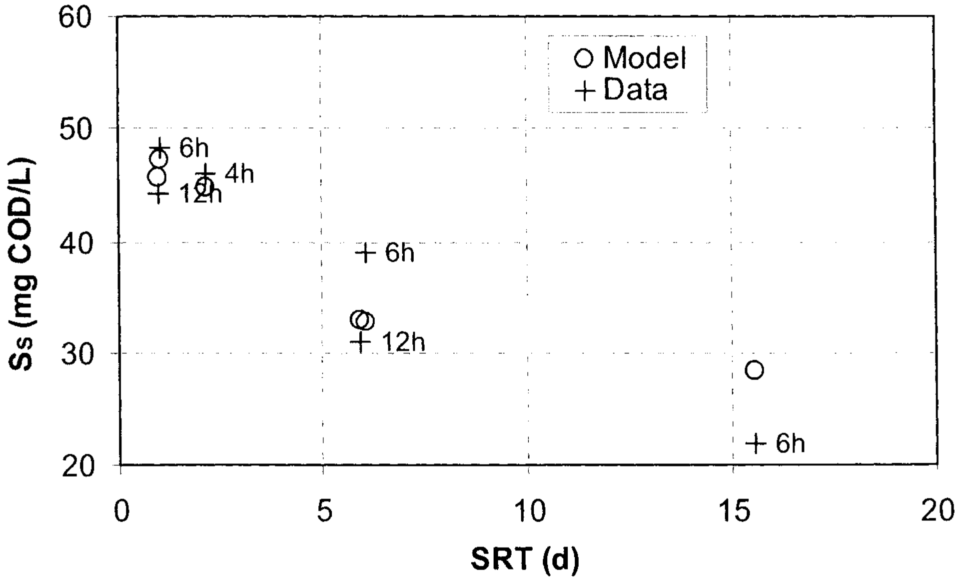


Fig. 5.5 Effluent Soluble Substrate Modeling According to ASM3

5.4.3 Sensitivity Analysis

It is worthwhile to perform a sensitivity analysis on the ASM3 model, because of limitations of the literature on this subject. Sensitivity analysis helps to assess the identifiability of the model parameters, which is a check if these parameters can be uniquely determined with the available data. AQUASIM was used to accomplish this task. AQUASIM has a feature that allows the user to calculate linear sensitivity analyses with respect to each of the parameters included in the model.

Four sensitivity functions are distinguished by AQUASIM. If y is an arbitrary variable calculated by AQUASIM and p is a model parameter, these functions are:

1) Absolute-absolute, $\delta_{y,p}^{a,a} = \partial y/\partial p$, which measures the absolute change in y per unit of change in p.
2) Relative-absolute, $\delta_{y,p}^{r,a} = (\partial y/\partial p)/y$, which measures the relative change in y per unit of change in p.
3) Absolute-relative, $\delta_{y,p}^{a,r} = p(\partial y/\partial p)$, which measures the absolute change in y for a 100% change in p.
4) Relative-relative, $\delta_{y,p}^{r,r} = p(\partial y/\partial p)/y$, which measures the relative change in y for a 100% change in p.

The most useful sensitivity function is a relative-relative function, because it is dimensionless. This makes possible the quantitative comparisons of the effect of different parameters on a common variable as well as the effect of different variables on a common parameter. However, the disadvantage of this function is that it does not give useful results if the value of the variable y is small. The larger the value and the more pronounced the differences in slope of sensitivity function shows that the model is more sensitive to the parameter. It also shows a higher identifiability of that parameter.

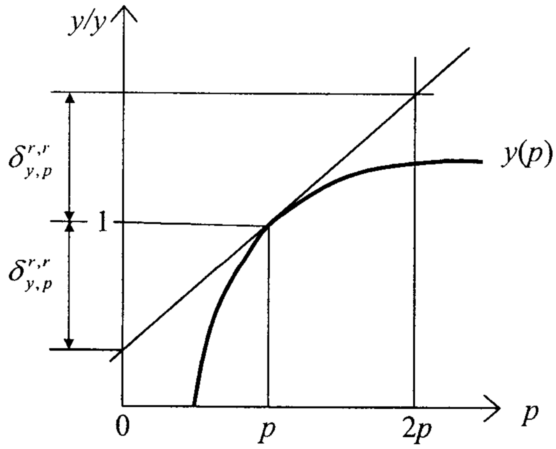


Fig. 5.6 Interpretation of Relative-Relative Sensitivity Analysis Function

It is of importance to note that the results of sensitivity analysis depend on the estimated values for model parameters. The result can be different if another set of parameters is selected. Sensitivity analysis results for X_V are shown in Fig. 5.7. In the sensitivity analysis of S_S (Fig. 5.8), parameters with a value of zero were removed for clarity. Separated points on these two figures are connected to improve clarity and to make comparison of the parameters easier.

These two figures contain notable amount of information about the behaviour of the system. For example Fig. 5.7 shows that 100% increase in Y_H results in 112% increase in X_V for the first run. According to Fig. 5.8 the same change results in 323% decrease in the value of S_S.

From Fig. 5.7 one can conclude that biomass modeling is sensitive to Y_H, Y_{STO}, b_H, $\hat{\mu}_H$, b_{STO}, f_{XI}, K_{STO} and k_{STO}, from the most to the least sensitive parameter. The sensitivity of the function to K_S, K_X and k_h is very low. It can be seen from Fig. 5.8 that soluble substrate modeling is sensitive to Y_H, Y_{STO}, k_{STO}, b_H, b_{STO}, $\hat{\mu}_H$, K_{STO} and K_S, from the most to the least sensitive parameter. The function is not sensitive to K_X. Considering both biomass and substrate, ASM3 for the system under investigation is most sensitive to Y_H, Y_{STO}, b_H, b_{STO}, k_{STO} and $\hat{\mu}_H$. The sensitivity of the model to f_{XI}, K_{STO}, K_S, K_X and k_h is low or very low.

The sensitivity functions of the parameters k_{STO}, b_{STO} and Y_{STO} have a similar shape on both figures (the negative sign indicate that the model variable decreases with increasing of the parameter). It shows a correlation between the estimations of these parameters, which means changes in calculated model variable caused by a change in Y_{STO} can be approximately be compensated by a change in b_{STO} *or* k_{STO}. The same correlation exists for $\hat{\mu}_H$ and K_{STO}. The following is an example of how useful a sensitivity analysis can be. The average of relative-relative sensitivity function for Y_{STO} and k_{STO} for biomass modeling is 0.95 and 0.11 respectively. While these two parameters exhibit the same behaviour. From the sensitivity analysis, it can be concluded that the model is almost six times more sensitive to Y_{STO} than k_{STO}. Therefore a relative change in Y_{STO} must be replaced with a relative change seven times larger in k_{STO}.

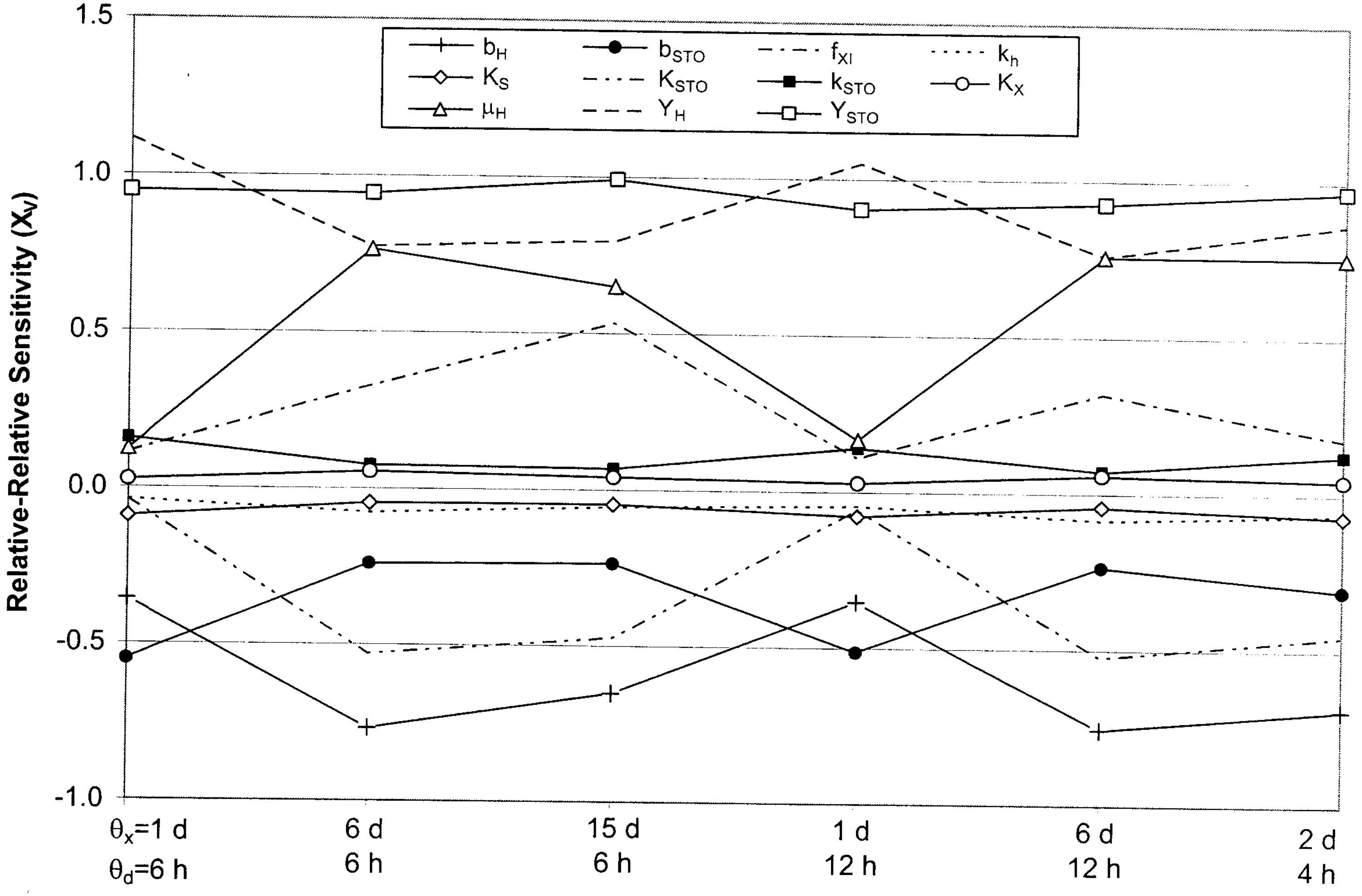


Fig. 5.7 Sensitivity Analysis for Biomass Modeling

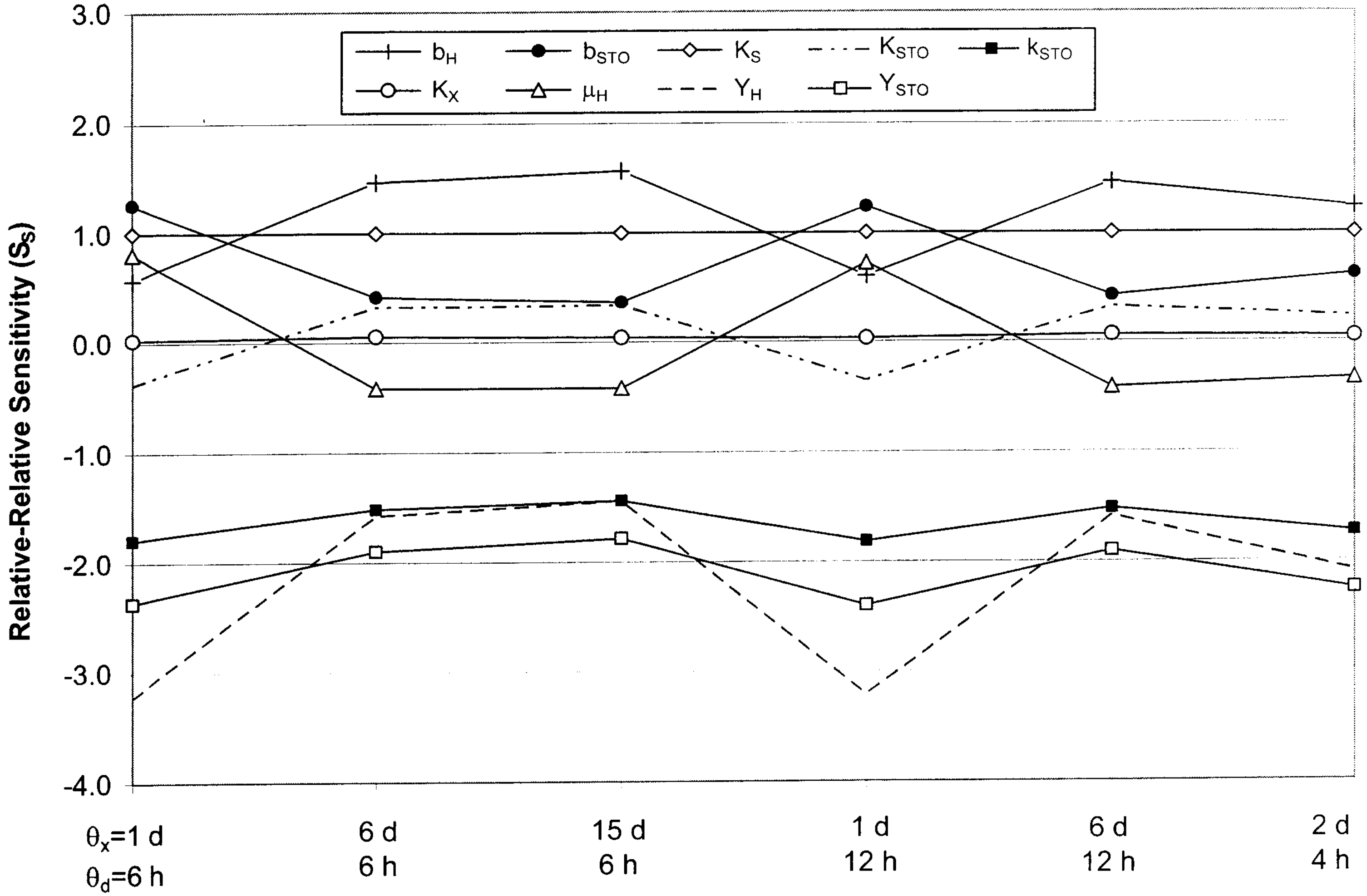


Fig. 5.8 Sensitivity Analysis for Substrate Modeling

5.5 ASM3: Nitrogen Processes

5.5.1 Derivations

In this section the equations necessary for modeling of nitrogen according to ASM3 are derived. Nitrogen in the system is presented in the form of nitrate and nitrite nitrogen S_{NO}, ammonium and ammonia nitrogen S_{NH} and dinitrogen N_2. Dinitrogen is in the form of gas and is produced in the anoxic processes, thus it can be neglected in the system under discussion.

Fundamental equations of the model in steady state are presented in Eqs. 5.35, 5.36 and 5.37. Mass balance of X_{BA}

$$\begin{aligned} &QX_{BA0} - Q_w X_{BA} - QX_{BAe} + \\ &\hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA} V - b_A X_{BA} V = 0 \end{aligned} \tag{5.35}$$

Mass balance of S_{NO}

$$QS_{NO0} - QS_{NO} + \frac{1}{Y_A} \hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} X_{BA} V = 0 \tag{5.36}$$

Mass balance of S_{NH}

$$\begin{aligned} &QS_{NH0} - QS_{NH} + \left(i_{NBM} - f_{XI} i_{NXI}\right)\left(b_A X_{BA} + b_H X_{BH}\right)V + \\ &\left[i_{NXS} - f_{SI} i_{NSI} - (1 - f_{SI}) i_{NSS}\right] k_h \left(\frac{X_S / X_{BH}}{K_X + X_S / X_{BH}}\right) X_{BH} V + \\ &i_{NSS} k_{STO} \left(\frac{S_S}{K_S + S_S}\right) X_{BH} V + \left(-i_{NBM} - \frac{1}{Y_A}\right) \hat{\mu}_A \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right) X_{BA} V - \\ &i_{NBM} \hat{\mu}_H \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right)\left(\frac{X_{STO} / X_{BH}}{K_{STO} + X_{STO} / X_{BH}}\right) X_{BH} V = 0 \end{aligned} \tag{5.37}$$

From Eq. 5.35 assuming $X_{BA0} = 0$, one can find an equation identical to Eq. 5.10 for prediction of S_{NO}. Dividing both sides of Eq. 5.37 by V results in the following relation for predicting S_{NH}

$$\begin{aligned}
S_{NH} &= S_{NH0} + \left(i_{NBM} - f_{XI} i_{NXI}\right)\left(b_A X_{BA} + b_H X_{BH}\right)\theta_d + \\
&\left[i_{NXS} - f_{SI} i_{NSI} - (1-f_{SI}) i_{NSS}\right] k_h \left(\frac{X_S/X_{BH}}{K_X + X_S/X_{BH}}\right) X_{BH}\theta_d + \\
&i_{NSS} k_{STO} \left(\frac{S_S}{K_S + S_S}\right) X_{BH}\theta_d + \left(-i_{NBM} - \frac{1}{Y_A}\right)\hat{\mu}_A \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right) X_{BA}\theta_d - \\
&i_{NBM}\hat{\mu}_H \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right)\left(\frac{X_{STO}/X_{BH}}{K_{STO} + X_{STO}/X_{BH}}\right) X_{BH}\theta_d
\end{aligned} \tag{5.38}$$

And from Eq. 5.36 the relation for predicting S_{NO} is

$$S_{NO} = S_{NO0} + \frac{\theta_d}{Y_A}\left(\frac{1}{\theta_X} + b_A\right) X_{BA} \tag{5.39}$$

5.5.2 Parameter Estimation

For the same reasons as ASM1 and ASM2, nitrogen processes modeling based on ASM3 does not yield good predictions. Complexity of the equation for S_{NH} is another reason for poor modeling. Table 5.8 shows the selected ranges for parameters involved in the modeling of nitrogen modeling. Table 5.9 shows three of the best parameter sets found.

Table 5.8 Range of ASM3 Parameters (Nitrogen Processes)

Parameter	f_{XBA}	Y_A	b_A	i_{NSI}	i_{NSS}	i_{NXI}	i_{NXS}	i_{NBM}	$\hat{\mu}_A$
U. Baund	0.01	0.15	0	0	0	0.01	0	0.01	0.1
L. Bound	0.05	0.25	0.3	0.02	0.05	0.25	0.05	0.05	2.0

Table 5.9 Parameters Estimation Results for Nitrogen Processes of ASM3

Parameter	f_{XBA}	Y_A	b_A	i_{NSI}	i_{NSS}	i_{NXI}	i_{NXS}	i_{NBM}	$\hat{\mu}_A$	ε of S_{NO}	ε of S_{NH}
Set 1	0.015	0.24	0.16	0	0.001	0.20	0	0.013	0.84	7.6	3.4
Set 2	0.014	0.24	0.20	0	0.003	0.21	0.001	0.001	0.84	7.6	5.0
Set 3	0.016	0.24	0.27	0	0.003	0.06	−0.044	0.004	0.84	8.3	4.5

Ammonia and ammonium prediction of ASM3 model based on parameter set 1 is shown in Fig. 5.9. ASM3 model for nitrate and nitrite behaviour of system based on parameter set 1 is shown in Fig. 5.10. The latter is based on the modified formula as presented in Chapter 4. The value of R^2 for S_{NH} and S_{NO} are –6.6 and 0.74, respectively.

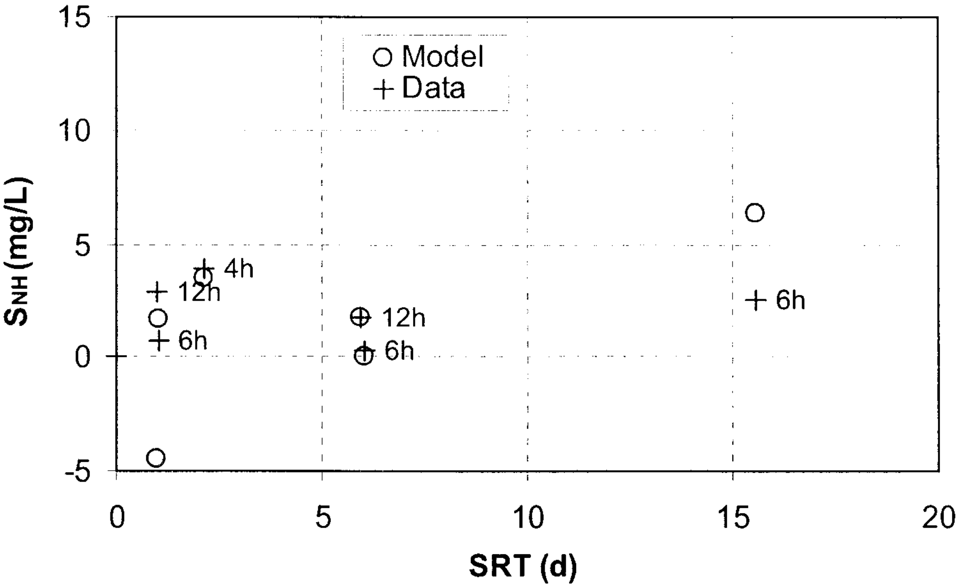


Fig. 5.9 Ammonia and Ammonium Nitrogen Based on the ASM3

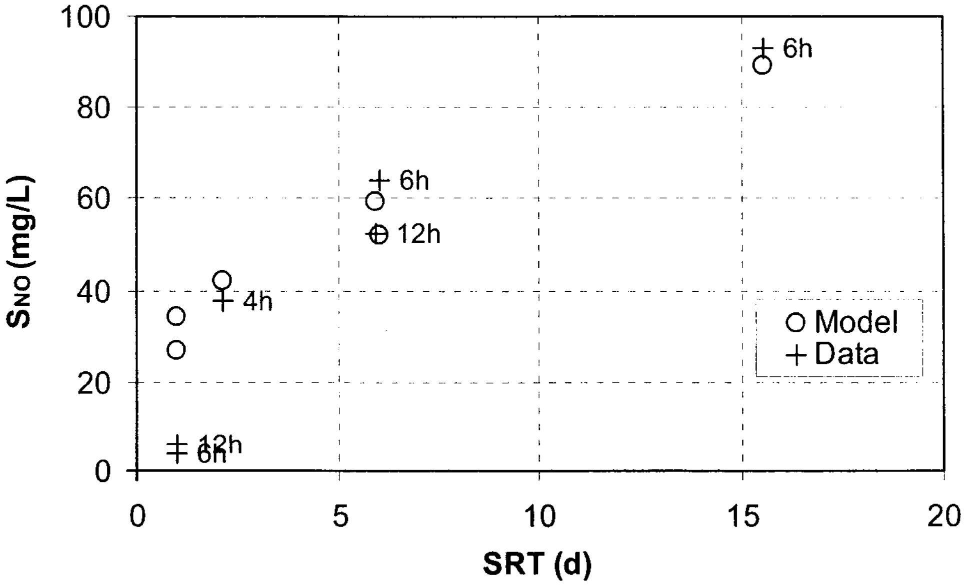


Fig. 5.10 Nitrate and Nitrite Nitrogen Based on the ASM3 (Modified Formula)

5.6 Empirical Model for Total Substrate (S_e)

None of the described models can predict the amount of total effluent substrate S_e as accurately as biomass predictions. The best coefficient of determination that can be attained is less than 0.3 by using these models. For that reason an attempt was made to find an empirical model capable of modeling total substrate.

This model is actually a modification of the McKinney model. This model is selected because of its simplicity. By neglecting inert COD, total substrate according to the McKinney model is

$$S_e = \frac{S_0}{1 + K_m \theta_d} \tag{5.40}$$

By solving Eq. 5.40 for K_m one can find

$$K_m = \frac{S_0 - S_e}{S_e \theta_d} \tag{5.41}$$

The value of K_m is calculated for each run. These are 20.1, 54.9, 78.8, 19.4, 37.2 and 27.4 mg/L, respectively. The values of K_m show a relation with SRT, because when SRT is high, K_m is high as well and vice versa. Standard deviation of the calculated values is 23.3 which is very high for the range. A function $f(\theta_X)$ that causes the transformed K_m as $K_m / f(\theta_X)$ to have a small standard deviation is sought. Different functions were tried such as $\ln \theta_x$, $\sqrt[3]{\theta_x}$, $\sqrt[3]{\theta_x^2}$, θ_x and $\sqrt{\theta_x}$. Finally the most suitable function was found to be $\sqrt{SRT}$. If the calculated values of K_m are divided by corresponding $\sqrt{\theta_x}$, the result will be 20.0, 19.8, 22.3, 19.5, 15.3 and 18.7 mg/L, respectively. Standard deviation and average of these new values are 2.3 and 19.3 mg/L, respectively. As a result an empirical model is proposed as

$$S_e = \frac{S_0}{1 + K_m \theta_d \sqrt{\theta_X}} \tag{5.42}$$

Equation 5.42 when $K_m = 19.3\ d^{-1}$ results in a model (Fig. 5.11) with coefficient of determination, $R^2 = 0.985$. This model was unable to be improved noticeably by including non-biodegradable substrate S_I.

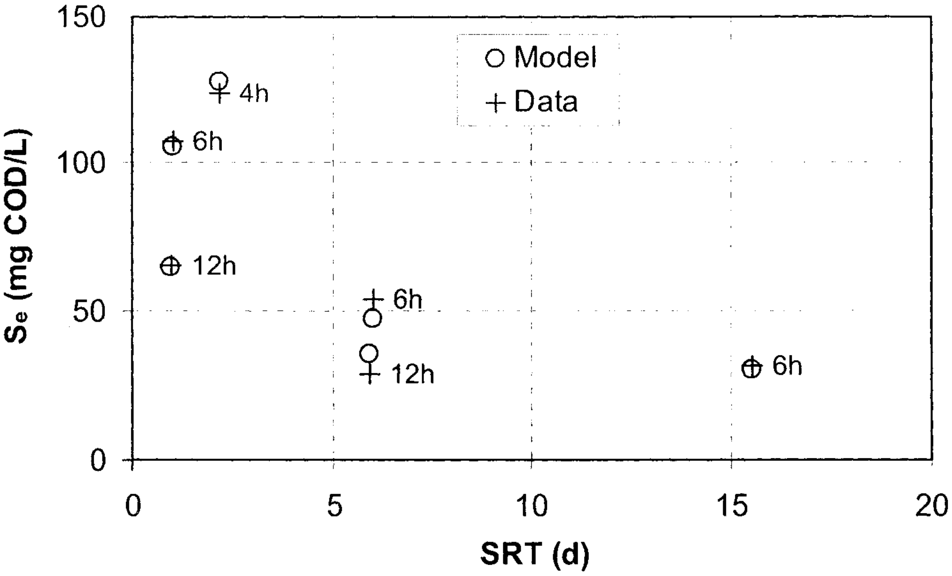


Fig. 5.11 Empirical Model for Substrate Removal (Total)

Although the empirical model yields near perfect results in this case, it needs more investigation to become reliable.

Chapter 6

Conclusions and Recommendations

Based on this study the principal conclusions are:

1) This membrane reactor is not efficient for low HRTs; also, performance was not good when HRT and SRT are high at the same time.
2) Over operating conditions where the membrane provided reasonable separation of solids, the system has COD removal between 93 and 97% with an average of 94%.
3) Substrate removal rates that are independent of biomass concentration X_V, cannot provide good prediction of system behaviour.

A comparison of the R^2 and ε criteria for different models of carbon and nitrogen processes are presented in Table 6.1 and Table 6.2, respectively. The model was developed based on the criterion without parenthesis.

Table 6.1 Comparison of $R^2(\varepsilon)$ for Different Models of Carbon Processes

Model	L&M	G&E	ASM1	ASM2	ASM3	Empirical
X_V	0.994 (0.357)	0.996 (0.164)	0.993 (0.162)	0.993 (0.162)	0.961 (0.493)	-
S_{Se}	0.691 (0.369)	0.721 (0.342)	0.602 (0.472)	0.602 (0.472)	0.830 (0.340)	-
S_e	-	-	-	-	-	0.985 (0.252)

Table 6.2 Comparison of ε (R^2) for Different Models of Nitrogen Processes

Model	ASM1	ASM2	ASM3
NH_3	13.6 (–20.5)	9.8 (–19.7)	3.4 (–6.6)
NO_3	5.6 (0.83)	9.8 (–0.54)	7.6 (0.74)
ON	1.7 (–0.01)	-	-

4) The best simple rate for substrate removal is $r_S = -KS_eX_V$ and replacement of X_V with X_a does not improve the model.
5) The empirical model fits well with data based on total COD.
6) Comparing X_{BH}, X_S and X_P in ASM1 and X_{BH}, X_S, X_I and X_{STO} in ASM3 shows X_{BH} in both are similar, X_P and X_S in ASM1 are equivalent to X_I and X_S+X_{STO} in ASM3, respectively. This is expected from the formulation and means that parameter estimation of these two models is not far from reality.
7) ASM3 predicts carbon removal of the system better than all other models. This modeling improvement is almost 12% compared to the Goodman and England model. The Lawrence and McCarty and Goodman and England models can predict biomass growth slightly better than IWA models. This signifies that in practice simple models are equivalent to IWA models, while IWA models are better for research purposes, because they give better insight into the system.
8) The ASM3 model for the system under investigation is most sensitive to Y_H, Y_{STO}, b_H, b_{STO}, $\hat{\mu}_H$ and k_{STO}, from the most to the least sensitive. The sensitivity of the model to f_{SI}, K_{STO}, K_S, K_X and k_h is low or very low.
9) ASM3 provides better prediction than ASM1 for nitrogen components of the system. The number of parameters in ASM1 is less than ASM3, while ASM3 does not need measurement of organic nitrogen. At the same time, ASM3 gives better understanding of the system.

Based on the research has been done, the following is suggested for future studies

1) Stoichiometric parameters should be measured experimentally based on IWA task group recommendations to assess the validity of the estimated values.
2) More runs with different operating conditions may be performed to finalize the developed models.
3) More studies should be done on nitrogen components of system, in order to find a reliable model.

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Appendix A: Raw Data

Table A.1 Test Data for 6 Hours HRT and 1 Day SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.28	1.1	620	91	410	47	438	49	360	16	1188	11	1080	6
13/Dec/01	6.25	1.0	719	114	427	45	456	50	300	23	1290	17	1160	13
15/Dec/01	6.20	1.0	621	110	334	53	392	42	204	11	1230	44	1080	20
Ave.	6.24	1.03	653.3	105.0	390.3	48.3	428.7	47.0	288.0	16.7	1236.0	24.0	1106.7	13.0
Std. dev.	0.03	0.05	46.4	10.0	40.4	3.4	26.9	3.6	64.2	4.9	41.9	14.4	37.7	5.7

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.28	1.1	7.6	7.6	19	254	77	199	27	1.9	9	4	22.8	4.8
13/Dec/01	6.25	1.0	7.2	7.5	19	189	61	113	32	0.0	9	3	29.8	0.6
15/Dec/01	6.20	1.0	7.3	7.1	20	218	114	139	29	0.1	16	5	30.0	1.2
Ave.			7.4	7.4	19.3	220.3	84.0	150.3	29.3	0.7	11.3	4.0	27.5	2.2
Std. dev.			0.2	0.2	0.5	26.6	22.2	36.0	2.1	0.9	3.3	0.8	3.3	1.9

Date	HRT	SRT	P*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.28	1.1	4.43	3.75	5.20	0.65	0	1.56	0.17	0.96	1.55	0.13	0	0.47
13/Dec/01	6.25	1.0	5.44	6.46	4.97	1.53	0.93	1.70	0.74	1.04	3.61	0.55	0.37	0.34
15/Dec/01	6.20	1.0	4.60	2.39	5.10	1.18	1.96	1.85	0.47	0.98	3.95	0.18	0.98	0.87
Ave.			4.8	4.2	5.1	1.1	1.0	1.7	0.5	1.0	3.0	0.3	0.5	0.6
Std. dev.			0.4	1.7	0.1	0.4	0.8	0.1	0.2	0.0	1.1	0.2	0.4	0.2

* Phosphorus (React = Reactive, A.H. = Acid Hydrolysed, A.D. = Acid Digested)

Table A.2 Test Data for 6 Hours HRT and 6 Days SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Nov/01	6.15	5.9	708	42	484	29	438	12	348	9	4530	13	3980	8
03/Dec/01	6.10	6.2	718	46	360	44	-	-	-	-	4680	8	4290	-
06/Dec/01	6.13	6.1	706	54	396	44	450	11	250	10	4920	8	4540	4
Ave.	6.13	6.07	710.7	47.3	413.3	39.0	444.0	11.5	299.0	9.5	4710.0	9.7	4270.0	6.0
Std. dev.	0.02	0.12	5.2	5.0	52.1	7.1	6.0	0.5	49.0	0.5	160.6	2.4	229.1	2.0

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Nov/01	6.15	5.9	5.7	4.2	20	218	117	101	25	0.2	15	87	26.1	1.5
03/Dec/01	6.10	6.2	6.5	3.6	23	216	99	120	24	0.4	7	46	24.2	2.0
06/Dec/01	6.13	6.1	6.7	5.4	20	168	62	80	26	0.3	8	59	25.1	2.7
Ave.			6.3	4.4	21.0	200.7	92.7	100.3	25.0	0.3	10.0	64.0	25.1	2.1
Std. dev.			0.4	0.7	1.4	23.1	22.9	16.3	0.8	0.1	3.6	17.1	0.8	0.6

Date	HRT	SRT	P*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Nov/01	6.15	5.9	6.31	5.98	6.31	1.37	0.90	2.75	3.28	3.20	4.81	2.75	2.46	3.99
03/Dec/01	6.10	6.2	6.27	6.61	6.27	2.02	1.95	3.20	3.18	3.47	3.98	2.88	3.30	2.59
06/Dec/01	6.13	6.1	5.87	6.21	5.87	2.08	2.01	2.18	3.23	3.56	3.36	2.99	2.91	2.96
Ave.			6.2	6.3	6.2	1.8	1.6	2.7	3.2	3.4	4.1	2.9	2.9	3.2
Std. dev.			0.2	0.3	0.2	0.3	0.5	0.4	0.0	0.2	0.6	0.1	0.3	0.6

Table A.3 Test Data for 6 Hours HRT and 15 Days SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.25	15.8	620	27	410	20	438	7	348	-	9300	0	8210	0
13/Dec/01	6.13	15.4	719	33	427	22	-	-	-	-	9810	2	8530	0
15/Dec/01	6.17	15.5	621	32	334	24	392	4	250	-	9110	4	8010	2
Ave.	6.18	15.57	653.3	30.7	390.3	22.0	415.0	5.5	299.0	-	9406.7	2.0	8250.0	0.7
Std. dev.	0.05	0.17	46.4	2.6	40.4	1.6	23.0	1.5	49.0	-	295.6	1.6	214.2	0.9

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.25	15.8	7.4	7.0	18	254	77	141	27	2.0	9	103	22.8	0.6
13/Dec/01	6.13	15.4	6.8	6.0	19	189	61	76	32	3.0	9	74	29.8	6.6
15/Dec/01	6.17	15.5	7.0	6.6	18	218	114	88	29	2.5	16	102	30.0	4.6
Ave.			7.1	6.5	18.3	220.3	84.0	101.7	29.3	2.5	11.3	93.0	27.5	3.9
Std. dev.			0.2	0.4	0.5	26.6	22.2	28.2	2.1	0.4	3.3	13.4	3.3	2.5

Date	HRT	SRT	P^*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
10/Dec/01	6.25	15.8	4.43	3.75	5.20	0.65	0.00	1.56	2.86	2.63	2.88	2.54	2.79	2.76
13/Dec/01	6.13	15.4	5.44	6.46	4.97	1.53	0.93	1.70	2.46	1.28	2.28	2.26	1.82	1.85
15/Dec/01	6.17	15.5	4.60	2.39	5.10	1.18	1.96	1.85	2.85	1.01	4.72	2.47	1.81	2.85
Ave.			4.8	4.2	5.1	1.1	1.0	1.7	2.7	1.6	3.3	2.4	2.1	2.5
Std. dev.			0.4	1.7	0.1	0.4	0.8	0.1	0.2	0.7	1.0	0.1	0.5	0.5

Table A.4 Test Data for 12 Hours HRT and 1 Day SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.87	1.0	756	65	435	45	462	32	330	27	530	44	530	30
03/Jan/01	12.97	1.0	711	70	385	49	496	27	314	8	585	25	565	12
05/Jan/01	12.55	1.0	732	59	433	39	455	11	321	5	630	12	625	6
Ave.	12.8	1.00	733.0	64.7	417.7	44.3	471.0	23.3	321.7	13.3	581.7	27.0	573.3	16.0
Std. dev.	0.18	0.00	18.4	4.5	23.1	4.1	17.9	9.0	6.5	9.7	40.9	13.1	39.2	10.2

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.87	1.0	7.5	8.3	17	203	104	162	31	5.4	15	7	33.1	13.1
03/Jan/01	12.97	1.0	8.2	8.8	16	341	209	289	24	1.4	21	5	29.0	5.4
05/Jan/01	12.55	1.0	7.5	9.5	17	284	184	213	28	1.9	14	6	33.6	4.5
Ave.			7.7	8.9	16.7	276.0	165.7	221.3	27.7	2.9	16.7	6.0	31.9	7.7
Std. dev.			0.3	0.5	0.5	56.6	44.8	52.2	2.9	1.8	3.1	1.0	2.1	3.9

Date	HRT	SRT	P^*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.87	1.0	5.92	5.71	6.50	0.99	1.07	1.64	0.87	0.99	1.80	1.04	0.91	0.96
03/Jan/01	12.97	1.0	6.13	5.87	6.35	1.71	1.36	1.73	0.27	0.71	0.84	0.34	0.22	0.25
05/Jan/01	12.55	1.0	5.25	5.83	6.26	0.72	1.18	1.82	0.14	0.32	0.61	0.04	0.22	0.35
Ave.			5.8	5.8	6.4	1.1	1.2	1.7	0.4	0.7	1.1	0.5	0.5	0.5
Std. dev.			0.4	0.1	0.1	0.4	0.1	0.1	0.3	0.3	0.5	0.4	0.3	0.3

Table A.5 Test Data for 12 Hours HRT and 6 Days SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.52	5.6	756	37	435	30	462	20	330	15	2180	20	2100	15
03/Jan/01	12.63	5.8	711	36	385	34	496	10	314	4	2550	11	2310	9
05/Jan/01	12.34	6.1	732	35	433	29	455	4	321	2	2300	10	2160	7
Ave.	12.5	5.85	733.0	36.0	417.7	31.0	471.0	11.3	321.7	7.0	2343.3	13.7	2190.0	10.3
Std. dev.	0.12	0.21	18.4	0.8	23.1	2.2	17.9	6.6	6.5	5.7	154.1	4.5	88.3	3.4

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.52	5.6	7.5	8.4	17	203	104	135	31	3.3	15	43	33.1	6.4
03/Jan/01	12.63	5.8	8.1	8.5	16	341	209	278	24	0.5	21	46	29.0	3.3
05/Jan/01	12.34	6.1	7.5	7.9	18	284	184	170	28	1.5	14	68	33.6	2.5
Ave.			7.7	8.3	17.0	276.0	165.7	194.3	27.7	1.8	16.7	52.3	31.9	4.1
Std. dev.			0.3	0.3	0.8	56.6	44.8	60.9	2.9	1.2	3.1	11.1	2.1	1.7

Date	HRT	SRT	P^*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
29/Dec/01	12.52	5.6	5.92	5.71	6.50	0.99	1.07	1.64	2.94	2.79	2.84	2.64	2.96	2.84
03/Jan/01	12.63	5.8	6.13	5.87	6.35	1.71	1.36	1.73	2.29	2.56	2.49	2.52	2.10	2.29
05/Jan/01	12.34	6.1	5.25	5.83	6.26	0.72	1.18	1.82	2.76	3.20	2.88	2.67	2.98	2.72
Ave.			5.8	5.8	6.4	1.1	1.2	1.7	2.7	2.9	2.7	2.6	2.7	2.6
Std. dev.			0.4	0.1	0.1	0.4	0.1	0.1	0.3	0.3	0.2	0.1	0.4	0.2

Table A.6 Test Data for 4 Hours HRT and 2 Days SRT

Date	HRT	SRT	Total COD		Soluble COD		Total BOD		Soluble BOD		TSS		VSS	
			Feed	Eff.	Feed	Eff.	Feed	Eff.	Feed	Eff.	Reactor	Eff.	Reactor	Eff.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
25/Jun/02	4.01	2.1	645	120	375	53					2735	48	2560	38
28/Jun/02	3.91	2.2	771	132	537	38	585	72	379	13	2923	85	2745	76
02/Jul/02	3.94	2.2	691	130	480	47				24	2990	70	2800	50
Ave.	4.0	2.17	702.3	127.3	464.0	46.0	585.0	72.0	379.0	18.5	2882.7	67.7	2701.7	54.7
Std. dev.	0.04	0.05	52.1	5.2	67.1	6.2	0.0	0.0	0.0	5.5	107.9	15.2	102.7	15.9

Date	HRT	SRT	pH	DO	Temp.	Alkalinity			NH_3-N		NO_3^--N		TKN	
						Feed(t)	Feed(p)	Eff.(t)	Feed	Eff.	Feed	Eff.	Feed	Eff.
	hours	days		mgL^{-1}	°C	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
25/Jun/02	4.01	2.1	7.0	5.8	19	210	88	90	29	4.4	20	61	36.7	8.5
28/Jun/02	3.91	2.2	6.8	6.4	21	240	145	104	30	3.7	21	31	27.1	9.2
02/Jul/02	3.94	2.2	7.0	5.8	20	225	125	111	27	3.6	18	21	26.7	11.9
Ave.			6.9	6.0	20.0	225.0	119.3	101.7	28.7	3.9	19.7	37.7	30.2	9.9
Std. dev.			0.1	0.3	0.8	12.2	23.6	8.7	1.5	0.4	1.2	17.0	5.7	1.8

Date	HRT	SRT	P^*, Feed (NF)			P, Feed (F)			P, Eff. (NF)			P, Eff. (F)		
			React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.	React.	A.H.	A.D.
	hours	days	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
25/Jun/02	4.01	2.1	6.31	4.01	7.31	3.76	2.79	4.27	1.81	0.00	1.74	2.57	1.68	3.68
28/Jun/02	3.91	2.2	5.92	6.13	7.12	2.43	2.96	4.06	0.11	0.35	0.54	0.14	1.44	2.50
02/Jul/02	3.94	2.2	5.00	5.57	7.79	4.49	4.28	4.58	0.78	1.44	2.82	0.35	0.10	1.36
Ave.			5.7	5.2	7.4	3.6	3.3	4.3	0.9	0.6	1.7	1.0	1.1	2.5
Std. dev.			0.5	0.9	0.3	0.9	0.7	0.2	0.7	0.6	0.9	1.1	0.7	0.9

Appendix B: IWA models

Appendix B: IWA Models

Symbol Definitions

Variables

Symbol	Definition
	Carbon
COD_{sol}	total soluble COD, mg/l
S_A	VFA (mg COD/l)
S_I	nbd (inert) soluble COD (mg/l)
S_S	degradable soluble COD (mg/l)
X_I	nbd particulate COD (mg/l)
X_S	degradable particulate organics (mg COD/l, mg BOD/l)
X_{STO}	stored COD (mg/l)
	Nitrogen
S_{N2}	N_2 (mg N/l)
S_{NH}	$NH_3 + NH_4^+$ (mg N/l)
S_{NI}	nbd soluble organic N (mg N/l)
S_{No}	degradable soluble organic N (mg N/l)
S_{NO2}	NO_2^- (mg N/l)
S_{NO3}	NO_3^- (mg N/l)
S_{NOX}	$NO_3^- + NO_2^-$ (mg N/l)
X_{NI}	nbd particulate organic N (mg N/l)
X_{No}	degradable particulate organic N (mg N/l)
	Phosphorus
S_{PI}	nbd soluble organic P (mg P/l)
S_{Po}	degradable soluble organic P (mg P/l)
S_{PO4}	PO_4^{3-} (sum of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) (mg P/l)
X_{MOH}	MeOH (metal hydroxide) (mg/l)
X_{MP}	MeP (metal phosphate) (mg P/l)
X_{PAO}	P accumulating microorganisms (mg/l)
X_{PHA}	PHA (mg/l)
X_{PI}	nbd particulate organic P (mg P/l)
X_{Po}	degradable particulate organic P (mg P/l)
X_{PP}	polyphosphate (mg/l)
	Other
Q	flowrate (Mgal/d or m^3/s)
r	ratio of recycled flow to influent flow
S_{ALK}	alkalinity (mmol/l)
S_O	DO/DO saturation concentration (mg O_2/l)
V	volume (gal) or (m^3)
X_A	autotrophs (mg/l)
X_{An}	nonviable autotrophs (mg/l)
X_H	heterotrophs (mg/l)
X_{Hn}	nonviable heterotrophs (mg/l)
X_{TSS}	TSS (mg/l)

X_V	VSS (mg/l)
v	stoichiometric coefficient (-)
θ_d	HRT (h)
θ_X	SRT (d)

Stoichiometric Symbols

Addition of the subscript "in" to any symbol identifies the location of the entity as the influent, e.g., $f_{CV,in}$ is COD:total VSS in the influent.

Symbol	Definition

Autotrophs (Nitrifiers)

f_{XI}, f_{XIA}	fraction of nbd COD generated in biomass lysis (-)
Y_A	Yield of aut. biomass per NO_3^--N (g COD/g N, g TSS/g N)

Carbon

f_{BOD}	BOD_5:ultimate BOD (-)
f_{BS}	BOD_5:degradable soluble COD (-)
f_{BX}	BOD_5:degradable particulate COD (-)
f_{CV}	COD:VSS (g COD/g VSS)
f_{OX}	O_2 consumed per BOD removed (-)
f_{SI}	fraction of S_I released in hydrolysis (-)

Nitrogen/Phosphorus

i_{NBM}	N content of biomass (g N /g COD, g N/g TSS)
$i_{N/O}$	NO_3^- consumed for BOD removed (g N/g BOD)
i_{NSI}, i_{PSI}	N (P) content of inert sol. COD, S_I [g N (P)/g COD]
i_{NSS}, i_{PSS}	N (P) content of deg. substrates, S_S [g N (P)/g COD]
i_{NXI}, i_{PXI}	N (P) content of inert part. COD, X_I [g N (P)/g COD]
i_{NXS}, i_{PXS}	N (P) content of slowly biodegradable substrate, X_S [g N (P)/g COD]
i_{PBM}	P content of biomass (g P /g COD)

TSS-VSS

f_{VT}	VSS to TSS ratio (g VSS/g TSS)
i_{IS}	nbd organics to total soluble COD (S_I to COD_{sol}) ratio
i_{IV}	nbd solids to VSS (X_I to X_V) ratio (g COD/g VSS)
i_{TSSBM}	TSS to COD ratio for biomass (g TSS/g COD)
i_{TSSBOD}	TSS to BOD ratio of particulate matter (g TSS/g BOD)
i_{TSSMM}	TSS to X_{MOH} ratio (g TSS/g Me)
i_{TSSMP}	TSS to X_{MP} ratio (g TSS/g Me)
i_{TSSXI}	TSS to COD ratio for X_I (g TSS/g COD)
i_{TSSXS}	TSS to COD ratio for X_S (g TSS/g COD)

Heterotrophic Biomass

f_{XI}, f_{XIH}, f_{XIP}	fraction of nbd particulate COD released in biomass decay (biomass/heterotroph/PAO) (-)
Y_B	yield coefficient of biomass (g VSS/g BOD_5)
Y_H, Y_{HNO}	aerobic/anoxic yield coefficient of heterotrophs (-, g TSS/g BOD)
Y_{net}	net or observed yield coefficient (g TSS/g BOD_5)
Y_{STONO}, Y_{STOO2}	anoxic/aerobic yield coefficient of stored COD (-)
Y_{VC}	yield coefficient of biomass (g VSS/g COD)

PAO

Y_{PAO}	yield coefficient (biomass/PHA) (-)
Y_{PHA}	PHA requirement for PP storage (g COD/g P)
Y_{PO4}	PP requirement (PO_4 release) per PHA stored (g P/g COD)

Kinetic Coefficients

Symbol	Definition
b_A, b_H	endogenous decay (lysis) coeff. of autotrophs/hetero. (h^{-1})
b_{ANO}, b_{HNO}	anoxic endogenous respiration coeff. of autotroph/hetero. (h^{-1})
b_{PAO}, b_{PHA}, b_{PP}	lysis coefficient for $X_{PAO}/X_{PHA}/X_{PP}$ (h^{-1})
b_{STONO}, b_{STOO2}	anoxic/aerobic endog. respiration coeff. of stored substrate (h^{-1})
f_{pH}	pH adjustment factor (-)
K_{ALKA}, K_{ALKH}, K_{ALKM}, K_{ALKP}	half-velocity coeff. for alkalinity for aut./heter./metal phosphate/PAO (mmol/l)
K_A	half-velocity coefficient for growth on S_A (mg COD/l)
K_{AP}	half-velocity coefficient for PAO growth on S_A (mg COD/l)
K_B	half-velocity coefficient for BOD (mg BOD/l)
K_{fe}	half-velocity coefficient for fermentation of S_S (mg COD/l)
k_h	hydrolysis rate coefficient (h^{-1}, g BOD/gTSS/h)
K_{IPP}	inhibition coefficient for poly-phosphate storage (-)
K_La	oxygen transfer coefficient (h^{-1})
k_{NH}	ammonification rate coefficient (h^{-1})
K_{NH}, K_{NHA}	het./aut. half-velocity coefficient for ammonia (mg N/l)
K_{NOX}	half-velocity coefficient for NO_x (mg N/l)
K_{NOXh}	NO_3^- half-rate constant (hydrolysis) (mg N/l)
K_{NOXH}, K_{NOXP}	NO_3^- half-rate constant (heterotrophs/PAO) (mg N/l)
K_{OA}, K_{OH}, K_{OP}	aut./het./PAO half-velocity coefficient for O_2 (mg O_2/l)
K_P	half-velocity coefficient for phosphate (mg P/l)
K_{PA}, K_{PH}	PO_4^{3-} half-rate coeff. (autotrophs/heterotrophs) (mg P/l)
K_{PHA}	half-velocity coefficient for PHA (-)
K_{Pmax}	maximum P storage for PAO (g P/g COD)
K_{PP}	half-velocity coefficient for PP (-)
K_{PPAO}	PO_4^{3-} half-rate constant (PAO) (mg P/l)
k_{PRE}	P precipitation rate constant (l/g $Fe(OH)_3$/h)
K_{PS}	P half-rate constant, PP storage (mg P/l)
k_{RED}	P redissolution rate constant (h^{-1})
k_{STO}	COD storage rate (h^{-1})
K_{STO}	half-velocity coefficient for stored COD (mg/l)
K_X	half-velocity coefficient for hydrolysis (mg/l)
M_O	maintenance rate (g O_2/g TSS/h)
q_{fe}	maximum anaerobic growth rate coeff. for heterotrophs (h^{-1})
q_{PHA}	rate coefficient for storage of X_{PHA} (g X_{PHA}/g X_{PAO}/h)
q_{PP}	rate coefficient for storage of X_{PP} (g X_{PP}/g X_{PAO}/h)
η_{fe}	anaerobic hydrolysis factor (-)
η_g	anoxic growth factor (-)
η_{gPAO}	fractional anoxic growth rate for PAO (-)
η_h	anoxic hydrolysis factor (-)
μ_A, μ_H	specific growth rate of autotrophs/heterotrophs (h^{-1})
μ_{Am}, μ_{Hm}, μ_{PAOm}	maximum specific growth rate of autotrophs/heterotrophs/PAO (h^{-1})

ASM1: Process kinetics and stoichiometry for carbon oxidation, nitrification, and denitrification

Component →	i	1	2	3	4	5	6	7	8	9	10	11	12	13[a]	
j	Process ↓	S_I	S_S	X_I	X_S	X_H	X_A	S_O	S_{NOX}	S_{NH}	S_{No}	X_{No}	S_{ALK}	X_{NI}	Process Rate, ρ_j [$ML^{-3}T^{-1}$]
1	Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1		$-\frac{1-Y_H}{Y_H}$		$-i_{NBM}$			$-\frac{i_{NBM}}{14}$		$\mu_{Hm}\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)X_H$
2	Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{2.86Y_H}$	$-i_{NBM}$			$\frac{1-Y_H}{14\cdot 2.86Y_H}$ $-i_{NBM}/14$		$\mu_{Hm}\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)$ $\times\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)\eta_g X_H$
3	Aerobic growth of autotrophs						1	$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{NBM}-\frac{1}{Y_A}$			$-\frac{i_{NBM}}{14}-\frac{1}{7Y_A}$		$\mu_{Am}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{OA}+S_O}\right)X_A$
4	Decay of heterotrophs			f_{XI}	$1-f_{XI}$	-1						$i_{NBM}-f_{XI}i_{NXI}$		$f_{XI}i_{NXI}$	$b_H X_H$
5	Decay of autotrophs			f_{XI}	$1-f_{XI}$		-1					$i_{NBM}-f_{XI}i_{NXI}$		$f_{XI}i_{NXI}$	$b_A X_A$
6	Ammonification of soluble org. nitrogen									1	-1		$\frac{1}{14}$		$k_a S_{No} X_H$
7	Hydrolysis of entrapped organics		1		-1										$k_h\left(\frac{X_S/X_H}{K_X+(X_S/X_H)}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)\right.$ $\left.+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)\right]X_H$
8	Hydrolysis of entrapped organic nitrogen										1	-1			$\rho_7(X_{No}/X_S)$
Observed conversion rates [$ML^{-3}T^{-1}$]		$r_i=\sum_j \nu_{ij}\rho_j$													

a. This column only applies to ASM1A.

Component Stoichiometric and Mass Balance Expressions (for each stage)

For a typical activated sludge process with a single stage CM aeration basin and only one RAS line from the underflow of the secondary clarifier to the aeration basin, $\frac{Q}{V}S_{S,in}$ would be equivalent to

$$\frac{Q}{V}S_{S,in} = \frac{Q_{in}}{V}S_{S,in} + \frac{rQ_{in}}{V}S_{S,r}$$

where rQ_{in} is the flowrate in the recycle line, Q_r.

Soluble Inert COD (S_I)

$$\frac{Q}{V}S_I = \frac{Q}{V}S_{I,in}$$

Soluble COD (S_S)

$$\frac{Q}{V}S_S = \frac{Q}{V}S_{S,in} - \frac{1}{Y_H}(\rho_1 + \rho_2) + \rho_7$$

Inert Particulate Organics (X_I)

$$\frac{Q}{V}X_I = \frac{Q}{V}X_{I,in} + f_{XI}\rho_4 + f_{XI}\rho_5$$

Particulate COD (X_S)

$$\frac{Q}{V}X_S = \frac{Q}{V}X_{S,in} + (1 - f_{XI})\rho_4 + (1 - f_{XI})\rho_5 - \rho_7$$

Heterotrophs (X_H)

$$\frac{Q}{V}X_H = \frac{Q}{V}X_{H,in} + \rho_1 + \rho_2 - \rho_4$$

Autotrophs (X_A)

$$\frac{Q}{V}X_A = \frac{Q}{V}X_{A,in} + \rho_3 - \rho_5$$

DO (S_O)

$$\frac{Q}{V}S_O = \frac{Q}{V}S_{O,in} + \alpha K_L a(\beta\Omega S_O^* - S_O) + \frac{Y_H - 1}{Y_H}\rho_1 + \frac{Y_A - 4.57}{Y_A}\rho_3$$

Nitrate + Nitrite (S_{NOX})

$$\frac{Q}{V}S_{NOX} = \frac{Q}{V}S_{NOX,in} + \frac{Y_H - 1}{2.86Y_H}\rho_2 + \frac{1}{Y_A}\rho_3$$

Ammonia (S_{NH})

$$\frac{Q}{V}S_{NH} = \frac{Q}{V}S_{NH,in} - i_{NBM}\rho_1 - i_{NBM}\rho_2 - \left(i_{NBM} + \frac{1}{Y_A}\right)\rho_3 + \rho_6$$

Soluble Organic Nitrogen (S_{No})

$$\frac{Q}{V}S_{No} = \frac{Q}{V}S_{No,in} - \rho_6 + \rho_8$$

Particulate Degradable Organic Nitrogen (X_{No})

$$\frac{Q}{V}X_{No}=\frac{Q}{V}X_{No,in}+\left(i_{NBM}-f_{XI}i_{NXI}\right)\rho_4+\left(i_{NBM}-f_{XI}i_{NXI}\right)\rho_5-\rho_8$$

Particulate Nondegradable Organic Nitrogen (X_{NI})

This equation only applies to ASM1A.

$$\frac{Q}{V}X_{NI}=\frac{Q}{V}X_{NI,in}+f_{XI}i_{NXI}\rho_4+f_{XI}i_{NXI}\rho_5$$

OUR and NUR

OUR and NUR are defined by the following equations.

$$\text{OUR} = \frac{Y_H-1}{Y_H}\rho_1+\frac{Y_A-4.57}{Y_A}\rho_3$$

$$\text{NUR} = \frac{Y_H-1}{2.86Y_H}\rho_2$$

ASM2: Stoichiometry for hydrolysis, carbon, nitrogen, and phosphorus

Component →	i	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
j	Process ↓	S_O	S_S	S_A	S_{NH}	S_{N2}	S_{NOX}	S_{PO4}	S_I	S_{ALK}	X_I	X_S	X_H	X_{TSS}	X_{PAO}	X_{PP}	X_{PHA}	X_A	X_{MOH}	X_{MP}
Hydrolysis Processes																				
1	Aer. hydrolysis		$1 - f_{SI}$		$v_{1,NH4}$			$v_{1,PO4}$	f_{SI}	$v_{1,ALK}$		-1		$-i_{TSSXS}$						
2	Anox. hydrol.		$1 - f_{SI}$		$v_{2,NH4}$			$v_{2,PO4}$	f_{SI}	$v_{2,ALK}$		-1		$-i_{TSSXS}$						
3	Anaer. hydrol.		$1 - f_{SI}$		$v_{3,NH4}$			$v_{3,PO4}$	f_{SI}	$v_{3,ALK}$		-1		$-i_{TSSXS}$						
Facultative Heterotrophic Organisms																				
4	Aerobic growth on S_S	$1-\frac{1}{Y_H}$	$-\frac{1}{Y_H}$		$\frac{i_{NSS}}{Y_H}-i_{NBM}$			$\frac{i_{PSS}}{Y_H}-i_{PBM}$		$v_{4,ALK}$			1	i_{TSSBM}						
5	Aerobic growth on S_A	$1-\frac{1}{Y_H}$		$-\frac{1}{Y_H}$	$-i_{NBM}$			$-i_{PBM}$		$v_{5,ALK}$			1	i_{TSSBM}						
6	Anoxic growth on S_S (denitrification)		$-\frac{1}{Y_H}$		$\frac{i_{NSS}}{Y_H}-i_{NBM}$	$\frac{1-Y_H}{2.86\cdot Y_H}$	$\frac{Y_H-1}{2.86\bullet Y_H}$	$\frac{i_{PSS}}{Y_H}-i_{PBM}$		$v_{6,ALK}$			1	i_{TSSBM}						
7	Anoxic growth on S_A (denitrification)			$-\frac{1}{Y_H}$	$-i_{NBM}$	$\frac{1-Y_H}{2.86\cdot Y_H}$	$\frac{Y_H-1}{2.86\cdot Y_H}$	$-i_{PBM}$		$v_{7,ALK}$			1	i_{TSSBM}						
8	Fermentation		-1	1	i_{NSS}			i_{PSS}		$v_{8,ALK}$										
9	Lysis				$v_{9,NH4}$			$v_{9,PO4}$		$v_{9,ALK}$	f_{XIH}	$1 - f_{XIH}$	-1	$v_{9,TSS}$						
Phosphorus-Accumulating Organisms																				
10	Storage of X_{PHA}			-1				Y_{PO4}		$v_{10,ALK}$				$v_{10,TSS}$		$-Y_{PO4}$	1			
11	Aerobic storage of X_{PP}	$-Y_{PHA}$						-1		$v_{11,ALK}$				$v_{11,TSS}$		1	$-Y_{PHA}$			
12	Anoxic storage of X_{PP}					$\frac{Y_{PHA}}{2.86}$	$-\frac{Y_{PHA}}{2.86}$	-1		$v_{12,ALK}$				$v_{12,TSS}$		1	$-Y_{PHA}$			
13	Aerobic growth of X_{PAO}	$1-\frac{1}{Y_{PAO}}$			$-i_{NBM}$			$-i_{PBM}$		$v_{13,ALK}$				$v_{13,TSS}$	1		$-\frac{1}{Y_{PAO}}$			
14	Anoxic growth of X_{PAO}				$-i_{NBM}$	$\frac{1-Y_{PAO}}{2.86\bullet Y_{PAO}}$	$\frac{Y_{PAO}-1}{2.86\bullet Y_{PAO}}$	$-i_{PBM}$		$v_{14,ALK}$				$v_{14,TSS}$	1		$-\frac{1}{Y_{PAO}}$			
15	Lysis of X_{PAO}				$v_{15,NH4}$			$v_{15,PO4}$		$v_{15,ALK}$	f_{XIP}	$1 - f_{XIP}$		$v_{15,TSS}$	-1					
16	Lysis of X_{PP}							1		$v_{16,ALK}$				-3.23		-1				
17	Lysis of X_{PHA}			1						$v_{17,ALK}$				-0.6			-1			
Growth and Decay of Nitrifying Organisms																				
18	Aer. growth of X_{AUT}	$-\frac{4.57-Y_A}{Y_A}$			$-i_{NBM}-\frac{1}{Y_A}$		$\frac{1}{Y_A}$	$-i_{PBM}$		$v_{18,ALK}$				i_{TSSBM}				1		
19	Lysis of X_{AUT}				$v_{19,NH4}$			$v_{19,PO4}$		$v_{19,ALK}$	f_{XIA}	$1 - f_{XIA}$		$v_{19,TSS}$				-1		
Processes Describing Simultaneous Precipitation of Phosphorus																				
20	Precipitation							-1		$v_{20,ALK}$				1.42					-3.45	4.87
21	Redissolution							1		$v_{21,ALK}$				-1.42					3.45	-4.87

Stoichiometric Equations for ASM2

$\nu(4, 1)$	$\nu_{1,NH4}$	$i_{NXS} - f_{SI}i_{NSI} - (1 - f_{SI})i_{NSS}$
$\nu(4, 2)$	$\nu_{2,NH4}$	$i_{NXS} - f_{SI}i_{NSI} - (1 - f_{SI})i_{NSS}$
$\nu(4, 3)$	$\nu_{3,NH4}$	$i_{NXS} - f_{SI}i_{NSI} - (1 - f_{SI})i_{NSS}$
$\nu(4, 9)$	$\nu_{9,NH4}$	$i_{NBM} - f_{XIH}i_{NXI} - (1 - f_{XIH})i_{NXS}$
$\nu(4, 15)$	$\nu_{15,NH4}$	$i_{NBM} - f_{XIP}i_{NXI} - (1 - f_{XIP})i_{NXS}$
$\nu(4, 19)$	$\nu_{19,NH4}$	$i_{NBM} - f_{XIA}i_{NXI} - (1 - f_{XIA})i_{NXS}$
$\nu(7, 1)$	$\nu_{1,PO4}$	$i_{PXS} - f_{SI}i_{PSI} - (1 - f_{SI})i_{PSS}$
$\nu(7, 2)$	$\nu_{2,PO4}$	$i_{PXS} - f_{SI}i_{PSI} - (1 - f_{SI})i_{PSS}$
$\nu(7, 3)$	$\nu_{3,PO4}$	$i_{PXS} - f_{SI}i_{PSI} - (1 - f_{SI})i_{PSS}$
$\nu(7, 9)$	$\nu_{9,PO4}$	$i_{PBM} - f_{XIH}i_{PXI} - (1 - f_{XIH})i_{PXS}$
$\nu(7, 15)$	$\nu_{15,PO4}$	$i_{PBM} - f_{XIP}i_{PXI} - (1 - f_{XIP})i_{PXS}$
$\nu(7, 19)$	$\nu_{19,PO4}$	$i_{PBM} - f_{XIA}i_{PXI} - (1 - f_{XIA})i_{PXS}$
$\nu(9, 1)$	$\nu_{1,ALK}$	$\frac{\nu_{1,NH4}}{14} - \frac{1.5\nu_{1,PO4}}{31}$
$\nu(9, 2)$	$\nu_{2,ALK}$	$\frac{\nu_{2,NH4}}{14} - \frac{1.5\nu_{2,PO4}}{31}$
$\nu(9, 3)$	$\nu_{3,ALK}$	$\frac{\nu_{3,NH4}}{14} - \frac{1.5\nu_{3,PO4}}{31}$
$\nu(9, 4)$	$\nu_{4,ALK}$	$\frac{\nu_{4,NH4}}{14} - \frac{1.5\nu_{4,PO4}}{31}$
$\nu(9, 5)$	$\nu_{5,ALK}$	$\frac{\nu_{5,NH4}}{14} - \frac{1.5\nu_{5,PO4}}{31} + \frac{1}{64Y_H}$
$\nu(9, 6)$	$\nu_{6,ALK}$	$\frac{\nu_{6,NH4}}{14} - \frac{1.5\nu_{6,PO4}}{31} + \frac{1 - Y_H}{14 \cdot 2.86Y_H}$
$\nu(9, 7)$	$\nu_{7,ALK}$	$\frac{\nu_{7,NH4}}{14} - \frac{1.5\nu_{7,PO4}}{31} + \frac{1 - Y_H}{14 \cdot 2.86Y_H} + \frac{1}{64Y_H}$
$\nu(9, 8)$	$\nu_{8,ALK}$	$\frac{\nu_{8,NH4}}{14} - \frac{1.5\nu_{8,PO4}}{31} - \frac{1}{64}$
$\nu(9, 9)$	$\nu_{9,ALK}$	$\frac{\nu_{9,NH4}}{14} - \frac{1.5\nu_{9,PO4}}{31}$
$\nu(9, 10)$	$\nu_{10,ALK}$	$\frac{1}{64} - 0.016Y_{PO4}$ [see $\nu(9, 11)$]
$\nu(9, 11)$	$\nu_{11,ALK}$	0.016 (based on $1.5H^+ + 3H_{1.5}PO_4^{1.5-} + K^+ + Mg^{2+} \rightarrow KMgP_3O_9 + 3H_2O$)
$\nu(9, 12)$	$\nu_{12,ALK}$	$\frac{Y_{PHA}}{14 \cdot 2.86} + 0.016$ [see $\nu(9, 11)$]
$\nu(9, 13)$	$\nu_{13,ALK}$	$\frac{\nu_{13,NH4}}{14} - \frac{1.5\nu_{13,PO4}}{31}$
$\nu(9, 14)$	$\nu_{14,ALK}$	$\frac{\nu_{14,NH4}}{14} - \frac{1.5\nu_{14,PO4}}{31} + \frac{1 - Y_{PAO}}{14 \bullet 2.86 \bullet Y_{PAO}}$
$\nu(9, 15)$	$\nu_{15,ALK}$	$\frac{\nu_{15,NH4}}{14} - \frac{1.5\nu_{15,PO4}}{31}$
$\nu(9, 16)$	$\nu_{16,ALK}$	-0.016 [see $\nu(9, 11)$]
$\nu(9, 17)$	$\nu_{17,ALK}$	$-\left(\frac{1}{64}\right) = -0.016$

ν(9, 18)	$\nu_{18,ALK}$	$\frac{\nu_{18,NH4}}{14}-\frac{1.5\nu_{18,PO4}}{31}-\frac{1}{14\bullet Y_A}$
ν(9, 19)	$\nu_{19,ALK}$	$\frac{\nu_{19,NH4}}{14}-\frac{1.5\nu_{19,PO4}}{31}$
ν(9, 20)	$\nu_{20,ALK}$	$-\frac{1.5\nu_{20,PO4}}{31}$ [based on $M(OH)_3 + H_{1.5}PO_4^{1.5-} \rightarrow MPO_4 + 1.5H^+ + 3OH^-$]
ν(9, 21)	$\nu_{21,ALK}$	$-\frac{1.5\nu_{21,PO4}}{31}$
ν(13, 9)	$\nu_{9,TSS}$	$-i_{TSSBM} + f_{XIH}i_{TSSXI} - (1 - f_{XIH})i_{TSSXS}$
ν(13, 10)	$\nu_{10,TSS}$	$0.6 - 3.23Y_{PO4}$
ν(13, 11)	ν_{11TSS}	$3.23 - 0.6Y_{PHA}$
ν(13, 12)	$\nu_{12,TSS}$	$3.23 - 0.6Y_{PHA}$
ν(13, 13)	$\nu_{13,TSS}$	$i_{TSSBM}-\frac{0.6}{Y_{PAO}}$
ν(13, 14)	$\nu_{14,TSS}$	$i_{TSSBM}-\frac{0.6}{Y_{PAO}}$
ν(13, 15)	$\nu_{15,TSS}$	$-i_{TSSBM} + f_{XIP}i_{TSSXI} - (1 - f_{XIP})\,i_{TSSXS}$
ν(13, 16)	$\nu_{16,TSS}$	−3.23 (assumes X_{PP} is $K_{0.33}Mg_{0.33}PO_3$)
ν(13, 17)	$\nu_{17,TSS}$	−0.60 (assumes 0.6 g TSS/g X_{PHA} COD; PHA is $C_4H_6O_2$)
ν(13, 19)	$\nu_{19,TSS}$	$-i_{TSSBM} + f_{XIA}i_{TSSXI} + (1 - f_{XIA})^*i_{TSSXS}$
ν(13, 20)	$\nu_{20,TSS}$	$i_{TSSMP} - i_{TSSMM}$
ν(13, 21)	$\nu_{20,TSS}$	$i_{TSSMM} - i_{TSSMP}$
ν(18, 20)	$\nu_{20,MM}$	$-i_{TSSMM}$ [assumes MOH is $Fe(OH)_3$]
ν(18, 21)	$\nu_{210,MM}$	i_{TSSMM}
ν(19, 20)	$\nu_{20,MP}$	i_{TSSMP} (assumes MP is $FePO_4$)
ν(19, 21)	$\nu_{210,MP}$	$-i_{TSSMP}$

ASM2: Process Rate Equations

j	Process	Process Rate, ρ_j $[ML^{-3}T^{-1}]$
Hydrolysis Processes		
1	Aerobic hydrolysis	$k_h\frac{S_O}{K_{OH}+S_O}\frac{X_S/X_H}{K_X+(X_S/X_H)}X_H$
2	Anoxic hydrolysis	$k_h\eta_h\frac{K_O}{K_{OH}+S_O}\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\frac{X_S/X_H}{K_X+(X_S/X_H)}X_H$
3	Anaerobic hydrolysis	$k_h\eta_{fe}\frac{K_O}{K_{OH}+S_O}\frac{K_{NOX}}{K_{NOX}+S_{NOX}}\frac{X_S/X_H}{K_X+(X_S/X_H)}X_H$
Heterotrophic Organisms		
4	Aerobic growth on S_S	$\mu_{Hm}\frac{S_O}{K_{OH}+S_O}\frac{S_S}{K_S+S_S}\frac{S_S}{S_S+S_A}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PH}+S_{PO4}}\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}X_H$
5	Aerobic growth on S_A	$\mu_{Hm}\frac{S_O}{K_{OH}+S_O}\frac{S_A}{K_A+S_A}\frac{S_A}{S_S+S_A}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PH}+S_{PO4}}\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}X_H$
6	Anoxic growth on S_S (denitrification)	$\mu_{Hm}\eta_g\frac{K_{OH}}{K_{OH}+S_O}\frac{S_{NOX}}{K_{NOXH}+S_{NOX}}\frac{S_S}{K_S+S_S}\frac{S_S}{S_S+S_A}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PH}+S_{PO4}}\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}X_H$
7	Anoxic growth on S_A (denitrification)	$\mu_{Hm}\eta_g\frac{K_{OH}}{K_{OH}+S_O}\frac{S_{NOX}}{K_{NOXH}+S_{NOX}}\frac{S_A}{K_A+S_A}\frac{S_A}{S_S+S_A}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PH}+S_{PO4}}\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}X_H$

8	Fermentation	$q_{fe}\frac{K_{OH}}{K_{OH}+S_O}\frac{K_{NOX}}{K_{NOXH}+S_{NOX}}\frac{S_S}{K_F+S_S}\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}X_H$
9	Lysis	$b_H X_H$
Phosphorus Accumulating Organisms		
10	Storage of X_{PHA}	$q_{PHA}\frac{S_A}{K_A+S_A}\frac{S_{ALK}}{K_{ALKP}+S_{ALK}}\frac{X_{PP}/X_{PAO}}{K_{PP}+(X_{PP}/X_{PAO})}X_{PAO}$
11	Aerobic storage of X_{PP}	$q_{PP}\frac{S_O}{K_{OP}+S_O}\frac{S_{PO4}}{K_{PS}+S_{PO4}}\frac{S_{ALK}}{K_{ALKP}+S_{ALK}}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+(X_{PHA}/X_{PAO})}\frac{K_{Pmax}-X_{PP}/X_{PAO}}{K_{IPP}+K_{Pmax}-(X_{PP}/X_{PAO})}X_{PAO}$
12	Anoxic storage of X_{PP}	$\rho_{11}\eta_{gPAO}\frac{K_{OP}}{S_O}\frac{S_{NOX}}{K_{NOXP}+S_{NOX}}$
13	Aerobic growth of X_{PAO}	$\mu_{PAO}\frac{S_O}{K_{OP}+S_O}\frac{S_{NH}}{K_{NHP}+S_{NH}}\frac{S_{PO4}}{K_{PPAO}+S_{PO4}}\frac{S_{ALK}}{K_{ALKP}+S_{ALK}}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}X_{PAO}$
14	Anoxic growth of X_{PAO}	$\rho_{13}\eta_{gPAO}\frac{K_{OP}}{S_O}\frac{S_{NOX}}{K_{NOXP}+S_{NOX}}$
15	Lysis of X_{PAO}	$b_{PAO}X_{PAO}$
16	Lysis of X_{PP}	$b_{PP}X_{PP}$
17	Lysis of X_{PHA}	$b_{PHA}X_{PHA}$
Nitrifying (Autotrophic) Organisms		
18	Aerobic growth of X_A	$\mu_{Am}\frac{S_O}{K_{OA}+S_O}\frac{S_{NH}}{K_{NHA}+S_{NH}}\frac{S_{PO4}}{K_{PA}+S_{PO4}}\frac{S_{ALK}}{K_{ALKA}+S_{ALK}}X_A$
19	Lysis of X_A	$b_A X_A$
Simultaneous Precipitation of Phosphorus with Metal Hydroxide		
20	Precipitation	$k_{PRE}S_{PO4}X_{MOH}$
21	Redissolution	$k_{RED}\frac{S_{ALK}}{K_{ALKM}+S_{ALK}}X_{MP}$

Component Stoichiometric and Mass Balance Expressions (for each stage)

$$\frac{Q}{V}S_{S,in}=\frac{Q_{in}}{V}S_{S,in}+\frac{rQ_{in}}{V}S_{S,r}$$

where rQ_{in} is the flowrate in the recycle line, Q_r.

DO (S_O)

$$\frac{Q}{V}S_O=\frac{Q}{V}S_{O,in}+\alpha K_L a\left(\beta\Omega S_O^*-S_O\right)+\frac{Y_H-1}{Y_H}(\rho_4+\rho_5)-Y_{PHA}\rho_{11}+\frac{Y_{PAO}-1}{Y_{PAO}}\rho_{13}+\frac{Y_A-4.57}{Y_A}\rho_{18}$$

Fermentable Soluble COD (S_S)

$$\frac{Q}{V}S_S=\frac{Q}{V}S_{S,in}+(1-f_{SI})(\rho_1+\rho_2+\rho_3)-\frac{1}{Y_H}(\rho_4+\rho_6)-\rho_8$$

Volatile Fatty Acids (S_A)

$$\frac{Q}{V}S_A=\frac{Q}{V}S_{A,in}-\frac{1}{Y_H}(\rho_5+\rho_7)+\rho_8-\rho_{10}+\rho_{17}$$

Ammonia (S_{NH})

$$\frac{Q}{V}S_{NH}=\frac{Q}{V}S_{NH,in}+\left[i_{NXS}-i_{NSI}f_{SI}-\left(1-f_{SI}\right)i_{NSS}\right]\left(\rho_1+\rho_2+\rho_3\right)+\left(\frac{i_{NSS}}{Y_H}-i_{NBM}\right)\left(\rho_4+\rho_6\right)$$
$$-i_{NBM}\left(\rho_5+\rho_7+\rho_{13}+\rho_{14}\right)+i_{NSS}\rho_8+\left[i_{NBM}-f_{XIH}i_{NXI}-\left(1-f_{XIH}\right)i_{NXS}\right]\rho_9$$
$$+\left[i_{NBM}-f_{XIP}i_{NXI}-\left(1-f_{XIP}\right)i_{NXS}\right]\rho_{15}-\left(i_{NBM}+\frac{1}{Y_A}\right)\rho_{18}+\left[i_{NBM}-f_{XIA}i_{NXI}-\left(1-f_{XIA}\right)i_{NXS}\right]\rho_{19}$$

Nitrate + Nitrite (S_{NOX})

$$\frac{Q}{V}S_{NOX}=\frac{Q}{V}S_{NOX,in}+\frac{Y_H-1}{2.86Y_H}\left(\rho_6+\rho_7\right)-\frac{Y_{PHA}}{2.86}\rho_{12}+\frac{Y_{PAO}-1}{2.86Y_{PAO}}\rho_{14}+\frac{1}{Y_A}\rho_{18}$$

Soluble Phosphorus (S_{PO4})

$$\frac{Q}{V}S_{PO4}=\frac{Q}{V}S_{PO4,in}+\left[i_{PXS}-i_{PSS}\left(1-f_{SI}\right)-i_{PSI}f_{SI}\right]\left(\rho_1+\rho_2+\rho_3\right)+\left(\frac{i_{PSS}}{Y_H}-i_{PBM}\right)\left(\rho_4+\rho_6\right)$$
$$-i_{PBM}\left(\rho_5+\rho_7+\rho_{13}+\rho_{14}+\rho_{18}\right)+i_{PSS}\rho_8+\left[i_{PBM}-f_{XIH}i_{PXI}-\left(1-f_{XIH}\right)i_{PXS}\right]\rho_9$$
$$+Y_{PP}\rho_{10}-\left(\rho_{11}+\rho_{12}-\rho_{16}+\rho_{20}-\rho_{21}\right)+\left[i_{PBM}-f_{XIP}i_{PXI}-\left(1-f_{XIP}\right)i_{PXS}\right]\rho_{15}$$
$$+\left[i_{PBM}-f_{XIA}i_{PXI}-\left(1-f_{XIA}\right)i_{PXS}\right]\rho_{19}$$

Soluble Inert COD (S_I)

$$\frac{Q}{V}S_I=\frac{Q}{V}S_{I,in}+f_{SI}\left(\rho_1+\rho_2+\rho_3\right)$$

Particulate Inert COD (X_I)

$$\frac{Q}{V}X_I=\frac{Q}{V}X_{I,in}+f_{XIH}\rho_9+f_{XIP}\rho_{15}+f_{XIA}\rho_{19}$$

Particulate Degradable COD (X_S)

$$\frac{Q}{V}X_S=\frac{Q}{V}X_{S,in}-\rho_1-\rho_2-\rho_3+\left(1-f_{XIH}\right)\rho_9+\left(1-f_{XIP}\right)\rho_{15}+\left(1-f_{XIA}\right)\rho_{19}$$

Heterotrophs (X_H)

$$\frac{Q}{V}X_H=\frac{Q}{V}X_{H,in}+\rho_4+\rho_5+\rho_6+\rho_7-\rho_9$$

PAO (X_{PAO})

$$\frac{Q}{V}X_{PAO}=\frac{Q}{V}X_{PAO,in}+\rho_{13}+\rho_{14}-\rho_{15}$$

PP (X_{PP})

$$\frac{Q}{V}X_{PP}=\frac{Q}{V}X_{PP,in}-Y_{PO4}\rho_{10}+\rho_{11}+\rho_{12}-\rho_{16}$$

Organic Storage Products of PAO (X_{PHA})

$$\frac{Q}{V}X_{PAO}=\frac{Q}{V}X_{PAO,in}+\rho_{10}-\rho_{17}-Y_{PHA}\left(\rho_{11}+\rho_{12}\right)-\frac{1}{Y_{PAO}}\left(\rho_{13}+\rho_{14}\right)$$

Autotrophs (X_A)

$$\frac{Q}{V}X_A = \frac{Q}{V}X_{A,in} + \rho_{18} - \rho_{19}$$

Total Suspended Solids (X_{TSS})

$$\begin{aligned}\frac{Q}{V}X_{TSS} = {} & \frac{Q}{V}X_{TSS,in} + i_{TSSXS}(\rho_1 + \rho_2 + \rho_3) + i_{TSSBM}(\rho_4 + \rho_5 + \rho_6 + \rho_7 + \rho_{18}) \\ & + \left[i_{TSSXI} f_{XIH} + (1 - f_{XIH}) i_{TSSXS} - i_{TSSBM}\right]\rho_9 + (0.6 - 3.23Y_{PP})\rho_{10} + (3.23 - 0.6Y_{PHA})(\rho_{11} + \rho_{12}) \\ & + \left(i_{TSSBM} - \frac{0.6}{Y_{PAO}}\right)(\rho_{13} + \rho_{14}) + \left[i_{TSSXI} f_{XIP} + (1 - f_{XIP}) i_{TSSXS} - i_{TSSBM}\right]\rho_{15} - 3.23\rho_{16} - 0.6\rho_{17} \\ & + \left[i_{TSSXI} f_{XIA} + (1 - f_{XIA}) i_{TSSXS} - i_{TSSBM}\right]\rho_{19} + (i_{TSSMP} - i_{TSSMM})(\rho_{20} - \rho_{21})\end{aligned}$$

Metal Hydroxide (X_{MOH})

$$\frac{Q}{V}X_{MOH} = \frac{Q}{V}X_{MOH,in} - i_{TSSMM}(\rho_{20} - \rho_{21})$$

Metal Phosphate (X_{MP})

$$\frac{Q}{V}X_{MP} = \frac{Q}{V}X_{MP,in} - i_{TSSMP}(\rho_{20} - \rho_{21})$$

OUR and NUR

OUR and NUR are defined by the following equations.

$$\text{OUR} = \frac{Y_H - 1}{Y_H}(\rho_4 + \rho_5) - Y_{PHA}\rho_{11} + \frac{Y_{PAO} - 1}{Y_{PAO}}\rho_{13} + \frac{Y_A - 4.57}{Y_A}\rho_{18}$$

$$\text{NUR} = \frac{Y_H - 1}{2.86Y_H}(\rho_6 + \rho_7) - \frac{Y_{PHA}}{2.86}\rho_{12} + \frac{Y_{PAO} - 1}{2.86Y_{PAO}}\rho_{14} + \frac{1}{Y_A}\rho_{18}$$

n subtle respects among the various models.

ASM3: Process kinetics and stoichiometry for carbon oxidation, nitrification, and denitrification

Component →		i 1	2	3	4	5	6	7	8	9	10	11	12	13	Process Rate, ρ_j [$ML^{-3}T^{-1}$]
j	Process ↓	S_O	S_I	S_S	S_{NH}	S_{N2}	S_{NOX}	S_{ALK}	X_I	X_S	X_H	X_{STO}	X_A	X_{TSS}	
1	Hydrolysis		f_{SI}	$1-f_{SI}$	$i_{NXS}-f_{SI}i_{NSI}$ $-(1-f_{SI})i_{NSS}$			$\frac{i_{NXS}-f_{SI}i_{NSI}-(1-f_{SI})i_{NSS}}{14}$		-1				$-i_{TSSXS}$	$k_h\left[\frac{X_S/X_h}{K_X+(X_S/X_H)}\right]X_H$
2	Aer. storage of COD	$-1+Y_{STOO2}$		-1	i_{NSS}			$\frac{i_{NSS}}{14}$				Y_{STOO2}		$0.6Y_{STOO2}$	$k_{STO}\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)X_H$
3	Anox. storage of COD			-1	i_{NSS}	$\frac{1-Y_{STONO}}{2.86}$	$-\frac{1-Y_{STONO}}{2.86}$	$\frac{i_{NSS}}{14}+\frac{1-Y_{STONO}}{14\bullet 2.86}$				Y_{STONO}		$0.6Y_{STONO}$	$\eta_g k_{STO}\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)X_H$
4	Aerobic growth of heterotrophs	$1-\frac{1}{Y_H}$			$-i_{NBM}$			$-\frac{i_{NBM}}{14}$			1	$-\frac{1}{Y_H}$		$i_{TSSBM}-\frac{0.6}{Y_H}$	$\mu_{Hm}\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}\right)$ $\times\left[\frac{X_{STO}/X_H}{K_{STO}+(X_{STO}/X_H)}\right]X_H$
5	Anoxic growth of heterotrophs				$-i_{NBM}$	$-\frac{1-1/Y_{HNO}}{2.86}$	$\frac{1-1/Y_{HNO}}{2.86}$	$-\frac{i_{NBM}}{14}-\frac{1-1/Y_{HNO}}{14\bullet 2.86}$			1	$-\frac{1}{Y_{HNO}}$		$i_{TSSBM}-\frac{0.6}{Y_{HNO}}$	$\mu_{Hm}\eta_g\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{ALKH}+S_{ALK}}\right)$ $\times\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)\left[\frac{X_{STO}/X_H}{K_{STO}+(X_{STO}/X_H)}\right]X_H$
6	Aer. end. resp. of heterotrophs	$f_{XI}-1$			$i_{NBM}-f_{XI}i_{NXI}$			$\frac{i_{NBM}-f_{XI}i_{NXI}}{14}$	f_{XI}		-1			$f_{XI}i_{TSSXI}$ $-i_{TSSBM}$	$b_H\left(\frac{S_O}{K_{OH}+S_O}\right)X_H$
7	Anox. end. resp. of heterotrophs				$i_{NBM}-f_{XI}i_{NXI}$	$\frac{1-f_{XI}}{2.86}$	$-\frac{1-f_{XI}}{2.86}$	$\frac{i_{NBM}-f_{XI}i_{NXI}}{14}+\frac{1-f_{XI}}{14\bullet 2.86}$	f_{XI}		-1			$f_{XI}i_{TSSXI}-$ i_{TSSBM}	$b_{HNO}\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)X_H$
8	Aer. resp. of stored organics	-1										-1		-0.6	$b_{STOO2}\left(\frac{S_O}{K_{OH}+S_O}\right)X_{STO}$ $b_{STOO2}>b_H$
9	Anoxic resp. of stored org.					$\frac{1}{2.86}$	$-\frac{1}{2.86}$	$\frac{1}{14\cdot 2.86}$				-1		-0.6	$b_{STONO}\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)X_{STO}$ $b_{STONO}>b_{HNO}$
10	Aer. growth of autotr.	$-\frac{4.57-Y_A}{Y_A}$			$-\frac{1}{Y_A}-i_{NBM}$		$\frac{1}{Y_A}$	$-\frac{i_{NBM}}{14}$					1	i_{TSSBM}	$\mu_{Am}\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NHA}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{ALKA}+S_{ALK}}\right)X_A$
11	Aer. endog. resp. of autotrophs	$f_{XI}-1$			$i_{NBM}-f_{XI}i_{NXI}$			$\frac{i_{NBM}-f_{XI}i_{NSI}}{14}$	f_{XI}				-1	$f_{XI}i_{TSSXI}-$ i_{TSSBM}	$b_A\left(\frac{S_O}{K_{OA}+S_O}\right)X_A$
12	Anox. endog. resp. of autotr.				$i_{NBM}-f_{XI}i_{NXI}$	$\frac{1-f_{XI}}{2.86}$	$-\frac{1-f_{XI}}{2.86}$	$\frac{i_{NBM}-f_{XI}i_{NXI}}{14}+\frac{1-f_{XI}}{14\bullet 2.86}$	f_{XI}				-1	$f_{XI}i_{TSSXI}-$ i_{TSSBM}	$b_{ANO}\left(\frac{K_{OA}}{K_{OA}+S_O}\right)\left(\frac{S_{NOX}}{K_{NOX}+S_{NOX}}\right)X_A$

All the of the concentration variables listed above have units of mg/l and all are either directly user specified or calculated internally from other data supplied by the user in the influent files.

The mass balances that incorporate the above variables are as follows.

Component Stoichiometric and Mass Balance Expressions (for each stage)

The influent flowrate and concentration terms take into account RAS, internal MLSS recycles, and influent distribution.

For a typical activated sludge process with a single stage CM aeration basin and only one RAS line from the underflow of the secondary clarifier to the aeration basin, $\frac{Q}{V}S_{S,in}$ would be equivalent to

$$\frac{Q}{V}S_{S,in} = \frac{Q_{in}}{V}S_{S,in} + \frac{rQ_{in}}{V}S_{S,r}$$

where rQ_{in} is the flowrate in the recycle line, Q_r.

DO (S_O)

$$\frac{Q}{V}S_O = \frac{Q}{V}S_{O,in} + \alpha K_L a\left(\beta\Omega S_O^* - S_O\right) + \left(-1 + Y_{STOO2}\right)\rho_2 + \left(1 - \frac{1}{Y_H}\right)\rho_4 + \left(f_{XI} - 1\right)\left(\rho_6 + \rho_{11}\right) - \rho_8$$
$$-\left(\frac{4.57 - Y_A}{Y_A}\right)\rho_{10}$$

Soluble Inert COD (S_I)

$$\frac{Q}{V}S_I = \frac{Q}{V}S_{I,in} + f_{SI}\rho_1$$

Soluble COD (S_S)

$$\frac{Q}{V}S_S = \frac{Q}{V}S_{S,in} + \left(1 - f_{SI}\right)\rho_1 - \rho_2 - \rho_3$$

Ammonia (S_{NH})

$$\frac{Q}{V}S_{NH} = \frac{Q}{V}S_{NH,in} + \left[i_{NXS} - f_{SI}i_{NSI} - \left(1 - f_{SI}\right)i_{NSS}\right]\rho_1 + i_{NSS}\left(\rho_2 + \rho_3\right) - i_{NBM}\left(\rho_4 + \rho_5\right)$$
$$+\left(i_{NBM} - f_{XI}i_{NXI}\right)\left(\rho_6 + \rho_7 + \rho_{11} + \rho_{12}\right) - \left(\frac{1}{Y_A} - i_{NBM}\right)\rho_{10}$$

Nitrogen Gas (S_{N2})

$$\frac{Q}{V}S_{N2} = \frac{Q}{V}S_{N2,in} + \left(\frac{1 - Y_{STONO}}{2.86}\right)\rho_3 - \left(\frac{1 - 1/Y_{HNO}}{2.86}\right)\rho_5 + \left(\frac{1 - f_{XI}}{2.86}\right)\left(\rho_7 + \rho_{12}\right) + \frac{\rho_9}{2.86}$$

Nitrate + Nitrite (S_{NOX})

$$\frac{Q}{V}S_{NOX} = \frac{Q}{V}S_{NOX,in} - \left(\frac{1 - Y_{STONO}}{2.86}\right)\rho_3 + \left(\frac{1 - 1/Y_{HNO}}{2.86}\right)\rho_5 - \left(\frac{1 - f_{XI}}{2.86}\right)\left(\rho_7 + \rho_{12}\right) - \frac{\rho_9}{2.86} + \frac{\rho_{10}}{Y_A}$$

Alkalinity (S_{ALK})

$$\frac{Q}{V}S_{ALK} = \frac{Q}{V}S_{ALK,in} + \frac{\left[i_{NXS} - f_{SI}i_{NSI} - \left(1 - f_{SI}\right)i_{NSS}\right]}{14}\rho_1 + \frac{i_{NSS}}{14}\rho_2 + \left(i_{NSS} + \frac{1 - Y_{STONO}}{2.86}\right)\frac{\rho_3}{14} - \frac{i_{NBM}}{14}\left(\rho_4 + \rho_{10}\right)$$
$$-\left(i_{NBM} + \frac{1 - 1/Y_{HNO}}{2.86}\right)\frac{\rho_5}{14} + \frac{\left(i_{NBM} - f_{XI}i_{NXI}\right)}{14}\left(\rho_6 + \rho_{11}\right) + \left(i_{NBM} - f_{XI}i_{NXI} + \frac{1 - f_{XI}}{2.86}\right)\frac{\left(\rho_7 + \rho_{12}\right)}{14} + \frac{1}{2.86}\frac{\rho_9}{14}$$

Inert Particulate Organics (X_I)

$$\frac{Q}{V}X_I = \frac{Q}{V}X_{I,in} + f_{XI}\left(\rho_6 + \rho_7 + \rho_{11} + \rho_{12}\right)$$

Particulate COD (X_S)

$$\frac{Q}{V}X_S = \frac{Q}{V}X_{S,in} - \rho_1$$

Heterotrophs (X_H)

$$\frac{Q}{V}X_H = \frac{Q}{V}X_{H,in} + \left(\rho_4 + \rho_5\right) - \left(\rho_6 + \rho_7\right)$$

Stored COD (X_{STO})

$$\frac{Q}{V}X_{STO} = \frac{Q}{V}X_{STO,in} + Y_{STOO2}\rho_2 + Y_{STONO}\rho_3 - \frac{1}{Y_H}\rho_4 - \frac{1}{Y_{HNO}}\rho_5 - \left(\rho_8 + \rho_9\right)$$

Autotrophs (X_A)

$$\frac{Q}{V}X_A = \frac{Q}{V}X_{A,in} + \rho_{10} - \rho_{11} - \rho_{12}$$

TSS (X_{TSS})

$$\frac{Q}{V}X_{TSS} = \frac{Q}{V}X_{TSS,in} - i_{TSSXS}\rho_1 + 0.6\left(Y_{STOO2}\rho_2 + Y_{STONO}\rho_3\right) + \left(i_{TSSBM} - \frac{0.6}{Y_H}\right)\rho_4 + \left(i_{TSSBM} - \frac{0.6}{Y_{HNO}}\right)\rho_5$$
$$+ \left(f_{XI}i_{TSSXI} - i_{TSSBM}\right)\left(\rho_6 + \rho_7 + \rho_{11} + \rho_{12}\right) - 0.6\left(\rho_8 + \rho_9\right) + i_{TSSBM}\rho_{10}$$

OUR and NUR

OUR and NUR are defined by the following equations.

$$\text{OUR} = \left(-1 + Y_{STOO2}\right)\rho_2 + \left(1 - \frac{1}{Y_H}\right)\rho_4 + \left(f_{XI} - 1\right)\left(\rho_6 + \rho_{11}\right) - \rho_8 - \left(\frac{4.57 - Y_A}{Y_A}\right)\rho_{10}$$

$$\text{NUR} = -\left(\frac{1 - Y_{STONO}}{2.86}\right)\rho_3 + \left(\frac{1 - 1/Y_{HNO}}{2.86}\right)\rho_5 - \left(\frac{1 - f_{XI}}{2.86}\right)\left(\rho_7 + \rho_{12}\right) - \frac{\rho_9}{2.86} + \frac{\rho_{10}}{Y_A}$$