MODIFIED MONOD AND LINEAR SUBSTRATE UTILIZATION RATE EQUATIONS FOR ACTIVATED SLUDGE BIODEGRADATION PROCESSES

by

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ABSTRACT

Substrate removal is most commonly modelled with a Monod (r_s= - kSX/(S+K_s) [mg/L/d]) or a linear (r_s= - kSX_v [mg/L/d]) rate equation. In these expressions the removal rate is most often assumed to be first order with respect to volatile suspended solids, which are used as an approximation of the active biomass in the reactor. Wastewater treatment systems are typically operated at sludge ages at which the biomass is in the condition of advanced endogenous decay. This results in the accumulation of dead biomass and other organic debris which reduces the accuracy of volatile suspended solids as a measure of active biomass. The active biomass percentage of volatile suspended solids decreases as sludge age increases.

To account for the those conditions, a modified substrate removal expression with volatile mass concentration (X_v) replaced with active biomass concentration (X_a) represented as AX_v^n (A - constant, n between 0 and 1) was hypothesized as an improved model. The resulting modified Monod and linear substrate utilization rate equations were as follows: $r_s = -kSX_v^n/(S+K_s)$ [mg/L/d], and $r_s = -kSX_v^n$ [mg/L/d], respectively (coefficient A was absorbed in k). Theoretically the expression AX_v^n in modified equations can represent accurately the actual active biomass concentration.

Activated sludge from sequencing batch reactors at steady state conditions was studied for substrate removal kinetics in batch utilization tests. Those tests were conducted on different initial substrate concentrations and different sludge dilutions. The best fitting exponent n, found from the experimental data from those tests, was equal to 0 in both equations. The fitting error (residual mean square) computed from modified equations with n equal to 0 was much lower then fitting error from unmodified equations in which n was equal to 1. The kinetic coefficients computed from modified equations were a better representation of the intrinsic kinetic coefficients (substrate and bacterial population specific) than coefficients computed from unmodified equations. The modified Monod equation provided better fit to the experimental data then the modified linear equation.

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GLOSSARY

A = constant

c_v = coefficient of variation

b_n = specific decay rate constant of nonviable cells [d^{-1}]

b_v = specific decay rate constant of viable cells [d^{-1}]

E = fitting error for sets of tests

EJ = fitting error for one test

ER = difference in fitting errors

E0 = fitting error for n = 0

E1 = fitting error for n = 1

d = specific death rate constant [d^{-1}]

f_d = biodegradable fraction of microbial mass

f_i = inert fraction of influent suspended solids

f_{ndi} = inorganic inert fraction of microorganisms

k = maximum specific substrate utilization rate, in general

k_1, k_2 = maximum specific substrate utilization rates, [mg COD/mg VSS/d], [d^{-1}]

k_3, k_4 = substrate utilization rate coefficients equal to k_2/K_s, and k_1/K_s, respectively, [L/mg VSS/d]

k_5 = substrate utilization rate coefficient, [d^{-1}]

k_a = maximum substrate utilization rate, based on active mass, [d^{-1}]

k_c = endogenous decay rate, VSS based, [mg VSS/mg VSS/d], [d^{-1}]

k_{ca} = endogenous decay rate, active mass based, [mg X_a/mg X_a/d], [d^{-1}]

$k_{ca(t_s)}$ = sludge oxidation rate coefficient at a specific sludge age (Goodman and Englande, 1974)

$k_{ca(1)}$ = sludge oxidation rate coefficient at sludge age 1 day equal to approximately to 0.5 d^{-1} (Goodman and Englande, 1974)

k_n = maximum specific substrate utilization rate, for a particular exponent n

$k_{(LH)}$ = the lowest and the highest values of k in data array

$k_{(op)}$ = value of k in data array for which fitting error was the lowest

K = overall coefficient equal to kX_v, [mg COD/L/d]

K_m = overall substrate removal rate in Goodman and Englande model

K_s = saturation constant, [mg COD/L]

$K_{s(LH)}$ = the lowest and the highest values of K_s in data array

$K_{s(op)}$ = value of K_s in data array for which fitting error was the lowest

M = number of observations

μ = maximum growth rate, [mg VSS/L/d]

μ_s = maximum specific growth rate, [mg VSS/mg VSS/d], [d^{-1}]

NK = number of k values in DA

NKS = number of K_S values in DA

P = number of parameters in regression model

Q = flow rate

r_i = residual (difference between observed and computed substrate concentrations)

r_s = substrate utilization rate, in general

r_{su} = specific substrate utilization rate, [d^{-1}]

$r_{ob.}$ = observed specific substrate utilization rate, [d^{-1}]

$r_{com.}$ = computed specific substrate utilization rate, [d^{-1}]

r_x = microorganisms growth rate, [mg VSS/L/d]

$r_{x,a}$ = microorganisms growth rate, active mass based, [mg VSS/L/d]

r_1, r_2, r_3 = ratios

R_s = specific loading rate

R_v = volumetric loading rate

s = standard deviation

S = substrate concentration, [mg/L]

S_c = computed substrate concentration, [mg/L]

S_e = effluent substrate concentration, or substrate concentration in CFSTR, [mg/L]

S_{ob} = observed substrate concentration, [mg/L]

S_{min} = minimum substrate concentration observed in a test, [mg/L]

S_r = residual substrate concentration, [mg/L]

SRA = the actual set of residual substrate concentrations

SR1 = set no. 1 of residual substrate concentrations

SR2 = set no. 2 of residual substrate concentrations

SK = coefficient defining the k dimension of the next DA

SKS = coefficient defining the K_s dimension of the next DA

S_Y = substrate concentration equal to $S_{ob} - S_r$, [mg/L]

S_0 = initial observed substrate concentration, [mg/L]

S_{0c} = initial computed substrate concentration, [mg/L]

S_{0Y} = initial substrate concentration, equal to $S_0 - S_r$

t_{da} = hydraulic detention time, based on aeration time

t_d = hydraulic detention time, based on full cycle time

t_{sa} = solids retention time, based on aeration time

t_s = solids retention time, based on full cycle time

v = viability

V_a = active volume of the reactor

V = reactor volume, in general

V_t = total reactor volume

X = total suspended solids, solids in general, [mg/L]

X_a = active mass concentration, [mg/L]

X_e = endogenous mass concentration, [mg/L]

X_i = inert solids concentration, [mg/L]

X_v = volatile mass concentration, [mg/L]

X_n = nonviable mass concentration, [mg/L]

X_{vv} = viable mass concentration, [mg/L]

X_o = influent suspended solids concentration, [mg/L]

Y = yield factor, [mg VSS/mg COD]

ABBREVIATIONS

ADR = actual dilution rate

DA = data array

CFSTR = continuous flow stirred tank reactor (continuous flow reactor)

HRT = hydraulic retention time

IS = iteration step

ISS = S_{0Y} iteration step

ISK = k iteration step

ISKS = K_s iteration step

ISTC = initial theoretical substrate concentration

MIS = minimum iteration step

MISS = S_{0Y} minimum iteration step

MISK = k minimum iteration step

MISKS = K_s minimum iteration step

OLR = organic loading rate

RMS = residual mean square

RMS_M = residual mean square computed from modified Monod model

RMS_L = residual mean square computed from modified linear model

SBR = sequencing batch reactor

SRT = sludge retention time

SRA = results array for sets of tests

SS = suspended solids

TDR = theoretical dilution rate

TRA = results array for tests

TSS = total suspended solids

VLR = volumetric loading rate

VSS = volatile suspended solids

CHAPTER 1

INTRODUCTION

Treatment of wastewaters is most often conducted in aerobic biological processes. This method allows for removal of colloidal and dissolved organic matter from sewage, in the most cost efficient manner. The rate of waste removal in this process depends on a number of conditions. The most important are the type of waste, the composition of the microbial population and environmental factors that limit the growth of bacteria, such as pH, temperature, and concentration of dissolved oxygen.

Rate of waste (substrate) removal is usually computed from an empirical model analogous to the Monod equation (Monod, 1949). This model is written in two forms, as $r_s = -kS/(S+K_s)$ [d^{-1}], or as $r_s = -kSX/(S+K_s)$ [mg/L/d]. In those equations S represents substrate concentration and X is volatile suspended solids (X_v), k is the maximum specific substrate utilization rate and K_s is the half velocity constant (equal to the substrate concentration at which $r_s = k/2$).

The order of the Monod model with respect to substrate concentration varies depending on the S/K_s ratio; it approaches unity and zero at low and high S/K_s ratios, respectively. Thus, the removal rate is often computed using a first order kinetic equation ($r_s = -kSX_v$), when describing biological treatment processes taking place at relatively low substrate concentrations in comparison to K_s. Usually the first order kinetic equation has its upper limit of applicability much below the substrate concentration at which microorganism limiting conditions occur (i.e., at which further increase in substrate

concentration does not cause significant increase in removal rate). However, the linear equation is sometimes employed to model the whole r_s range.

Maximum specific substrate utilization rate (k) computed from the Monod equation represents the maximum substrate utilization rate usually normalized with respect to volatile suspended solids (X_v). This does not reflect the actual substrate utilization conditions, for the reason that only the part of X_v, the active microorganisms exhibiting metabolic activity (X_a), are able to participate in substrate utilization. Volatile suspended solids is a measure of all particulate organic matter in suspension, and beside the active mass it accounts also for influent solids and nonactive bacteria at different stages of decay. Because biological treatment systems are operated at conditions of excess biomass to achieve maximum rate of substrate removal, the mixed liquor (ML) contains a considerable amount of nonactive bacteria and bacterial debris. Accordingly, the use of X_v instead of X_a in substrate utilization rate equations, leads to computation of kinetic coefficients (k and K_s) which poorly represent the actual kinetics of the treatment process.

The objective of this study was to test modified Monod ($r_s = -kSX_v^n/(S+K_s)$ [mg/L/d]), and modified linear ($r_s = -kSX_v^n$ [mg/L/d]), substrate utilization rate equations, in which active biomass was represented by X_v concentration raised to a power n between 0 and 1, and multiplied by constant A (A was absorbed in k). It was expected that the expression AX_v^n would model better the actual active biomass concentration in the sludge than the often used expression X_v. This assumption was based on the fact that when sludge retention time (SRT) increases causing an increase in the X_v concentration, the ratio AX_v^n/X_v decreases. This reflects the actual conditions occurring in biological processes in which ratio X_a/X_v decreases with increase in SRT and X_v. More accurate representation of the active biomass would result in an equation yielding kinetic coefficients more representative of the actual kinetics of the treatment process and would better describe process performance across a broader range of operating conditions.

Experimentally the optimal value of exponent n was found based on results from batch substrate degradation tests. Those tests were performed on activated sludge acclimatized in sequencing batch reactors.

CHAPTER 2

LITERATURE REVIEW

The purpose of this review is to analyze kinetic coefficients from other studies, computed from most commonly used substrate utilization rate equations (Monod and linear). The representation of active biomass as X_v, in those equations, leads to kinetic coefficients which were usually a poor representation of the actual kinetics of the utilization process. This indicated a requirement for improvement of Monod and linear equations that would lead to the kinetic coefficients reflecting better the substrate utilization kinetics of the active biomass, instead of being based on volatile solids concentration.

The substrate utilization rate equations and sludge models employing Monod and linear equations are presented in following sections. Active biomass concentrations computed from those models, and according to modified expression AX_v^n (A constant) are compared in Chapter 3.

2.1 Monod and Linear Substrate Utilization Rate Equations

The most often used substrate utilization rate equation (eq. 2.1, Metcalf and Eddy, 1991) is analogous to the Monod equation ($\mu = \mu_s S/(S+K_s)$) describing growth of homogenous bacterial cultures (Monod, 1949).

$$r_{s1} = -\frac{k_1 S}{S + K_S} \; [d^{-1}] \qquad (2.1)$$

where:
r_{s1} = specific substrate utilization rate [mg COD/L/d per mg VSS/L, $[d^{-1}]$]
k_1 = maximum specific substrate utilization rate [mg COD/L/d per mg VSS/L, $[d^{-1}]$]

The other form of this equation, which is often used, is obtained by multiplying both sides of eq. 2.1 by X_v (eq. 2.2).

$$r_{s2} = -\frac{k_2 S X_v}{S + K_S} \; [mg/L/d] \qquad (2.2)$$

where:
r_{s2} = substrate utilization rate [mg COD/L/d]
k_2 = maximum specific substrate utilization rate $[d^{-1}]$

The most often used linear equation is given by eq. 2.3.

$$r_{s3} = -k_3 X_v S \; [mg/L/d] \qquad (2.3)$$

where:
r_{s3} = substrate utilization rate [mg COD/L/d]
k_3 = maximum specific substrate utilization rate [L/mg/d]

The other equations used in modelling of substrate utilization kinetics are presented below (eqs. 2.4 and 2.5).

$$r_{s4} = -k_4 S \; [d^{-1}] \qquad (2.4)$$

where:
r_{s4} = specific substrate utilization rate $[d^{-1}]$
k_4 = maximum specific substrate utilization rate [L/mg/d]

$$r_{s5} = -k_5 X_v \text{ [mg/L/d]} \tag{2.5}$$

where:
r_{s5} = substrate utilization rate [mg COD/L/d]
k_5 = maximum specific substrate utilization rate [d^{-1}]

Substrate utilization rate r_{s1} (eq 2.1) represents observed substrate utilization rate r_{s2} (eq. 2.2) normalized with respect to X_v (eq. 2.6), and the maximum specific substrate utilization rates k_1 and k_2 represent the observed maximum substrate utilization rate normalized with respect to X_v (maximum r_{s2}/X_v). Thus, eqs. 2.1 and 2.2 are equivalent and yield the same kinetic coefficients.

$$r_{s1} = \frac{r_{s2}}{X_v} = \frac{k_1 S}{S + K_s} [d^{-1}] \tag{2.6}$$

where:
X_v = biomass concentration [mg VSS/L]
k_1 = maximum specific substrate utilization rate [d^{-1}]

Equations 2.3, 2.4, and 2.5 are Monod models for specific conditions. Equations 2.3 and 2.4 are reductions of eqs. 2.2 and 2.1 respectively, for very low substrate concentrations, when $S << K_s$ ($k_3 = k_2/K_{s2}$, $k_4 = k_1/K_{s1}$). Equation 2.5 represents reduced eq. 2.2 for microorganism limited conditions, for $S >> K_s$ ($k_5 = k_2$).

Equations 2.3 and 2.4 are sometimes applied as linear sludge models, to model the whole range of r_s, from zero to microorganism limiting conditions.

2.2 Sludge Models

Sludge models presented in the following sections were used in Chapter 3 to generate data on which the modified Monod and modified linear equations were tested.

2.2.1 General Sludge Model (Lawrence McCarty)

The general sludge model for microbial growth and substrate utilization, is represented by eq. 2.7 (Lawrence and McCarty, 1970; Goodman and Englande, 1974).

$$r_x = -Yr_s - k_e X \tag{2.7}$$

where:
r_x = biomass accumulation rate [mg/L/d]
r_s = substrate utilization rate [mg/L/d]
X = mixed liquor biomass concentration [mg/L]
Y = sludge yield factor [-]
k_e = endogenous decay rate [1/d]

In the Lawrence and McCarty model (LM) biomass concentration (X) is represented by average VSS concentration. Mass accumulation coefficients Y and k_e, are usually computed from the linearization of eq. 2.7 (eq. 2.8)

$$\mu = \frac{r_x}{X} = -Y\frac{r_s}{X} - k_e = \frac{1}{t_s} \tag{2.8}$$

where:
μ = specific growth rate [d^{-1}]
t_s= sludge retention time (SRT) [d]

Knowing the mass accumulation coefficients which are usually assumed constant for the same feed and sludge, biomass concentration is computed (eq. 2.11), by substituting eq. 2.9 (based on mass balance) for r_s in eq. 2.8, and rearranging the resulting eq. 2.10.

$$r_s = -\frac{(S_0 - S_e)}{t_d} \tag{2.9}$$

where:
S_0= influent substrate concentration [mg/L/d]
S_e= effluent substrate concentration [mg/L/d]
t_d = hydraulic retention time (HRT) [d]

$$\frac{1}{t_s} = Y\frac{(S_0 - S_e)}{Xt_d} - k_e \tag{2.10}$$

$$X = Y\frac{t_s(S_0 - S_e)}{t_d(1 + k_e t_s)} \tag{2.11}$$

2.2.2 Goodman and Englande, and Christensen and McCarty Models

The sludge models presented by Goodman and Englande (1974), and Christensen and McCarty (1975) are similar, because both models are based on the eq. 2.12.

$$r_{xa} = -Y_a r_s - k_{ea} X_a \tag{2.12}$$

where:
r_{xa} = active biomass growth rate [mg/L/d]
X_a = active mass concentration [mg/L]
k_{ea} = endogenous decay rate, based on active mass [d^{-1}]
Y_a = Yield, active mass based [--]

Rearranging the above equation leads to the equation for active mass concentration (eq. 2.13).

$$X_a = Y_a\frac{t_s(S_0 - S_e)}{t_d(1 + k_{ea} t_s)} \tag{2.13}$$

The differences between Goodman and Englande (GE) and Christensen and McCarty (CM) models are in the type of substrate utilization rate equation used, method of computing the endogenous decay rate coefficient, and the division of suspended solids (SS) into components.

In CM model, Monod type substrate utilization rate equation (eq. 2.2) was used, while GE model employed a linear equation (eq. 2.14).

$$r_s = -K_m S_e \tag{2.14}$$

where:
S_e = effluent substrate concentration in a CFSTR (equal to the substrate concentration in the reactor)
K_m = overall substrate removal rate

Coefficient K_m represents kX_v (Goodman and Englande, 1974), where k is the specific VSS based substrate removal rate. Substituting kX_v for K_m in eq. 2.14 results in eq. 2.15 (which is analogous to eq. 2.3).

$$r_s = -kX_v S_e \tag{2.15}$$

In the GE model the k_{ca} (endogenous decay rate, a sludge oxidation rate) value is computed from an empirical equation (eq. 2.16).

$$k_{ca(t_s)} = k_{ca(1)}(0.75^{\ln t_s / \ln 2}) \tag{2.16}$$

where:
$k_{ca(t_s)}$ = sludge oxidation rate coefficient at a specific sludge age [d^{-1}]
$k_{ca(1)}$ = sludge oxidation rate coefficient at sludge age 1 day equal to approximately to 0.5 d^{-1}

While in the CM model k_{ca} is assumed to be constant with a value of 0.2 d^{-1}.

In both models the same equation is used to compute X_e, which is defined as "endogenous mass accumulation" in GE model and "inert remains of active microorganisms" in CM model (eq. 2.17).

$$X_e = (1 - f_d) k_{ea} X_a t_s \quad (2.17)$$

where:
f_d = biodegradable fraction of microorganisms

The value of the biodegradable fraction of microorganisms as used by those authors varies from 0.76 - 0.77 in GE model to 0.8 in CM model.

In both models volatile mass is computed as the sum of active biomass and endogenous mass (inert organic remains) (eq. 2.18).

$$X_v = X_a + X_e \quad (2.18)$$

In the GE model there is one more SS component, inert inorganic mass (eq. 2.19).

$$X_i = f_i X_0 t_s / t_d + f_{ndi} (X_a + X_e) \quad (2.19)$$

where:
X_i = inert inorganic mass concentration
X_o = influent SS concentration
f_i = inert fraction of influent SS
f_{ndi} = inorganic inert fraction of microorganisms

Values of coefficients f_i and f_{ndi} are 0.55 and 0.1 respectively (Goodman and Englande, 1974). Total SS concentration in GE model is the sum of active, endogenous and inert mass concentrations (eq. 2.20).

$$X_t = X_a + X_e + X_i \quad (2.20)$$

2.2.3 Grady and Roper's Model

In Grady and Roper's (1973) model sludge is divided into viable and nonviable microorganisms. In this model viable microorganisms (X_w) produced from the process of substrate utilization are lost due to wasting from the system, natural death, decay (which is due to endogenous metabolism, to provide maintenance energy), lysis and predation.

Decay is assumed to be first order kinetics ($b_v X_{vv}$) with respect to viable cells concentration with a constant specific rate b_v (Lawrence and McCarty, 1970). Rate of death (as loss of viability) was assumed to follow first order kinetics (dX_{vv}) with a constant specific rate d (Grady and Roper, 1973). The rate of change of viable mass can be expressed by the following equation.

$$\frac{dX_{vv}}{dt} = -Yr_s - b_v X_{vv} - dX_{vv} \tag{2.21}$$

where:
b_v = specific decay rate constant of viable cells, [d^{-1}]
d = specific death rate constant, [d^{-1}]

By rearranging eq. 2.21 and substituting eq. 2.9 for r_s, viable mass concentration is computed.

$$X_{vv} = Y\frac{t_s(S_0 - S_e)}{t_d(1 + b_v t_s + dt_s)} \tag{2.22}$$

Production of nonviable microorganisms in this model is due to death rate of viable microorganisms $(dX_{vv}/dt)_d$. Loss of nonviable microorganisms is due to wastage $(dX_n/dt)_w$ and decay ($b_n X_n$) (which is due to endogenous metabolism, lysis and predation). Concentration of nonviable microorganisms is computed from the rate of change of nonviable mass (eq. 2.23).

$$\left(\frac{dX_n}{dt}\right)_w = \left(\frac{dX_{vv}}{dt}\right)_d - b_n X_n \tag{2.23}$$

where:
b_n = specific decay rate constant of nonviable cells, [d^{-1}]

Substituting viable microorganism death rate $(dX_{vv}/dt)_d$ in eq. 2.23, with first order kinetics (eq. 2.24), and dividing both sided of resulting equation by X_n yields eq. 2.25. Rearranged eq. 2.25 gives an expression for nonviable mass concentration (eq. 2.26).

$$\left(\frac{dX_{vv}}{dt}\right)_d = dX_{vv} \tag{2.24}$$

$$\frac{\left(\frac{dX_n}{dt}\right)_w}{X_n} = \frac{dX_{vv}}{X_n} - b_n = \frac{1}{t_s} \tag{2.25}$$

$$X_n = \frac{t_s dX_{vv}}{1 + b_n t_s} \tag{2.26}$$

Total cell concentration in the reactor is the sum of the viable and nonviable cell concentrations (eqs. 2.27, 2.28).

$$X = X_{vv} + X_n \tag{2.27}$$

$$X = Y\frac{t_s(S_0 - S)(1 + b_n t_s + dt_s)}{t_d(1 + b_n t_s)(1 + b_v t_s + dt_s)} \tag{2.28}$$

2.3 Kinetic Studies

In Monod (eq. 2.2) and linear (eq. 2.3) substrate utilization rate equations, biomass concentration is usually represented by VSS. Often this results in misrepresentation of the actual active mass concentration, because VSS represents all suspended organic mass in the mixed liquor (ML). Specific substrate utilization and growth rates (k and μ_s) computed from those equations usually represent the observed substrate utilization or growth rates normalized with respect to volatile mass concentration (X_v). Usually those coefficients do not reflect the actual kinetics of the process conducted at a particular SRT, because substrate utilization kinetics depends on X_a (Weddle and Jenkins, 1971). Coefficients computed from tests conducted at different SRTs exhibit variability due to different X_v concentrations in those tests.

The comparison between specific kinetic rates computed from eqs 2.2 or 2.3 from tests performed at different SRTs, may have little meaning because the ratio between X_v and X_a is not constant at different SRTs. Thus, even if those studies were conducted on a

sludge with similar bacterial composition of active mass and the same substrate, specific rates computed from those equations usually would not reflect this fact. However, if under the same experimental conditions specific kinetic rates were computed as observed rates normalized with respect to X_a, the variability of those coefficients due to X_v would be eliminated.

Summarizing, the computation of one set of specific kinetic rates from Monod or linear equations for a number of processes conducted at different sets of conditions, often results in kinetic coefficients which are an imprecise approximation of the actual sludge kinetics occurring at each set of conditions, because the actual X_a concentrations and the decrease in X_a/X_v ratio with increase in SRT are not being represented in those equations.

The improvement of kinetic equations in the direction of finding "intrinsic" kinetic coefficients, finds support in recent studies. Intrinsic, meaning: "depending on the structure of the compound and degrading microbial community, not on the configuration of the experimental setup" (Tabak et al., 1992). This approach is presented by Tabak et al. (1992), in the development of predictive structure-biodergadation models, in which the contribution coefficients of different substrates were found. The overall Monod coefficients were calculated based on those contribution coefficients. Similarly Cooney and McDonald (1993) evaluated "intrinsic" Monod constant K_s as a function of the type of substrate.

Sun (1993), tested the modified Monod and linear equations proposed in this study for continuos flow (CMSTR) and sequencing batch reactors (SBR), and found that the best fit was obtained for n = 0.1 in both modified equations ($r_s = -kSX_v^{0.1}/(S+K_s)$, and $r_s = -kSX_v^{0.1}$). Computed kinetic coefficients k, K_s depended on the type of reactor. Exponent n was independent of the reactor type, this indicated that at a particular SRT the X_a/X_v ratios in SBR and CMSTR were the same.

A number of studies were conducted over the years, in which either eq. 2.1 or eq. 2.2 was used to model sludge kinetics. The results from some of these studies are presented and evaluated below.

Equation 2.1 ($\mu = -\mu_s S/(S+K_s)$ [d^{-1}]) was applied to model aerobic substrate utilization kinetics of a heterogeneous bacterial population, in laboratory scale batch reactors (Peil and Gaudy, 1971). Thirteen different substrates were used, and each except cysteine was tested at least twice. Computed plots of substrate concentration vs. specific growth rate (μ [d^{-1}]) fitted experimental data very well for each individual test. Maximum specific growth rates (μ_s) and half velocity coefficients (K_s), computed for each test, are presented in Table 2.1. The X_v and SRT experimental data were not provided. The values of kinetic coefficients were significantly different for tests conducted on the same substrate at different times. These differences were attributed to a change in species predominance in the mixed culture, during the interval of several weeks between replicate experiments. However, the differences in computed μ_s and K_s from tests conducted on the same substrate might have resulted as well from different X_v in those tests.

Table 2.1 Kinetic coefficients, Peil and Gaudy, 1971

Substrate	Exp. #	μ_s h^{-1}	K_s mg COD/L
Glucose	1	0.49	29
	2	0.38	11
Lactose	1	0.53	55
	2	0.44	37
	3	0.21	--
	4	0.43	33
Sucrose	1	0.55	17
	2	0.28	6
Sorbitol	1	0.60	18
	2	0.44	13
Alanine	1	0.33	27
	2	0.18	15
Glutamic acid	1	0.78	47
	2	0.59	95
Serine	1	0.43	50
	2	0.54	30
Histidine	1	0.50	17
	2	0.67	50
Phenylalanine	1	0.33	41
	2	0.33	54
Cysteine	1	0.16	23
Acetic acid	1	0.36	41
	2	0.29	47
Propionic acid	1	0.38	6
	2	0.37	16
Sewage	1	0.49	41
	2	0.43	62

Results from batch substrate utilization tests were fitted with eq. 2.1 in study on activated sludge by Gaudy et al., (1967). Seed sludge was obtained from a municipal wastewater treatment plant. Sludge was acclimatized in a CFSTR on a synthetic substrate containing 1000 mg/L of glucose and essential minerals. HRT was the same as the SRT because sludge exiting from the reactor was not recirculated. For each SRT, a set of batch experiments was performed with initial substrate concentrations ranging from 50 to 800 mg/L of glucose, and SRTs from 1.5 to 24 h. Initial growth rates from those series of experiments were plotted vs. substrate concentrations, and fit with the kinetic model. Resulting values of μ_s and K_s for each SRT were very different (Table 2.2). This could indicate lack of applicability of eq. 2.1 to fit data from tests for all SRTs lumped together.

The Monod equation fitted data very well for experiments conducted at the same SRT (fitting errors were not provided, only plots of μ vs. S).

Table 2.2 Kinetic coefficients, Gaudy et al., 1967

SRT	μ_x	K_s
h	h^{-1}	mg COD/L
24	0.416	68
18	0.384	87
12	0.588	91
6	0.715	145
4	0.555	97
3	0.770	181
2	0.600	116
1.5	0.530	30

The relationship between maximum specific substrate utilization rate (k) and SRT was investigated for activated sludge utilizing xenobiotics (Chudoba et al., 1989). Transformed eq. 2.2 ($r_{s2} = -k_2SX_v/(S+K_s)$) in which k_2 times X_v was substituted by overall coefficient K was employed to model substrate utilization rate ($r_s = -KS/(S+K_s)$). The experiments were carried out in a completely mixed system at two different constant volumetric loading rates (VLR) and various SRTs for each substrate. The first series of experiments were conducted for VLR = 12.8 mg COD/L/h, and the second series for VLR = 41.7 mg COD/L/h. Results from the first series of experiments are presented in Table 2.3. It was found that maximum specific substrate utilization rates ($k_2[h^{-1}] = K/X_v$) were generally higher for low SRTs, for the same substrate. It was concluded that the increase observed for younger sludges was caused by the fact that slow growing organisms were washed out of the system. This led to relative enrichment of the culture with organisms responsible for removal of a particular substrate. It was also concluded that the increase in k_2 with decrease in SRT could be also due to the fact that younger cells of responsible microorganisms were more active in removing xenobiotics. Those conclusions do not have any support in the data presented. The coefficients k_2 were not the values which were

observed, they were computed by dividing observed coefficient K (equal to the maximum r (mg COD/L/d)) by X_v. Thus the increase in k_2 relative to decrease in K with decrease in SRT, was simply due to decreasing X_v concentration with decrease in SRT (Table 2.3). In this experiment, it could not be assumed that all X_v was composed of active mass, which would validate those conclusions, because SRT varied from 0.7 to 3.4 days. Results from this study indicated that eq. 2.2 with constant k_2 and K_s would not fit the data well from the experiments performed at different SRTs (because k_2 were different for different SRT for tests on the same substrate, Table 2.3).

Table 2.3 Kinetic coefficients, Chudoba J. et al. (1989)

Compound	SRT	K	k_2	K_s
	d	mg COD/L/d	$d^{-1}\cdot10^3$	mg COD/L
morpholine	2.5	10.5	17.3	--
	1.3	3.7	13.6	--
	0.7	0.6	9.2	--
sulphanilic	3.4	17.7	21.1	2.0
acid	2.5	12.6	24.3	--
	1.3	5.4	24.9	--
	0.7	2	34.2	--
nitrilotriacetic	3.4	22.7	26.2	1.6
acid	2.5	18.6	33.5	--
	1.3	10.7	37.7	2.6
	0.7	3.6	53.8	--
methanol	3.4	37.4	45.0	0.4
	2.5	31.1	55.0	0.4
	1.3	22.0	103.3	--
	0.7	12.7	121.3	--

Braha and Hafner (1987) fitted eq. 2.2 to a set of data, obtained from batch utilization tests. Those tests were conducted on activated sludge, fed with low concentrations of industrial wastewater. Sludge was acclimatized in a CFSTR, with HRT between 4 and 17.5 hours. Seven batch experiments were conducted with initial sludge concentrations ranging from 3880 to 5880 mg VSS/L and SRTs between 3.6 and 11.4 days. Initial feed concentrations in the batch experiments were between 270 and 308 mg

TOC/L, falling steadily to around 50 mg TOC/L at hour 15 of the test. According to the authors, eq 2.2 with microorganisms concentration equal to the average MLVSS concentration, fitted data poorly from all experiments lumped together (R^2=0.541). A zero order (with respect to substrate concentration) substrate utilization rate equation (eq 2.4, $r_{sS} = -k_5 X_v$) correlated the same data with $R^2 = 0.86$ ($k_5 = 0.0245$). Kinetic coefficients computed for each test separately, based on X_v from each test, are presented in Table 2.4.

Table 2.4 Kinetic Coefficients, Braha and Hafner (1987)

Test	K_s	μ_s	X_0	S_0	SRT
#	g TOC/L	d^{-1}	g VSS/L	g TOC/L	d
1	14	0.400	5.88	0.277	11.4
2	13	0.482	4.31	0.281	9.3
3	13	0.500	4.19	0.319	8.0
4	14	0.568	4.02	0.296	6.4
5	15	0.776	3.68	0.281	4.9
6	16	0.548	5.02	0.273	4.0
7	14.8	0.383	3.88	0.228	3.6

Equation 2.2 with constant kinetic coefficients would not fit data well from all tests, as it was indicated by variability of μ_s (Table 2.4).

Equation 2.2 was fitted to results from batch experiments (Speitel and DiGiano, 1988) in which microorganisms were utilizing a phenol based feed at very low concentrations. In order to prepare sludge for batch experiments, a chemostat (batch reactor) was seeded with a mixture of activated sludge from a wastewater treatment plant, runoff from a coal pile, and activated sludge used in the treatment of coal gasification wastewater. The chemostat operated at a feed concentration of 0.5 mg/L of phenol and an HRT of 5 h. After several weeks of acclimatization sludge was diluted in two proportions, 1:3 and 1:5, for use in substrate utilization batch experiments. Before those tests, the sludge was spiked with phenol to stimulate microbial activity and reduce the lag time at the beginning of the experiments. In batch tests each of the two sludge dilutions were fed with 12 different initial substrate concentrations. Equation 2.2 was fitted to the r_s vs. S data from experiments performed on different concentrations of the same sludge lumped

together. The authors do not provide some data, from tests performed, such as: microorganism concentration, SRT, mass accumulation and kinetic coefficients, and fitting errors. It would be useful to fit eq. 2.2 to tests conducted for each sludge dilution separately, and compare the resulting k, K_s and fitting errors with results from fitting procedure performed by Speitel and DiGiano. From plots of r_s vs. S provided in that study it could be concluded that such an exercise would be worthwhile, because data points from tests for each dilution exhibited different patterns. This meant that eq. 2.2 did not fit well results from two dilutions lumped together.

Batch phenol degradation tests (Beltrame et al., 1979) were conducted on sludge which was acclimatized in a CFSTR with an influent phenol concentration of 360 mg/L. Under CFSTR conditions the substrate removal rate followed Monod type kinetics according to equation 2.1 (or eq. 2.2). Three experimental procedures for batch tests were implemented: a) mixed liquor was transferred from a CFSTR to a batch vessel, and substrate degradation was observed, b) additional phenol was added to the ML taken from continuous flow reactor, and degradation was measured, c) substrate degradation in ML transferred from CFSTR was carried out to depletion, after that phenol was added and the kinetic run was performed. Equation 2.1 with the kinetic coefficients computed from CFSTR run ($k = 0.140\ h^{-1}$, $K_s = 247$ mg/L), was used to model batch runs. Specific substrate degradation rates computed at the initial substrate concentration ($r_{com.}(S_0)$) were much higher than the observed specific substrate degradation rates at S_0 ($r_{ob.}(S_0)$), in procedures b) and c). This phenomenon was judged to be caused by the inhibitory character of phenol. Because of the high phenol concentrations in procedures b) and c), and its inhibitory effect on sludge, results from those procedures cannot be used for the purpose of evaluating applicability of eq. 2.1. Out of 28 runs, some experimental results like substrate concentration, MLVSS, and specific substrate utilization rates, were provided for 18 runs only. SRTs were not presented, and it was not indicated whether the sludge concentration was hydraulically changed. In procedure a) (Table 2.5) in runs 2, 6,

25 and 19 computed specific substrate degradation rates $r_{com.}(S_0)$ and observed specific substrate degradation rates $r_{obs.}(S_0)$ were similar, in runs 21, 29, and 14 differences between $r_{com.}(S_0)$ and $r_{obs.}(S_0)$ were significant (Table 2.5, col. 4 and 5). Thus, it can be concluded that the results from this procedure do not support the applicability of eq. 2.1 with constant coefficients, to model substrate utilization at conditions of different substrate and microbial concentrations.

Table 2.5 Substrate utilization rates, Beltrame et al. (1979), (procedure a)

Run no.	S_0^*	X_0^{**}	$r_{obs.}(S_0)$	$r_{com.}(S_0)$
	mg Phenol/L	mg VSS/L	$(10^2)h^{-1}$	$(10^2)h^{-1}$
2	115	3180	4.56	4.47
21	134	2390	6.03	4.95
28	135	2870	3.46	4.97
6	169	2260	5.48	5.72
25	173	2220	5.44	5.79
14	188	2140	4.25	6.08
19	220	1550	7.65	6.62

*substrate concentration at zero time
**MLVSS concentration at zero time

Based on the above review it can be concluded that eq. 2.2 (or 2.1), with constant kinetic coefficients, in which maximum specific substrate utilization rates (or growth rates) were computed by normalizing maximum substrate utilization rates (or growth rates) with respect to X_v (or total biomass concentration) failed to model sludge kinetics at different SRTs. The coefficients k (or μ) and K_s in those equations were far from being intrinsic to the substrate and microbial population tested. They tended to be setup specific (depended on SRT), and exhibited high variability. The same conclusions may be drawn for the linear equation (eq. 2.3) and its coefficients because it is also based on X_v.

CHAPTER 3

DEVELOPMENT AND TESTING OF THE MODIFIED EQUATIONS

3.1 Active Mass Representation as AX_v^n in the Modified Monod and Linear Equations

It would be an improvement, if biomass was represented in kinetic equations by active biomass, which is the mass of microorganisms responsible for substrate removal from the ML. In this case sludge substrate utilization kinetics would be directly proportional to the concentration of active organisms (Weddle and Jenkins, 1971).

Concentration of active biomass in sludge can be determined by a number of methods. However, each of these methods is lengthy and complicated. For these reasons it would be convenient and time saving if active biomass was represented as a function of VSS concentration (X_v), which is easy to measure.

The proposed modification had to represent the changing ratio between active and volatile mass concentrations (X_a/X_v) which accompanies change in SRT. Variation of this ratio with respect to SRT is shown on the example of the sludge viability data ((X_w/X_v)· 100%), obtained from the Nelson and Lawrence (1980) study (Fig. 3.1).

It was assumed that the proposed modified equations with constant coefficients, will be valid only for sludges fed with the same substrate and having practically the same composition of active biomass. This approach would result in a set of k, and K_s that would approximate the "intrinsic" kinetic coefficients (related to the type of substrate and microbial population, not to the SRT).

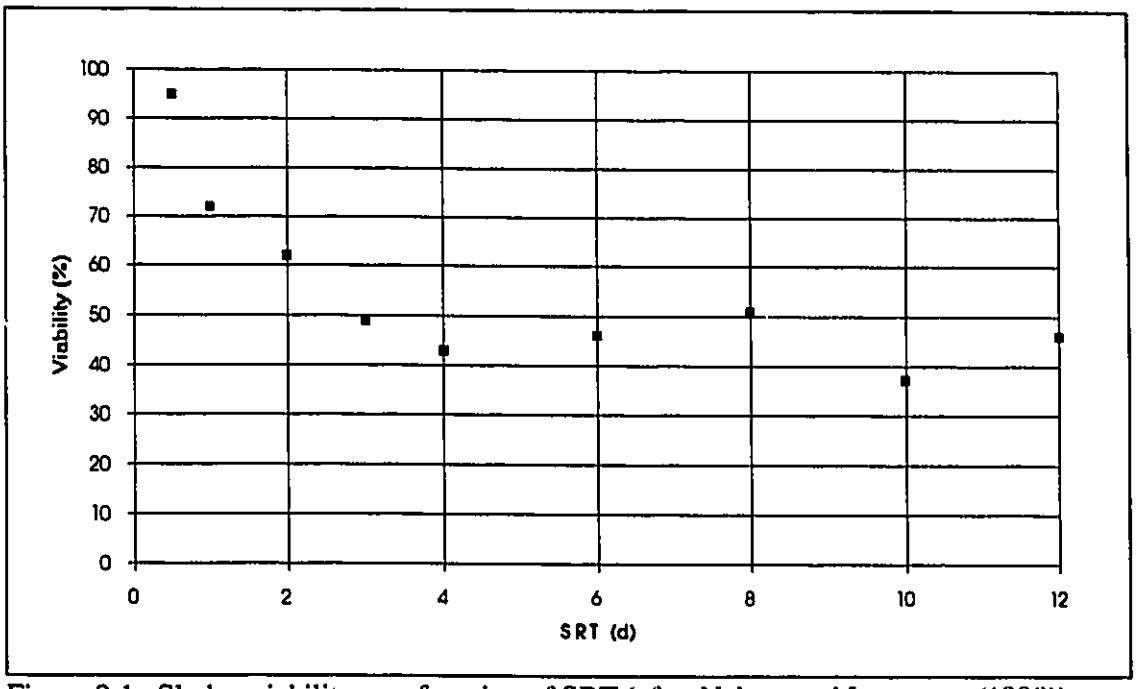

Figure 3.1. Sludge viability as a function of SRT (after Nelson and Lawrence (1980))

In order to account for the above requirements it was proposed to represent X_a as AX_v^n (A constant). This resulted in replacing X_v in eqs. 2.2 and 2.3 by X_v^n, (constant A was absorbed in coefficient k). This modification exhibits the desired behavior of relatively diminishing the influence of increased X_v due to SRT increase on substrate removal kinetics. Modified Monod and linear models are represented by eqs. 3.1 and 3.2, respectively.

$$r_s = -\frac{kSX_v^n}{S+K_s}[mg/L/d] \tag{3.1}$$

$$r_s = -kSX_v^n[mg/L/d] \tag{3.2}$$

The expression X_v^n can be easily fitted to model the decrease in X_a/X_v ratio with increase in SRT, because X_v^n/X_v ratio decreases with increase in X_v. Thus X_v^n is a better representation of active mass concentration in substrate utilization rate equations than usually used X_v.

3.2 Properties of the Modified Model

Kinetic coefficients computed from modified Monod equation (eq. 3.1) and eq. 2.2 are the same only for the conditions of constant X_v. However, when those equations are fitted to the same set of r_s vs. S data from tests conducted at different X_v, kinetic coefficients and fitting error (E) obtained from both equations are different. This is due to the fact that the X_v^n/X_v ratio is not constant for different values of X_v.

Kinetic coefficients k, K_s are usually computed from the linearization of the substrate utilization rate equations. Examination of this procedure, shows the differences between eqs. 2.2 and 3.1. Equations 3.3 and 3.4 represent linearizations of eqs. 2.2 and 3.1, respectively, fitted to the same set of experimental data r_s vs S.

$$\frac{X_v}{r_s} = \frac{1}{S}\frac{K_{s2}}{k_2} + \frac{1}{k_2} \tag{3.3}$$

$$\frac{X_v^n}{r_s} = \frac{1}{S}\frac{K_s}{k} + \frac{1}{k} \tag{3.4}$$

The data to which eqs. 3.3 and 3.4 are fitted are transformations of the r_s vs. S data (set 1) which are experimentally determined. Equation 3.3 is fitted to X_v/r_s vs. 1/S set (set 2), and eq. 3.4 is fitted to X_v^n/r_s vs. 1/S set (set 3). Under the conditions of different X_v (at different SRT) corresponding to different r_s, kinetic coefficients computed from those two sets are not the same. Those two sets of data are equivalent only when X_v is constant for every r_s observed. In this case ratio of corresponding $(X_v^n/r_s)/(X_v/r_s) = X_v^n/X_v$, and set 3 is the transformation of set 2 by constant coefficient X_v^n/X_v. However when X_v is not constant for every r_s observed, the ratio of corresponding inverted normalized substrate utilization rates $(X_v^n/r_s)/(X_v/r_s) = X_{v1}^n/X_{v1}$, X_{v2}^n/X_{v2}... X_{vm}^n/X_{vm} is not constant, and set 3 is not a transformation of set 2 with a constant coefficient. Thus, in this case, set

2 and set 3 are not equivalent, and computed coefficients k, K_s from eqs. 2.2 and 3.1 will be different. The same reasoning applies to eqs. 2.3 and 3.2.

The meaning of the coefficient k computed from modified models and the relation between X_v^n, X_a, k, k_a and A are shown in eq. 3.5.

$$kX_v = k_a A X_v^n = (k_a A)(X_a / A) = k_a X_a \qquad (3.5)$$

where:
k = maximum specific substrate utilization rate based on X_v
k_a = maximum specific substrate utilization rate based on X_a

The actual k_a and X_a are misrepresented by a factor of A in eqs. 3.1 and 3.2. However, because the result of eq. 3.5 is constant for a particular concentration and composition of active mass, it is not necessary to compute factor A and the true values of k_a and X_a, in order to arrive at the correct value of substrate utilization rate r_s. Coefficient A has to be computed only for the purpose of approximating the actual concentration of active mass (according to equation $X_a = AX_v^n$).

Application of the modified model gives the best results, when the kinetic coefficients are computed for the conditions of similar organic loading rates, in addition to the conditions of practically the same substrate and microbial population (section 3.1). The reason for this is that the ratio of X_v^n/X_v approximates different X_a/X_v ratios at different SRTs. However, this makes modeling of the same ratio less accurate for the conditions of the same SRT and different organic loading rates (OLR). Under those conditions the computed X_v^n/X_v (X_a/X_v) ratio increases with increasing ORL (because X_v increases), while the actual X_a/X_v ratio may remain the same.

The conditions of applicability of the modified model determined the experimental conditions for which k, K_s coefficients were computed in this study. Those coefficients were computed based on tests conducted on sludge developed on the same substrate and the same OLR, and at different SRT.

3.3. The Modified Models fitted to the Theoretical Data

In the following section, the best fitting exponent n, in the modified Monod ($r_s = -kSX_v^n/(S+K_s)$) and linear ($r_s = -kSX_v^n$) substrate utilization rate equations will be computed for assumed theoretical conditions based on data generated from sludge models presented in Chapter 2.

Finding the optimum n allowed for computation of active mass concentrations as a function of X_v, according to the expression AX_v^n.

3.3.1 Computational Procedure

Computations were conducted for GE, CM and GR sludge models for continuous flow processes. Values of parameters specific to a particular sludge model, and coefficients Y_a, k_{ca}, k_a, and K_s, were the same as used by authors of the model. Other parameters such as S_0, t_d, together with SRTs, and exponents n at which sludge parameters were computed, were assumed by the author. The models were applied over a range of SRTs to predict effluent substrate concentration, active mass in the reactor and other process variables.

To find the optimal value of n, coefficient k in eqs. 3.1 or 3.2 (depended on sludge model) had to be found for each pair of SRT and n. Thus, for each sludge model, a two dimensional array of maximum substrate utilization rates normalized with respect to X_v^n (k_n) was computed. Each row in this array corresponded to different SRT, and each column to different exponent n.

The first step in this procedure was to compute, for different SRTs, active mass (X_a) or viable mass (X_w), and effluent (S_e) concentrations, based on parameters: S_0, Y_a, k_{ca}, k_a, K_s, and t_d. It is usually assumed that substrate removal coefficients do not change as SRT varies. Therefore active mass based, mass accumulation and kinetic coefficients Y_a, k_{ca}, k_a, and K_s were set constant at different SRTs, on the assumption (which is an

approximation) that the bacterial composition of active mass also remained constant. Using the value of computed X_a the concentrations of other sludge components (X_a, X_i, X_e, X_v, X_w) were computed. Using the effluent concentrations along with the sludge component data the array of k_n coefficients was derived.

To solve the GE, CM, and GR models active mass and effluent concentrations at each SRT were computed using the iteration method. First, the value of active mass was assumed and the corresponding effluent concentration was computed by combining eq. 2.2, or 2.3 in which X_v was substituted by X_a with eq. 2.9, into eq. 3.6 or 3.7 (eq. 2.3 was used in GE model, eq. 2.2 was used in CM and GR models).

(eq. 2.2) $$r_s = -\frac{k_2 S X_v}{S + K_s}$$

(eq. 2.3) $$r_s = -k_3 S X_v$$

(eq. 2.9) $$r_s = -\frac{(S_0 - S_e)}{t_d}$$

$$r_s = -\frac{(S_0 - S_e)}{t_d} = -\frac{k_2 S_e X_a}{S_e + K_s} \qquad (3.6)$$

$$r_s = -\frac{(S_0 - S_e)}{t_d} = -k_3 S_e X_a \qquad (3.7)$$

The rearranged eq. 3.6 (eqs. 3.8 and 3.9) or eq. 3.7 (eq. 3.10), was then solved for S_e.

$$S_e^2 + S_e(X_a k t_d + K_s - S_0) - S_0 K_s = 0 \qquad (3.8)$$

$$S_e = \{-(X_a k t_d + K_s - S_0) + [(X_a k t_d + K_s - S_0)^2 + 4 S_0 K_s]^{0.5}\} / 2 \quad (3.9)$$

$$S_e = \frac{S_0}{1 + t_d k X_a} \quad (3.10)$$

Once S_e was determined, assumed and computed (eq. 3.11) active mass concentrations were compared.

$$X_a = Y_a \frac{t_s (S_0 - S_e)}{t_d (1 + k_{ea} t_s)} \quad (3.11)$$

Iterations were carried out until the assumed and computed X_a values matched within a 0.1 mg/L error margin. The value of S_e obtained for the resulting X_a represented effluent concentration for that particular SRT.

In the next step X_v concentrations were computed according to a particular sludge model. Maximum specific substrate utilization rates, X_v based, were computed from rearranged eqs. 3.6 or 3.7 in which X_a was replaced by X_v (eqs. 3.12 and 3.13).

$$k_2 = \frac{(S_0 - S_e)(S_e + K_s)}{t_d S_e X_v} \quad (3.12)$$

$$k_3 = \frac{(S_0 - S_e)}{t_d S_e X_v} \quad (3.13)$$

Next, for the same SRT, active mass concentrations represented as X_v^n were computed according to eq. 3.14, with exponent n ranging from 0 to 1 in increments of 0.1.

$$kX_v = k_n X_v^n \quad (3.14)$$

where:
$k = k_2$ or k_3

The procedure described above was repeated for each SRT, resulting in k_n array, in which each row represented a set of k_n for a particular SRT, and each column represented a set of k_n for a particular n.

After computing the k_n array, the best fitting exponent n was found based on coefficients of variation (c_v) computed from set of k_n at each n (c_v was equal to the standard deviation of k_n in a column divided by the average k_n in that column, times 100%). The k_n set with the lowest c_v indicated the best exponent n.

The above method was used for the purpose of demonstrating the decreasing variability of k_n computed at different values of exponent n (approaching the zero variability of k_a) as the X_a represented as X_v^n was approaching the X_a computed from the sludge model. If n equal to 1 was found to be the optimal value then the unmodified equation would best describe the rate of substrate removal.

After the optimal exponent n was found, the active mass concentrations represented as AX_v^n were computed at each SRT. Coefficient A was computed by dividing the average k_n (k_{nav}) of the k_n set at the optimum n by coefficient k_a (eqs. 3.15 and 3.16).

$$(k_a A)X_v^n = k_{nav}X_v^n \tag{3.15}$$

$$A = \frac{k_{nav}}{k_a} \tag{3.16}$$

The expression AdX_v^n/dt_s approximated dX_a/dt_s, and the value of exponent n was an indication of the rate of change in concentration of active biomass in the sludge, with respect to SRT.

3.3.2 GE and AX_v^n Models

Following are the computations based on GE model (parameters are given in Table 3.1). The values of parameters Y_a, $k_{ac(1)}$, k_a, K_s, f_d, f_{ndi}, and f_i, were presented by Goodman and Englande (1974) as typical coefficients for domestic sewage treatment.

Table 3.1 Parameters, GE Model

S_0	250	mg COD/L
Y_a	0.47	--
$k_{ac(1)}$	0.5	d^{-1}
k_a	0.073	L/mg/d
t_d	0.25	d
f_d	0.24	--
f_{ndi}	0.1	--
f_i	0.55	--
t_s	0.125	d

Computed effluent substrate concentrations (S_e) and solids concentrations X_a, X_e, X_i, X_t, and X_v at different SRTs are presented in Table 3.2. The last column in this table represents active biomass concentrations, computed according to modified model $X_a = AX_v^n$. Exponent n in this equation corresponded to the set of the maximum substrate utilization rates k_n, which had the lowest coefficient of variation (c_v in Table 3.3). Coefficient A was computed by dividing the average k_n (k_{nav}) of this set by k_a = 0.073 L/mg/d. Comparison between values in fourth and last column (Table 3.2), shows good agreement between X_a computed from the sludge model and X_a computed as AX_v^n.

Table 3.2 Computed X_a concentrations, GE and AX_v^n model

t_x	S_e	k_e	X_a	X_e	X_i	X_t	X_v	AX_v^n
d	mg/L	d^{-1}	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	44	0.500	517	62	58	637	579	548
2	25	0.375	965	174	114	1252	1138	941
3	19	0.317	1336	305	164	1805	1641	1260
4	15	0.281	1660	448	211	2319	2108	1540
5	13	0.256	1950	600	255	2805	2550	1794
7	11	0.223	2460	921	338	3720	3381	2248
10	9	0.192	3106	1434	454	4994	4540	2845
12	8	0.178	3484	1789	527	5799	5272	3207
15	7	0.162	3992	2335	633	6960	6328	3711
20	6	0.144	4731	3275	801	8806	8005	4479

Table 3.3 k_n array for n from 1 to 0, GE and AX_v^n model

SRT\n	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
1	37.7	20.0	10.6	5.60	2.96	1.57	0.830	0.439	0.233	0.123	0.065
2	70.4	34.9	17.2	8.53	4.22	2.09	1.033	0.511	0.253	0.125	0.062
3	97.5	46.5	22.2	10.58	5.05	2.41	1.148	0.548	0.261	0.125	0.059
4	121.2	56.4	26.2	12.20	5.67	2.64	1.228	0.571	0.266	0.124	0.057
5	142.4	65.0	29.7	13.53	6.18	2.82	1.287	0.587	0.268	0.122	0.056
7	179.6	79.7	35.4	15.69	6.96	3.09	1.370	0.608	0.270	0.120	0.053
10	226.7	97.7	42.1	18.13	7.81	3.37	1.450	0.625	0.269	0.116	0.050
12	254.3	107.9	45.8	19.44	8.25	3.50	1.487	0.631	0.268	0.114	0.048
15	291.4	121.4	50.6	21.09	8.79	3.66	1.527	0.636	0.265	0.111	0.046
20	345.4	140.6	57.2	23.30	9.48	3.86	1.571	0.640	0.260	0.106	0.043
c_v(%)=	57.0	51.1	45.0	38.7	32.1	25.4	18.4	11.2	4.3	5.6	13.3

The optimum exponent n in equation $X_a = AX_v^n$ was equal to 0.8, as indicated by the lowest coefficient of variation (4.3%) of the corresponding set of k_n (Table 3.3, Fig. 3.2), the coefficient A was equal to 3.38. The active mass concentrations, computed from this sludge model and according to the modified equation $AX_v^n = 3.38X_v^{0.8}$, were compared on Fig. 3.3. (X_a fit. = AX_v^n on this figure). According to this sludge model the best fitting modified linear equation was given by eq. 3.17, in which coefficient k was equal to k_s times A (computed according to eq. 3.5, as 0.073[L/mg/d]·3.38 = 0.247[L/mg/d].

$$r_s = -0.247 S X_v^{0.8} \qquad (3.17)$$

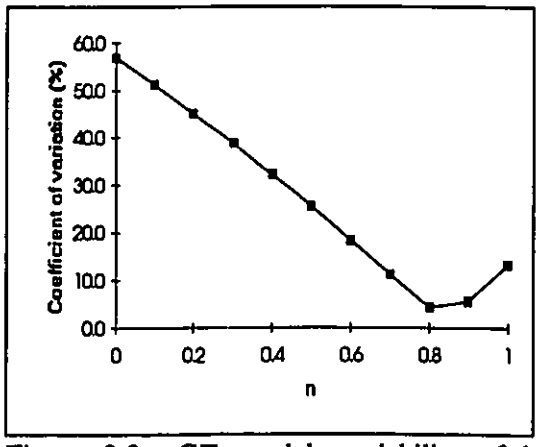

Figure 3.2 GE model, variability of k_n coefficients, as a function of n

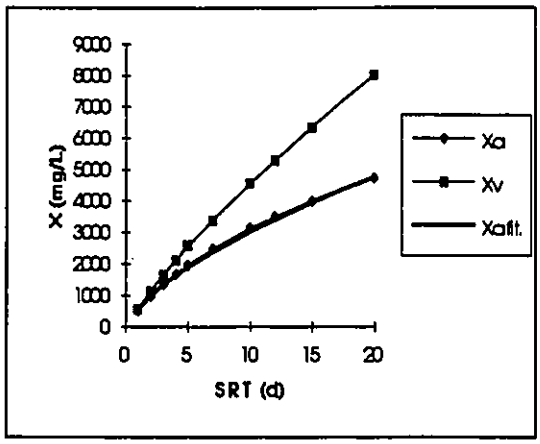

Fig. 3.3 GE model, active mass concentration as AX_v^n

3.3.3 CM and AX_v^n Model

The same computations as in the previous section were repeated for the CM model (parameters are in Table 3.4). The values of parameters Y_a, k_{ea}, k_a, K_s and f_d were used by Christensen and McCarty (1975).

Table 3.4 Parameters, CM model

S_0	250	mg COD/L
Y_a	0.5	--
k_{ea}	0.2	d
k_a	22	d^{-1}
K_s	200	mg COD/L
f_d	0.2	
t_d	0.125	d

Computed effluent substrate concentration (S_e) and biomass concentrations X_a, X_e, and X_v at different SRTs are presented in Table 3.5. The last column in this table represents active biomass concentrations computed according to modified model $X_a = AX_v^n$. Exponent n in this equation corresponded to the set of the substrate utilization rates k_n with the lowest coefficient of variation (c_v in Table 3.6). Coefficient A was computed by dividing average k_n of this set by $k_a = 22\ d^{-1}$.

Table 3.5 Computed X_a concentrations, CM and AX_v^n model

t_c	S_o	X_a	X_o	X_v	AX_v^n
d	mg/L	mg/L	mg/L	mg/L	mg/L
1	24	752	30	782	713
2	14	1351	108	1459	1175
3	10	1799	216	2014	1521
4	9	2146	343	2490	1802
5	8	2425	485	2909	2041
7	6	2842	796	3637	2440
10	6	3259	1303	4562	2925
12	5	3455	1658	5113	3204
15	5	3675	2205	5881	3584
20	5	3926	3140	7066	4151

Table 3.6 k_n array for n from 1 to 0, CM and AX_v^n model

SRT\n	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
1	16544	8498	4365	2242	1152	592	304	156	80.2	41.2	21.2
2	29722	14344	6923	3341	1612	778	376	181	87.5	42.2	20.4
3	39578	18494	8642	4038	1887	882	412	193	90.0	42.0	19.6
4	47212	21599	9881	4521	2068	946	433	198	90.6	41.4	19.0
5	53350	24030	10824	4875	2196	989	446	201	90.4	40.7	18.3
7	62524	27540	12131	5343	2354	1037	457	201	88.6	39.0	17.2
10	71698	30874	13295	5725	2465	1062	457	197	84.8	36.5	15.7
12	76010	32360	13776	5865	2497	1063	453	193	82.0	34.9	14.9
15	80850	33942	14249	5982	2511	1054	443	186	78.0	32.7	13.7
20	86372	35600	14674	6048	2493	1028	424	175	72.0	29.7	12.2
c_v(%)=	41.1	36.4	31.5	26.5	21.4	16.3	11.4	7.5	7.4	11.5	17.4

The optimum exponent n in equation $X_a = AX_v^n$ was equal to 0.8, as indicated by the lowest coefficient of variation (7.4%) of the corresponding set of k_n (Table 3.6, Fig. 3.4), the coefficient A was equal to 3.84. The active mass concentrations computed from this sludge model, and according to the modified equation $AX_v^n = 3.84X_v^{0.8}$, were compared on Fig. 3.5 (X_a fit. = AX_v^n). According to this sludge model, the best fitting modified Monod model was given by eq. 3.18, in which coefficient k was equal to k_a times A (computed according to eq. 3.5, as $22[d^{-1}]\cdot 3.84 = 84.48[d^{-1}]$).

$$r_s = -\frac{84.48SX^{0.8}}{S+200} \tag{3.18}$$

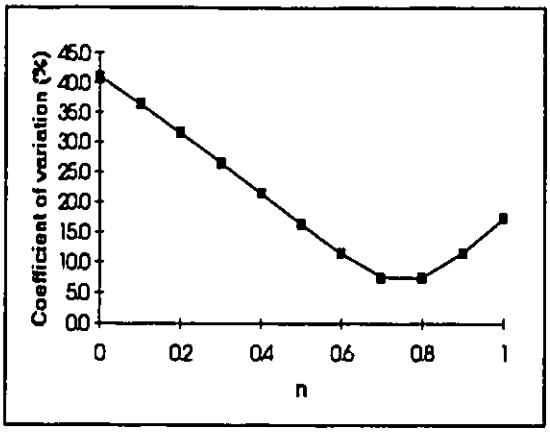

Figure 3.4 CM model, variability of k_n coefficients, as a function of n

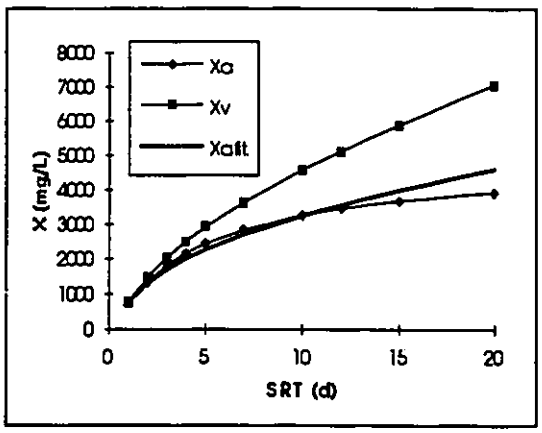

Fig. 3.5 CM model, active mass concentration as AX_v^n

3.3.4 GR and AX_v^n Model

Results obtained from Grady and Roper's model are presented in Tables 3.8 and 3.9, (parameters are in Table 3.7). The same computational procedure as for GE and CM models was used. The values of Y_a, k_a, K_s b_v, b_n, d, and f_d were presented by Grady and Roper (1974).

Table 3.7 Parameters, GR model

S_o	250	mg	COD/L
Y_a	0.5	--	
b_v	0.192	d^{-1}	
b_n	0.024	d^{-1}	
d	0.24	d^{-1}	
k_a	22	d^{-1}	
K_s	200	mg	COD/L
f_d	0.24		
t_d	0.125	d	

Computed effluent substrate concentration (S_e) and biomass concentrations X_{vv}, X_n, and X at different SRTs are presented in Table 3.8. The last column in this table represents active biomass concentrations computed according to modified model $X_a = AX^n$. Exponent n in this equation corresponds to the set of the substrate utilization rates k_n with the lowest coefficient of variation (Table 3.8). Coefficient A was computed by dividing the average k_n of this set by $k_a = 22\ d^{-1}$.

Table 3.8 Computed X_w concentrations, GR and AX^n model

SRT	S_r	X_w	X_n	X	AX^n
d	mg/L	mg/L	mg/L	mg/L	mg/L
1	30	615	144	759	688
2	19	993	455	1448	891
3	15	1228	825	2053	1025
4	13	1389	1216	2605	1127
5	12	1505	1613	3118	1211
7	11	1663	2392	4055	1345
10	10	1803	3490	5293	1497
12	10	1864	4168	6033	1577
15	9	1929	5107	7036	1677
20	9	1999	6482	8481	1807

Table 3.9 k_n array for n from 1 to 0, GR and AX^n model

SRT\n	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
1	13530	6971	3591	1850	953	491	253	130.4	67.2	34.6	17.83
2	21846	10551	5096	2461	1189	574	277	133.9	64.7	31.2	15.08
3	27016	12600	5877	2741	1278	596	278	129.7	60.5	28.2	13.16
4	30558	13917	6338	2887	1315	599	273	124.2	56.6	25.8	11.73
5	33110	14811	6625	2964	1326	593	265	118.7	53.1	23.7	10.62
7	36586	15941	6946	3026	1319	575	250	109.1	47.5	20.7	9.02
10	39666	16828	7140	3029	1285	545	231	98.1	41.6	17.7	7.49
12	41008	17172	7191	3011	1261	528	221	92.6	38.8	16.2	6.80
15	42438	17499	7216	2976	1227	506	209	86.0	35.5	14.6	6.03
20	43978	17799	7204	2915	1180	478	193	78.2	31.7	12.8	5.19
c_v(%)	29.9	24.3	18.7	13.3	9.0	8.3	12.3	18.4	25.3	32.7	40.4

The optimum exponent n in equation $X_a = AX^n$ was equal to 0.5, as indicated by the lowest coefficient of variation (8.3%) of the corresponding set of k_n (Table 3.9, Fig. 3.6), the coefficient A was equal to 24.93. The active mass concentrations, computed from this sludge model, and according to the modified equation $AX^n = 24.93X^{0.5}$, were compared on Fig. 3.7 (X_w fit. = AX^n). According to this sludge model, the best fitting modified Monod equation was given by eq. 3.19, in which coefficient k was equal to k_s times A (computed according to eq. 3.5, as $22[d^{-1}] \cdot 24.93 = 548.5[d^{-1}]$).

$$r_s = -\frac{548.5SX^{0.5}}{S+200} \tag{3.19}$$

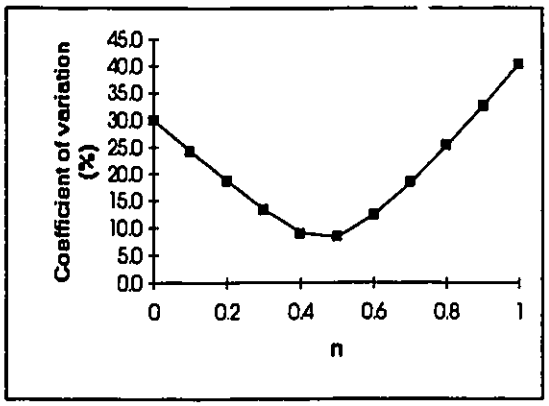

Figure 3.6 GR model, variability of k_n coefficients, as a function of n

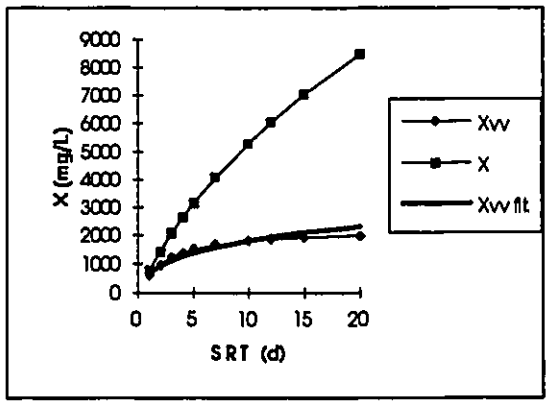

Fig. 3.7 GR model, viable mass concentration as AX^n

3.3.5 Conclusions

The optimum exponent n found from each sludge model (GE, CM, and GR), for the utilization of domestic sewage at the same S_0, t_d and t_s range, was different from 1 or 0. According to these models and for the conditions assumed, the active mass concentrations were better represented by $AX_v^{0.8}$ or $AX_v^{0.5}$ than by AX_v^1 as in eqs. 2.2 or 2.1.

3.4 The Modified Models fitted to the Experimental Data

In this section the sludge active mass[1] concentrations from two experiments were fitted by the modified model AX_v^n. In the third example the experimental data set r_s vs. S, was fitted by eq. 3.1.

---

[1]Terms indicating microorganisms which participate in substrate utilization process are different in different studies, active mass (as used in previous sections) or viable mass are often used. In presented reviews, terms used are the same as in the study under review. The term active mass is used in other parts of this thesis.

1. Experiments were performed by Upadhyaya and Eckenfelder, (1973) on continuous flow stirred tank reactors (CFSTR) with an 8 L volume. A suspension of powdered skim milk in autoclaved tap water was used as a substrate. Excess sludge was wasted regularly to keep MLVSS concentration at an approximate level of 2400 mg/L. Data in Table 3.10 in columns 1, 2, 3, 4, 5, and 7 were taken from that experiment; values in columns 6, 8, and 9 were computed to show the relation between SRT and viable (active) biomass concentration. Active mass concentration was measured according to plate count, and ATP (adenosine triphosphate) methods. Amount of ATP was approximately constant in viable microbial cells at different SRT (col. 8, Table 3.10).

Table 3.10 Experimental and computed viable mass concentration, Upadhyaya and Eckenfelder (1973)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
unit #	TOC	X_v	SRT	c*/Xv	c/TOC	ATP/X_v	ATP/c	X_v/TOC	AX_v^n
-	g/d	g/L	d	c/g ($\times 10^{-11}$)	c/g/d ($\times 10^{-11}$)	g/g ($\times 10^{3}$)	g ($\times 10^{8}$)	g/L/g/d	c/g/d ($\times 10^{-11}$)
1	1.15	2.23	40.7	1.49	2.89	0.531	0.356	1.939	0.305
2	1.78	2.27	23.4	2.10	2.68	0.746	0.355	1.275	0.269
3	2.59	2.35	14.6	2.63	2.39	0.915	0.348	0.907	0.243
4	3.33	2.60	12.1	2.91	2.27	0.987	0.339	0.781	0.232

*cell
(2) - organic loading rate
(6) - col. (5) multiplied by col. (3) and divided by col. (2)
(8) - col. (7) divided by col. (5)
(9) - col. (3) divided by col. (2)
(10) - $A\times$(c/TOC (col. 6))^n

Viable and volatile mass concentrations, normalized with respect to the organic loading rate (col. 6 and 9, Table 3.10), and active mass concentration represented as AX_v^n (col. 10, Table 3.10) were presented on Fig. 3.8 ($AX_v^n = X_a$ fit. on graph legend).

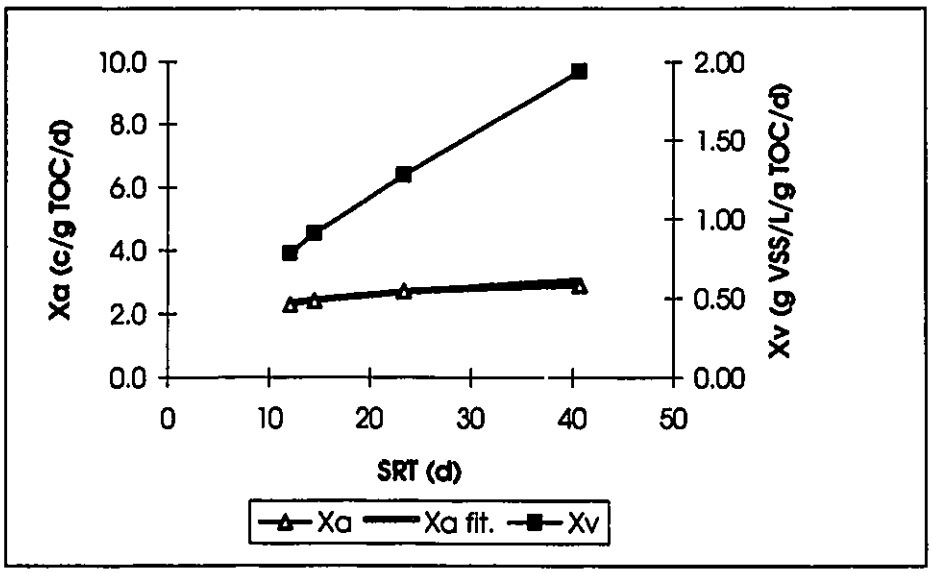

Figure 3.8 Viable and volatile mass as a function of SRT

On Fig. 3.8 X_a represented number of viable cells per g TOC/d times 10^{-11}, X_v represented g MLVSS/g TOC/d. The ratio between active and volatile mass concentrations in sludge decreased as SRT increased. The active mass concentration was fitted with the expression $2.5X_v^{0.3}$ (X_a fit. on Fig. 3.8).

Normalized active and volatile mass concentrations were obtained by dividing the concentration of viable mass by the total amount of TOC per day, not by the amount of substrate utilized per day. This however, did not skew the computed X_a/X_v ratios as long as TOC biodegradable percentage remained constant (which was most likely the case, because synthetic feed of constant composition was used) and hydraulic retention time (HRT) was long enough to achieve complete biodegradation of substrate. Hydraulic retention time in these experiments varied between 2.1 and 6.1 days, thus, it could be assumed that the utilization of biodergadable substrate (glucose) was almost complete at each SRT.

2. Based on mass accumulation coefficients from the Nelson and Lawrence (1980) study, viable mass computed as AX_v^n was compared to the viable mass concentration as computed from equation 2.13.

$$\text{(eq. 2.13)}\quad X_a = Y_a \frac{t_s(S_0 - S_e)}{t_d(1 + k_{ea} t_s)}$$

where:
t_s-SRT
t_d-HRT
S_0-initial substrate concentration
S_e-effluent substrate concentration
k_{ea}-viable mass based endogenous decay rate
Y_a-yield, based on viable mass

In that study viable mass concentration was determined by the ATP method. Mass accumulation coefficients were computed from eq. 2.12 ($r_x/X_a = - Y_a r_s/X_a - k_{ea}$) and assumed constant for the whole experiment (Table 3.11). Other conditions were; t_d = 1 day, and the volumetric loading rate (VLR) equal to 1000 mg COD/L/d.

Viable mass concentration as computed from the modified equation $X_a = AX_v^n = 8X_v^{0.6}$ (A and n fitted), approximated very closely viable mass concentration as computed according to eq. 2.13, for SRTs from 0.5 to 12 days (Table 3.12, cols. 6 and 4). Active mass concentration fitted by $8X_v^{0.6}$ is presented on Fig. 3.9 (X_{vv} fit.).

Table 3.11 Mass accumulation coefficients, Nelson and Lawrence (1980)

Y	k_e	Coeff. basis
mg/mg	d^{-1}	
0.327	0.019	X_v
0.310	0.228	X_{vv}

Table 3.12 Viable mass concentrations; observed (Nelson and Lawrence, 1980), and computed as equal to AX_v^n

SRT	X_{vv}(ob.)	X_v	X_{vv}	X_{vv}(com.)	$8X_v^{0.6}$	$4.5X_v^{0.7}$	$39X_v^{0.4}$
d	%	mg/L	mg/L	%	mg/L	mg/L	mg/L
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
0.5	95	153.9	132.2	86	164.2	152.8	292.4
1	72	304.9	239.8	79	247.5	246.6	384.3
2	62	598.6	404.5	68	371.0	395.5	503.4
3	49	881.7	524.6	60	468.0	518.7	587.7
4	43	1154.8	616.1	53	550.3	626.6	654.7
6	46	1673.2	746.2	45	687.4	812.2	759.4
8	51	2157.3	834.3	39	800.6	970.4	840.7
10	37	2610.5	897.9	34	897.7	1109.0	907.3
12	46	3035.7	945.9	31	982.7	1232.5	963.8

(2)-observed percent viability.
(3)-computed VSS concentration (eq. 2.11).
(4)-computed viable mass concentration (eq. 2.13).
(5)-computed percent viability (X_{vv}/X_v 100%).

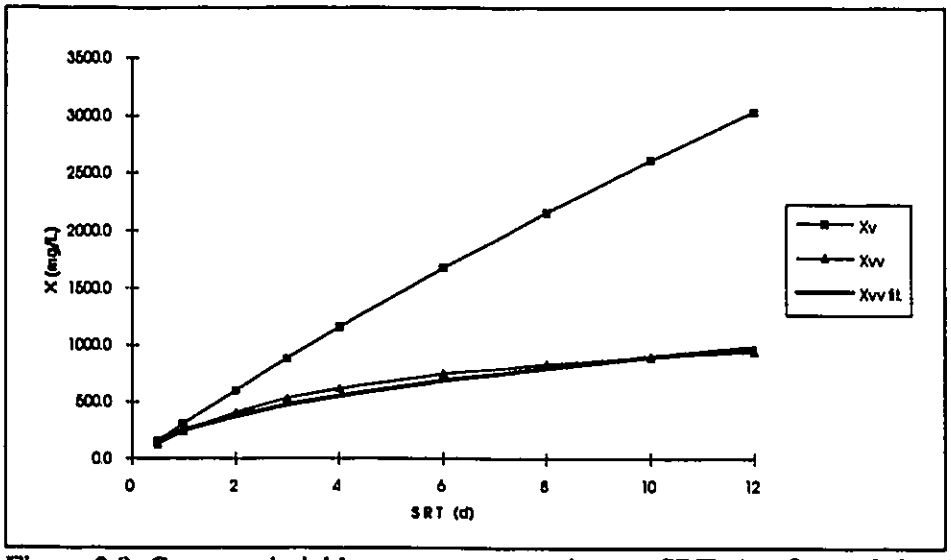

Figure 3.9 Computed viable mass concentration vs. SRT, A = 8, n = 0.6

To demonstrate the influence of the range of SRT on the computed exponent n and coefficient A in the expression AX_v^n, equation AX_v^n was fitted to the experimental data (X_{vv}) from the following SRT ranges: 0.5 to 4 days (X_{vv} fit. 1) and 6 to 12 days (X_{vv} fit. 2) (Fig. 3.10).

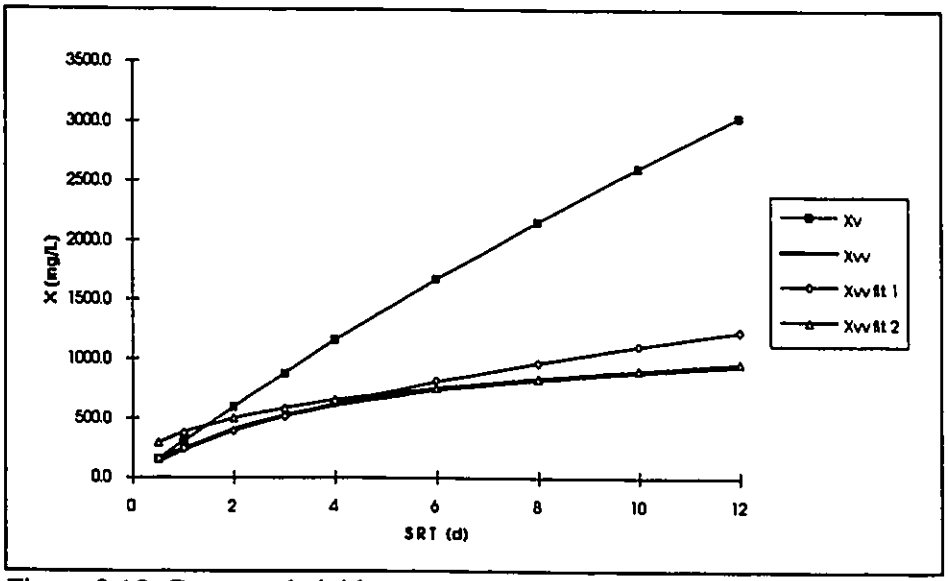

Figure 3.10 Computed viable mass concentrations, SRT ranges 0.5 - 4 and 6 - 12 days

Expressions AX_v^n with coefficients A and n computed from a particular data range fitted well the experimental data only in that range (Fig. 3.10). The fitted coefficients A and n were equal to: 4.5 and 0.7, and to 39 and 0.4, from SRT range 1 and 2, respectively.

3. Based on the experimental data from Yenke et. al. (1992) study, kinetic coefficients k and K_s and the fitting errors (E) computed from the best fitting eqs. 2.1 and 3.1 were compared. In that study experiments were performed on continuos flow, high performance compact reactor (HCR). Sludge was fed with synthetic glucose based feed, 18 runs were conducted. Loading rates, biomass concentrations, influent concentrations, and SRTs were different in each run (Table 3.13). In Yenke's study specific substrate utilization rates (r_{su} in Table 3.13) at each SRT were computed by dividing observed growth rates (r_g) by X. In that study, kinetic coefficients k and K_s were computed from the r_g/X vs. S data set, from the fitted Monod equation (eq. 2.1), and were equal to 0.33 kg BOD_5/kg TSS/h and 80 mg BOD_5/L, respectively. Authors did not include runs 1, 2, 3, and 4 in these computations.

Table 3.13. Activated sludge process parameters (Yenke at. el. 1992)

run	Q	td	S_0	S	X	SRT	r_{su}	r_s
#	L/h	h	g BOD/L	g BOD/L	g TSS/L	h	h^{-1}	g/L/h
1	27	0.56	0.164	0.036	7.00	---	0.033	0.230
2	25	0.60	0.151	0.028	5.88	38.26	0.035	0.205
3	27	0.56	0.207	0.028	6.40	59.62	0.050	0.322
4	24	0.63	0.333	0.060	6.76	57.80	0.065	0.437
5	27.5	0.55	0.397	0.030	6.28	23.01	0.107	0.673
6	27	0.56	0.422	0.053	6.44	24.39	0.103	0.664
7	27	0.56	0.810	0.092	6.40	9.64	0.202	1.292
8	25	0.60	0.892	0.102	6.96	12.77	0.189	1.317
9	27	0.56	0.791	0.162	6.24	17.09	0.181	1.132
10	27	0.56	0.864	0.094	9.36	17.26	0.148	1.386
11	27	0.56	0.796	0.083	7.04	14.75	0.182	1.283
12	27	0.56	0.768	0.083	8.28	16.45	0.149	1.233
13	25	0.60	1.660	0.332	7.68	8.32	0.288	2.213
14	25	0.60	1.536	0.177	7.24	7.70	0.313	2.265
15	27	0.56	1.734	0.437	7.44	7.83	0.314	2.335
16	28	0.54	2.350	0.507	9.48	7.76	0.363	3.440
17	26	0.58	2.054	0.290	10.80	9.20	0.283	3.058
18	26.5	0.57	2.252	0.490	11.36	8.87	0.274	3.113

The modified Monod equation proposed in this study (eq. 3.1; $r_s = -kSX_v^n/(S+K_s)$, with X_v substituted with X) was fitted to the same set of data on which computations in Yenke's study were performed (set 1, runs 1, 2, 3, and 4 not included), and to the set of data in which only runs 1 and 2 were excluded (set 2). Coefficients k, K_s, end fitting error (E) computed from eq. 3.1 for different n are presented in Tables 3.14 and 3.15, for sets 1 and 2, respectively, in cols. 4-13. Kinetic coefficients k and K_s computed from the eq. 2.1 are in col. 2 (Tables 3.14 and 3.15). Fitting error E was computed from nonlinear fitting method from r_s vs. S data.

Table 3.14 Computed kinetic coefficients and fitting errors (E) for different exponent n for set1

coeff.	eq. 2.1	eq. 3.1										
n	--	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
k	0.328	3.114	2.486	1.984	1.584	1.265	1.010	0.806	0.644	0.514	0.410	0.328
K_s	0.076	0.129	0.123	0.117	0.111	0.106	0.100	0.095	0.090	0.085	0.081	0.076
R^{2*}	0.792	0.819	0.821	0.823	0.824	0.824	0.823	0.821	0.817	0.811	0.803	0.792
E	0.283	0.407	0.387	0.367	0.349	0.332	0.317	0.304	0.294	0.287	0.283	0.283

*computed from linearization of eq. 2.1 (col. 2), and eq. 3.1 (cols. 3-13)
Units:
k [g BOD_5/L/d]
K_s [g BOD_5/L]
E [mg BOD_5/L/d]

Table 3.15 Computed kinetic coefficients and fitting errors (E) for different exponent n for set2

coeff.	eq. 2.1	eq. 3.1										
n	--	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
k	0.428	4.752	3.717	2.911	2.283	1.793	1.409	1.109	0.873	0.688	0.543	0.428
Ks	0.166	0.309	0.289	0.271	0.255	0.239	0.225	0.211	0.199	0.187	0.176	0.166
R^{2*}	0.518	0.580	0.576	0.572	0.567	0.562	0.556	0.550	0.543	0.536	0.527	0.518
E	0.277	0.352	0.333	0.316	0.301	0.289	0.278	0.271	0.267	0.267	0.270	0.277

The best fit for set 1 was obtained for n in the range of 0.9 – 1. Thus it can be assumed that the best fitting equation for this set was eq. 2.2 (or eq. 2.1, or modified Monod model with n = 1), which meant that the representation of active mass as X was reflecting the best the actual conditions in this set. This was equivalent to practically all X in the sludge being composed of active mass, which was expected because the SRT in this set was between 7.76 and 24.39 h. Sludge in those tests was in a growth state with very little endogenous decay.

The best fitting equation for set 2 was the modified model with exponent n in the range of 0.7 – 0.8. Those results were compatible with only part of X being composed of active mass, and were in agreement with actual experimental conditions of SRT between

7.76 and 59 h. Data set 2, in comparison to data set 1, contained additional two tests conducted on sludge with SRT equal 59 and 57 h.

The above results showed that the decrease in fitting error and improvement in values of kinetic coefficients can be achieved by using the proposed modified substrate utilization rate equation (eq 3.1). The improvement would be more visible for treatment facilities and experimental setups with longer SRTs. Under those conditions the differences between X_a and X_v (or X) would be greater.

CHAPTER 4

EXPERIMENTAL DESIGN

4.1 General Description of the Experiment

The experimental part of this project was performed in two stages. The goal of the first stage was to cultivate activated sludge in sequencing batch reactors (SBR). In the second stage, SBR sludge was tested in series of batch substrate utilization tests.

Seed sludge was obtained from the secondary stage of a municipal waste water treatment plant. Before being distributed to the reactors, seed sludge was fed with synthetic protein based substrate for one week.

Before being used in batch experiments sludge was acclimatized in reactors for several weeks until steady state was achieved (indicated by steady MLSS and S_e concentrations).

4.2 Experimental Setup

4.2.1 Sequencing Batch Reactors Set Up

SBRs were maintained at three SRTs: 5, 10 and 15 days (based on amount of sludge wasted per day to the total amount of sludge in the reactor). Treatment cycle timing was the same for each SRT, and was divided in phases as given in Table 4.1.

Table 4.1 Phases of SBR cycle

phase	duration (h)
Fill	2
React	3
Settle	0.75
Draw	0.25
Total cycle length	6.0

Reactors were manufactured from Plexiglas tubes (15 cm i.d.). Each reactor had 12 L total volume (V_t) and 8 L active volume (V_a). Hydraulic retention time (HRT, t_d) based on total cycle time was 0.375 d, HRT based on aeration time (t_{da}) was 0.3125 d. The total aeration time was 20 h per day in 4 cycles at 5 h each.

$$t_d = V_a/Q = 12/(8 \cdot 4) = 0.375 \text{ d } (9 \text{ h})$$

$$t_{da} = 12/(8 \cdot 4)/(24/20) = 0.3125 \text{ d } (7.5 \text{ h})$$

Influent feed concentration was 250 mg COD/L. Flow rates and loadings are listed below.

Influent flow rate (fill phase),

$$Q_{inf} = V_a/t_f = 8 \text{ [L]} / 2 \text{ [h]} = 4 \text{ L/h} = 66.7 \text{ ml/min}$$

where:
V_a = active volume
t_f = fill time

Supernatant withdrawal rate,

$$Q_{eff} = V_a/t_w = 8 \text{ [L]} / 15 \text{ [min]} = 32 \text{ L/h} = 533 \text{ ml/min}$$

where:
V_a = active volume
t_f = draw time

Volumetric loading rate (R_v),

$$R_v = Q\ S/V_t = 32 \text{ [L/d]} \cdot 250 \text{ [mg COD/L]} / 12 \text{ [L]} = 666.7 \text{ mg COD/L/d}$$

SRT was controlled by manual withdrawal of a portion of mixed liquor at rates of 0.8 L, 1.2 L, and 2.4 L daily from 15, 10, and 5 day SRT reactors respectively. Withdrawal was conducted once a day always at the same time of the day, and time of the

cycle, at the end of the reaction phase. The cycle was controlled by an electronic timer (Fig. 4.1).

Feed was supplied by a metering pump and a Masterflex pump was used to withdraw supernatant. At the end of the draw line an overflow dish was installed (4 L volume) to retain sludge which left the reactor in the supernatant. Aeration and mixing were achieved by supplying compressed air through double diffusing stones. Walls of the reactors were scraped manually on a daily basis to prevent growth of attached bacteria. Reactors were kept at room temperature, approximately 20° C.

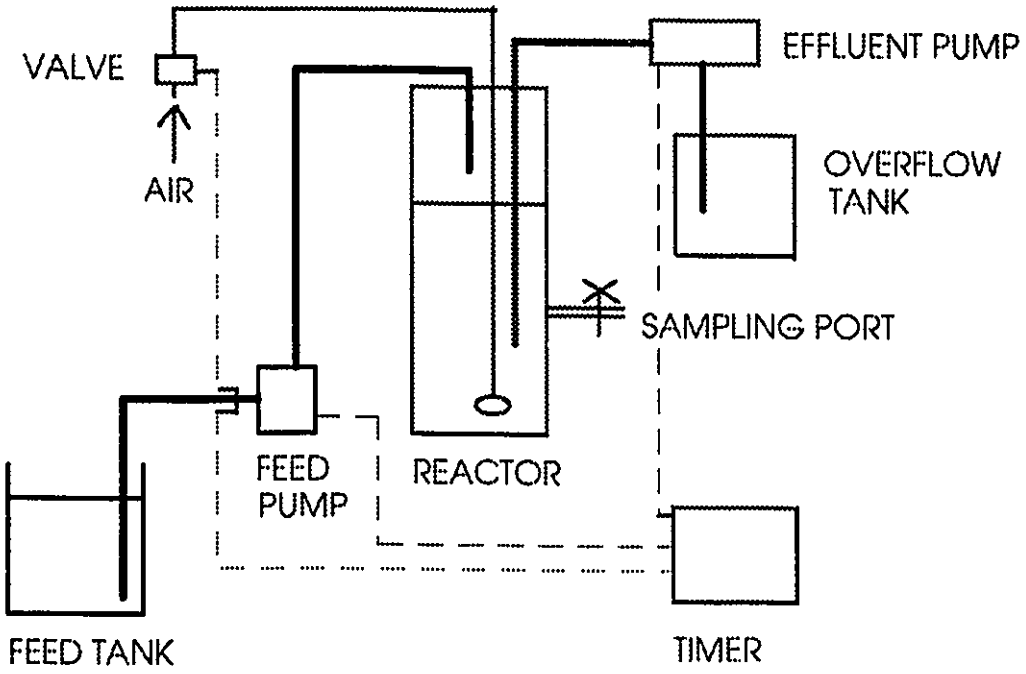

Figure 4.1 SBR experimental setup

4.2.2 Batch Tests Setup

Batch tests were performed in 2 L beakers on 1 L of ML. Nine batch tests were conducted for each sludge age, 27 for the whole experiment. The mixed liquor concentrations used in batch tests were; X - initial MLVSS concentration of full reactors, X/2 - half diluted MLVSS and, 2X - twice concentrated MLVSS. Batch test conditions

are listed in Table 4.2. One liter of ML of all of the above concentrations was fed instantaneously with 250, 500, and 1000 mg COD. Substrate and solids concentrations (COD and VSS) were monitored during the test.

Table 4.2 Description of sets of tests

2X set	X set	X/2 set	SRT	ITSC*
test #	test #	test #	d	mg COD/L
1	4	7	15	1000
2	5	8	15	500
3	6	9	15	250
10	13	16	10	1000
11	14	17	10	500
12	15	18	10	250
19	22	25	5	1000
20	23	26	5	500
21	24	27	5	250

*initial theoretical substrate concentration.

After ML was distributed into the beakers, the desired ML substrate concentrations were achieved by instantaneous injection of concentrated feed. Beakers were aerated with compressed air through a diffuser stone. The contents were stirred with a magnetic stirrer.

Sludge was concentrated to 2X concentration by settling ML sludge in 2 L glass cylinders. After sludge settled to a level below 1 L, 1 L of supernatant was withdrawn.

Sludge was diluted to X/2 concentration by adding supernatant remaining from concentrated samples to mixed liquor withdrawn from the reactor in 1 to 1 proportion.

4.3 Feed Solution

Concentrated feed was prepared from a mixture of 90% protein powder (Joe Weider 100% vegetable protein mix) and 10% PVA (polyvinyl alcohol), on a COD basis. Protein powder was dissolved in tap water at the temperature approaching the boiling point and at a pH above 10.5. Stock solution of 83 g/L protein was made (1 g of protein

stock was equivalent to 1.5 g COD) and stored at 4° C. PVA was dissolved in tap water at the water temperature approaching the boiling point. A 50 g/L PVA solution was made (1 g of PVA solution was equivalent to 2.3 g COD) and stored at room temperature. Composition of the actual feed is presented in Table 4.3, and its properties in Table 4.4.

Table 4.3 Feed composition

Ingredient	amount (mg/L)
proteins	150.3
polyvinyl alcohol	10.9
$NaHCO_3$	150
KH_2PO_4	15

Table 4.4 Feed Properties

COD	250 mg/L
Alkalinity	79.7 mg/L as $CaCO_3$ at pH 7.0 103.9 mg/L as $CaCO_3$ at pH 9.0
pH	9.3

4.4 Experimental Tests

4.4.1 Sequencing Batch Reactor Sampling

4.4.1.1 Sampling Schedule

The following tests were performed on the sequencing batch reactors: influent and effluent COD, MLVSS, ML pH and DO.

The COD of every new batch of feed was measured immediately after preparation.

Reactor effluent COD was measured on a daily basis at the end of the acclimatization time. The end of the acclimatization time was defined by steady MLVSS, and effluent COD concentrations.

MLVSS concentration was tested on a daily basis. Mixed liquor pH and dissolved oxygen concentrations were checked every second day.

4.4.1.2 Sampling Procedure

Mixed liquor samples for suspended solids were always taken at the same time of the day at the end of the react period. A sampling port at half of the reactor height was used.

COD feed samples were taken from the feed container immediately after a new batch of feed was prepared. Effluent samples for COD and SS measurement were taken from the overflow dish, after its contents were well stirred. The samples were taken with wide mouth 20 ml syringes.

4.4.2 Batch Tests Sampling

4.4.2.1 Sampling Schedule

Samples for COD were taken on average every 1 hour, more frequently at the beginning of the test (every 0.5 hour), and less frequently at the end of the test (up to 2 h between the last and the second last sample). The sampling period varied between 6 and 8 hours.

Samples for SS were taken at least 4 times during the test.

4.4.2.2 Sampling Procedure

The same samples were used for COD and MLSS tests. Samples were withdrawn from the beaker with a 20 ml syringe without a needle. Samples were prepared by centrifuging mixed liquor at 10,000 rpm for 10 minutes. Supernatant was used for COD tests, and compacted sludge for MLVSS tests.

4.5 Analytical Methods

COD tests were performed according to Standard Methods (1989), the colorimetric method was used to measure COD in samples with COD higher than 50 mg/L. Samples were cooled overnight. A Bausch & Lomb Spectronic 20

spectrophotometer was used. Effluent samples with COD content less than 50 mg/L were tested by the titrimetric method.

Suspended solids tests were performed according to Standard Methods (1989). Sludge cake from centrifuge tubes was transferred to evaporation dishes and dried overnight in an oven at 103°C.

pH was measured by Fisher Accumet meter, model 210 with combination electrode. Dissolved oxygen concentration was measured by a YSI model 57 DO meter with a YSI BOD membrane probe 5720A.

CHAPTER 5

COMPUTATIONAL PROCEDURE

The objective of this project was to find the best fitting exponents n, in the modified Monod and the modified linear substrate utilization rate equations (eqs. 3.1 and 3.2).

$$\text{(eq. 3.1)}\quad r_S = -\frac{kSX_v^n}{S+K_s} = \frac{dS}{dt}$$

$$\text{(eq. 3.2)}\quad r_s = -kSX_v^n = \frac{dS}{dt}$$

The experimental data fitted with those equations consisted of COD concentrations vs. time obtained from 27 batch tests. To find the best fitting exponent n, the results were divided into three sets, according to biomass concentration ratio between SBR MLVSS and MLVSS in the batch tests (B MLVSS). Each set contained nine tests performed on a sludge with one of the following B MLVSS / SBR MLVSS ratios: 2X, X and 0.5X (where X was the SBR MLVSS). For each set of tests, the best fitting kinetic coefficients were computed for assumed exponents n from 0 to 1 with increments of 0.1. Those computations were conducted on data from all tests belonging to a particular set of tests lumped together. The best value of exponent n in eqs. 3.1 and 3.2 was indicated by the lowest fitting error. For the best fitting exponent n, and kinetic coefficients k and K_s, computed from a set of tests, fitting errors were computed for each test in that set (by fitting modified equations with those coefficients to the experimental data from a test), to

evaluate the fit of equations with coefficients computed from the set of tests to the individual tests.

In addition to those computations, the modified equations were fitted to each test separately (coefficients k and K_s computed from each test were different). This last set of computations was conducted for the purpose of comparison between kinetic coefficients and fittings errors computed from each test (section 6.3.3).

5.1 The Computational Criterion of Fit

Optimum kinetic coefficients at a particular exponent n, were found from the least squares method. According to this method, the best fit is obtained when the sum of squares of residuals (eq. 5.1) is at its minimum (Draper and Smith, 1981).

$$SUM(p) = \sum_{m=1}^{M} [S_{ob(m)} - f(t_m; p)]^2 \qquad (5.1)$$

where:
$S_{ob(m)}$ = values observed at time t_m
$f(t_m;p)$ = regression function representing values at time t_m
M = number of observations
p = parameters

In this method, when a nonlinear equation is fitted to the experimental data, fit is represented by the residual mean square (RMS) which represents the "deviation of residuals about the regression" and is computed according to eq. 5.2 (Bates and Watts, 1988).

$$RMS = \left[\frac{SUM(k, K_s, n)}{M-P}\right]^{1/2} = \left[\frac{\sum_{m=1}^{M}(S_{ob(m)} - S_{c(m)})^2}{M-P}\right]^{1/2} \quad (5.2)$$

where:
M = number of observations
P = number of parameters in regression model
$S_{ob(m)}$ = values observed
$S_{c(m)}$ = values computed

The denominator, M – P, in eq. 5.2 represents the number of degrees of freedom associated with sum of squares of residuals.

In this project the modified Monod equation had two parameters, k and K_s; exponent n was not treated as a parameter because computations were performed for assumed values of n. The modified linear equation had one parameter k. Thus, the residual mean squares for the modified Monod and linear equations (RMS_M and RMS_L, respectively) were computed according to eqs. 5.3 and 5.4.

$$RMS_M = \left[\frac{\sum_{m=1}^{M}(S_{ob(m)} - S_{c(m)})^2}{M-2}\right]^{1/2} \quad (5.3)$$

$$RMS_L = \left[\frac{\sum_{m=1}^{M}(S_{ob(m)} - S_{c(m)})^2}{M-1}\right]^{1/2} \quad (5.4)$$

where:
M = number of observations
$S_{ob(m)}$ = observed substrate concentrations
$S_{c(m)}$ = computed substrate concentrations

RMS computed from sets of tests and from individual tests were defined as the fitting errors, E and EJ, respectively.

5.2 Residual COD Concentrations

It was observed that at the end of every test non-biodegradable COD remained. Non-biodegradable COD concentrations (S_r) were usually indicated by leveling off of the graph. To account for remaining COD, the data used for computations (S_Y) represented COD experimental results (S_{ob}) adjusted according to equation $S_Y = (S_{ob} - S_r)$. The values of S_r for every test are listed in Table 6.2 (Chapter 6).

5.3 Modified Monod Equation

5.3.1 Computational Procedure

The Monod type differential equation (eq. 3.1) was solved numerically, using a variable order Adams predictor-corrector method (integration formula). Computations were performed on the University of Ottawa mainframe computer. The computer program was written by the author in VS FORTRAN. This program incorporated the IMSL DGEAR subroutine as a differential equation solver (program flowchart and code are presented in Appendix C).

The description of the algorithm of the DGEAR subroutine (IMSL library, June 1982) is as follows: "Dgear finds approximations to the solution of a system of first order ordinary differential equations of the form y' = f(x, y) with initial conditions. The basic methods used for the solution are the implicit linear multistep type. There are two classes of such methods available to the user. The first is the implicit Adams method (up to order twelve), and the second is the backward differentiation (BDF) method (up to order twelve), also called Gear's stiff method". DGEAR was called into the program as an "on line" subroutine. For the purpose of this project only one differential equation, S' = f(S), had to be solved.

The best fitting kinetic coefficients k and K_s, for each exponent n (from 0 to 1 with the increment of 0.1) in computations on sets of data, and for n = 0 for computations on tests, were found using a grid search method. Most of the input and output data used by

the program were arranged into arrays. The input data included coefficients k, and K_s arranged into one dimensional arrays, with NK and NKS number of values, respectively. This resulted in NK times NKS number of k, K_s pairs, for which the values of fitting error were computed and evaluated. Those pairs formed two dimensions of the data array (DA) and are shown on Fig. 5.1.

$$\begin{bmatrix} k_{(1)}, K_{s(1)} & \cdot & \cdot & & \cdot & \cdot & k_{(1)}, K_{s(NKS)} \\ \cdot & & & & & & \cdot \\ & & & & & & \\ \cdot & & & & & & \cdot \\ k_{(NK)}, K_{s(1)} & \cdot & \cdot & & \cdot & \cdot & k_{(NK)}, K_{s(NKS)} \end{bmatrix}$$

Fig. 5.1 Data array of k, K_s coefficients, DA

Two initial data arrays with different values of kinetic coefficients were used in computations, one for the sets of tests and one for the individual tests (values of those coefficients are described in sections 5.3.2 and 5.3.3).

For each k, K_s pair, a substrate utilization rate equation (eq. 3.1) was fitted to the experimental data from each test for a number of assumed initial COD concentrations defined as S_{0Y}. Those values were effectively the third dimension of the DA. The values of S_{0Y} in the initial array were from 50% to 150% of the experimental initial COD concentration.

Each pair of k and K_s coefficients corresponded to one value of computed fitting error (RMS, section 5.1). The best fitting coefficients were those for which the value of the fitting error was the lowest.

The two dimensions results array computed for one individual test (TRA), for best fitting S_{0Y} values is shown on Fig. 5.2. Each fitting error (EJ) in this array corresponded to one pair of k, K_s coefficients from DA (Fig. 5.1).

$$\begin{bmatrix} EJ_{(1,1)} & \cdot & \cdot & & \cdot & \cdot & EJ_{(1,NKS)} \\ \cdot & & & & & & \cdot \\ & & & & & & \\ \cdot & & & & & & \cdot \\ EJ_{(NK,1)} & \cdot & \cdot & & \cdot & \cdot & EJ_{(NK,NKS)} \end{bmatrix}$$

Fig. 5.2 Results array for tests, TRA

In computations on set of tests, a substrate utilization rate equation (eq. 3.1) with one pair of kinetic coefficients k and K_s was fitted to each test in the set, for initial COD concentrations S_{0Y} defined based on the observed initial substrate concentration from each test. The procedure of defining S_{0Y} arrays was the same as in computations for tests. The two dimensions of results array for computations on sets of tests (SRA) are shown on Fig. 5.3. This array consisted of fitting errors (E) corresponding to each pair of k, K_s from DA (Fig. 5.1), computed from one set of tests. The fitting error E represented RMS computed for data from all tests in a set of tests (eq. 5.2 in which M represented sum of the number of observation from all tests in a set).

$$\begin{bmatrix} E_{(1,1)} & \cdot & \cdot & & \cdot & \cdot & E_{(1,NKS)} \\ \cdot & & & & & & \cdot \\ & & & & & & \\ \cdot & & & & & & \cdot \\ E_{(NK,1)} & \cdot & \cdot & & \cdot & \cdot & E_{(NK,NKS)} \end{bmatrix}$$

Fig. 5.3 Results array for sets of tests, SRA

In this grid search method, fitting errors were computed for a number of consecutive data arrays, before the desired accuracy in evaluating the best fitting k and K_s

was obtained. Each data array was built around the values of k, K_s from the preceding DA, for which the computed fitting error was the lowest. This procedure is described below.

The difference between two neighboring values of the same coefficient (k or K_s) in a particular data array (DA), was the iteration step (IS). The lowest and the highest values of k and K_s in each consecutive DA were computed according to eqs. 5.5 and 5.6, based on $k_{(op)}$ and $K_{s(op)}$ which symbolizes the k and K_s coefficients from the previous DA for which the fitting error was the lowest. The lowest value of k was $k_{(op)} - SK(k_{(j)} - k_{(j-1)})$ and the highest was $k_{(op)} + SK(k_{(j)} - k_{(j-1)})$. The lowest and highest values of K_s were calculated in a similar manner. Symbols $k_{(LH)}$ and $K_{s(LH)}$ were used to designate the limits on the two parameters.

$$k_{(LH)} = k_{(op)} \pm SK(k_{(j)} - k_{(j-1)}) \tag{5.5}$$

$$K_{s(LH)} = K_{s(op)} \pm SKS(K_{s(i)} - K_{s(i-1)}) \tag{5.6}$$

where:
SK, SKS = coefficients

Differences $(k_j - k_{(j-1)})$ and $(K_{s(i)} - K_{s(i-1)})$ in eqs. 5.5 and 5.6 were equal to the iteration step of the k and K_s dimension from the preceding DA, respectively (abbreviated as ISK and ISKS). These iteration steps were decreasing with each consecutive DA. The coefficients SK and SKS (for k and K_s dimension respectively) were found experimentally by performing different trials. The lowest limit of both kinetic coefficients, in any DA was set at 0.

An example of the first three DAs from computations on the set with "X" mixed liquor concentration is given in Tables 5.1a-c. In Table 5.1a, the first column and the first row represent values of k and K_s coefficients in the initial DA. In this DA, the iteration steps of k (ISK) and K_s (ISKS) were equal to 1290 – 100 = 1190 mg/L/d, and to 104.29 – 5 = 99.29 mg/L, respectively. The coefficients SK and SKS, in computations on sets were

equal to 2.25 and 1.75, respectively. The lowest and the highest values of k and K_s in the second DA, computed according to eqs. 5.5 and 5.6 were:

$$k_{(LH)} = 2480 \pm (2.25 \cdot 1190)$$

$$K_{s(LH)} = 5 \pm (1.75 \cdot 99.29)$$

The lowest values of computed coefficients k and K_s were less than zero, and for that reason they were set to 0 in the second DA. The highest values of k and K_s in the second DA were: 2480 + 2.25 · 1190 = 5157.5 mg/L/d and 5 + 1.75 · 99.29 = 178.75 mg/L, respectively (Table 5.1b). The k and K_s values in the second DA were uniformly spaced with a new lower iteration step over the interval 0 to 5157.5 mg/L/d and 0 to 178.75 mg/L, respectively.

The iteration step at which the computations were terminated was the minimum iteration step (MIS). Terms MISS, MISK, and MISKS represented the minimum iteration step for Y, k, and K_s dimensions, respectively. The minimum iteration step defined the accuracy of computations.

The procedure of defining the dimensions of consecutive S_{0Y} arrays was analogous to the process of defining k and K_s data array (DA). In computations for each k, K_s pair in each data array, iteration step of S_{0Y} dimension (ISS) was decreasing until reaching the first value smaller than MISS. The ISK and ISKS were decreasing with each consecutive DA until both of those values were smaller than a corresponding MISK and MISKS. Values of minimum iteration steps were set at: MISS = 1 mg COD/L, MISK = 1 mg COD/L/d (for n = 0), and MISKS = 0.1 mg COD/L. The accuracy with which S_{0Y}, k, and K_s were computed always exceeded the corresponding minimum iteration step. In computations on a particular DA, when for each pair of k, K_s the ISS decreased below MISS procedure was advancing to the next DA. When both ISK and ISKS reached value

lower than MISK and MISKS in a particular DA, the computational procedure was terminated, and results printed.

The first three results arrays for sets (SRAs), computed on "X" set of tests, for exponent n = 0, are presented in Tables 5.1a-c (set containing tests performed on SBR MLVSS concentration). In those tables the presented fitting errors for set of tests are the lowest for each k, K_s pair (computed for different S_{0Y} values in each test for which fitting error in each test was the lowest and what follows the fitting error for the whole set of tests were the lowest).

Table 5.1a First SRA for X set of tests, modified Monod model, n = 0

k\Ks	5	104.29	203.57	302.86	402.14	501.43	600.71	700.00
100	84.28	85.76	86.60	87.15	87.55	87.85	88.09	88.28
1290	34.33	46.12	53.38	58.37	62.03	64.87	67.18	69.09
2480	17.69	21.91	31.09	38.24	43.70	48.06	51.63	54.6
3670	37.22	22.29	20.72	25.05	30.26	35.02	39.12	42.65
4860	52.59	36.69	27.00	23.34	24.02	26.79	30.17	33.54
6050	63.93	49.04	37.94	30.41	26.32	25.14	25.97	27.9
7240	71.03	59.04	47.80	39.20	32.93	28.90	26.88	26.49
8430	79.36	66.63	56.11	47.32	40.27	34.87	31.03	28.66
9620	86.22	73.10	63.06	54.43	47.16	41.17	36.39	32.79
10810	91.00	79.06	69.04	60.61	53.34	47.13	41.91	37.63
12000	94.82	84.41	74.33	66.04	58.86	52.60	47.17	42.53

SRA	k	Ks	E
1	2480	5	17.69

Table 5.1b Second SRA for X set of tests, modified Monod model, n = 0

k\Ks	0.00	25.54	51.07	76.61	102.14	127.68	153.21	178.75
0.0	90.14	90.14	90.14	90.14	90.14	90.14	90.14	90.14
515.8	61.93	64.30	66.20	67.80	69.16	70.34	71.38	72.30
1031.5	42.58	45.30	48.18	50.68	52.85	54.76	56.45	57.96
1547.2	32.60	30.13	33.63	36.79	39.57	42.02	44.20	46.15
2063.0	38.43	19.48	22.33	25.41	28.38	31.14	33.66	35.96
2578.8	56.04	17.06	17.12	18.51	20.57	22.89	25.24	27.53
3094.5	78.860	22.87	20.03	18.60	18.37	19.04	20.29	21.87
3610.2	105.38	31.41	27.18	24.01	21.82	20.53	20.04	20.18
4126.0	134.30	39.77	35.04	31.08	27.89	25.40	23.57	22.35
4641.8	164.62	45.90	41.80	37.90	34.36	31.32	28.77	26.71
5157.5	196.54	52.06	47.62	43.82	40.33	37.13	34.28	31.78

SRA	k	Ks	E
2	2578.8	25.54	17.06

Table 5.1c Third SRA for X set of tests, modified Monod model, n = 0

k\Ks	0.000	10.030	20.060	30.100	40.130	50.160	60.190	70.220
1418.31	33.812	31.355	32.817	34.244	35.616	36.924	38.167	39.345
1650.40	32.390	25.447	26.786	28.179	29.569	30.927	32.238	33.497
1882.49	34.543	20.683	21.849	23.073	24.355	25.659	26.955	28.225
2114.58	39.823	17.562	18.300	19.221	20.254	21.369	22.532	23.716
2346.66	47.260	16.704	16.717	17.058	17.638	18.391	19.266	20.226
2578.75	56.041	18.089	17.310	16.938	16.884	17.089	17.501	18.075
2810.84	65.761	20.825	19.615	18.640	17.972	17.581	17.435	17.502
3042.92	76.389	24.264	22.843	21.525	20.409	19.529	18.880	18.448
3275.01	87.780	28.347	26.574	25.017	23.617	22.398	21.372	20.539
3507.10	99.830	32.760	30.640	28.819	27.201	25.748	24.459	23.336
3739.19	112.445	37.225	34.820	32.754	30.937	29.303	27.827	26.499

SRA	k	Ks	E
3	2346.66	10.03	16.704

The first column and the first row in Table 5.1a, represented values of coefficients k and K_s, respectively, in the initial assumed data array.

The values of the best fitting coefficients k and K_s in this initial DA were equal to 2480 mg COD/L/d and 5 mg COD/L, respectively, and corresponded to fitting error of 17.69 mg COD/L (intersection of first column and third row, Table 5.1a). In the second and third results arrays, computed values of E decreased to 17.06 and 16.70 mg COD/L, respectively (Tables 5.1b and 5.1c).

5.3.2 Computational Parameters for Sets of Tests

The ranges of the first k - K_s DA, for each set of data, were set at: k between 100 and 12000 mg COD/L/d (for n = 0), and K_s between 5 and 700 mg COD/L. Those values covered the ranges of the best fitting coefficients in each set of tests and were found after number of trials were performed. Each data array (DA) had 11 by 8 values of k and K_s, respectively (NK = 11, NKS = 8). Iteration steps were equal to: ISK = 1190 mg/L/d, and ISKS = 99.29 mg/L, and computed as follows:

$$ISK = (12000 - 100) / (NK - 1) = (12000 - 100) / 10 = 1190 \text{ [mg COD/L/d]}$$

$$ISKS = (700-5)/(NKS-1) = (700-5)/7 = 99.29 \text{ [mg COD/L]}$$

Coefficients SK and SKS were equal to 2.25 and 1.75, respectively (see eqs. 5.5 and 5.6), those values were found experimentally as optimal.

5.3.3 Computational Parameters for Individual Tests

The variation in results from individual tests was larger than from a set of tests as a whole, thus, a larger initial DA with higher k and K_s values was required to find the optimal k and K_s coefficients from each test. The range of the first DA, for each test, was set at k between 100 and 24000 mg/L/d COD (n = 0), and K_s between 5 and 1400 mg/L COD. Those values allowed to cover (in a consecutive DAs) the whole range of the best fitting kinetic coefficients computed from tests and were found after number of trials were performed. Each data array (DA) had 22 by 16 values of k and K_s, respectively (NK = 22, NKS = 16). Iteration steps were equal to: ISK = 1138 mg/L/d, and ISKS = 93 mg/L.

Coefficients SK and SKS were equal to 4.5 and 3.5, respectively (see eq. 5.6 and 5.7), those values were found experimentally as optimal.

5.4 Modified Linear Equation

5.4.1 Computational Procedure

In principle the grid search computational procedure for a modified linear equation was the same as that for the modified Monod equation (section 5.3). The differences between these two procedures were in the values of the parameters used, and in the method of solving the substrate utilization rate differential equation. The ranges of DA, and values of IS and MIS were different in each procedure (modified Monod equation - two dimensional matrix (k, K_s), modified linear equation - one dimensional matrix (k)). In computations for the linear equation, the value of MISS was set at 1 mg COD/L and value of MISK at 0.00144 L/mg/d (0.000001 L/mg/min), for n = 0. The modified linear substrate utilization rate equation (eq. 3.2) was solved by integration, resulting in the following expression for substrate concentration vs. time (eq.5.7).

$$S = S_{0Y} e^{(-kX^{n_1})} \tag{5.7}$$

where:

S_{0Y} = initial substrate concentration, equal to $S_0 - S_r$

The above equation was fitted to experimental data using a grid search method for a one dimensional array.

5.4.2 Computational Parameters for Sets of Tests and Individual Tests

For computations on both sets of tests and individual tests, the range of the first k array (DA) was from 0 to 144 L/mg/d. Coefficients NK and SK were equal to 11 and 1, respectively.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Sequencing Batch Reactors

6.1.1. Experimental Results

SBR MLVSS and effluent TSS and substrate concentrations (S_e) were measured as an indicator of steady state conditions. Values of effluent TSS concentrations were negligible. The ML pH level was in the 6.0 - 7.0 range, feed pH was between 8.8 and 9.3. ML DO concentration was at the level of 4.0 - 5.0 mg O_2/L during the react phase. Data from the SBR phase of the experiment (MLTSS, influent and effluent COD and TSS) are presented in Appendix A. SRT based on total cycle time (t_s), and aeration time (t_{ae}), average MLVSS concentration, and influent and effluent COD concentrations are presented in Table 6.1. MLVSS were measured at the end of reaction period.

Table 6.1 Average SBR MLVSS and S concentrations

t_s	t_{ae}	MLVSS	S_i	S_e
d	d	mg/L VSS	mg COD/L	mg COD/L
5.00	4.17	816	217	32
10.00	8.33	1240	201	34
15.00	12.50	2003	205	30

At the end of the acclimatization period the growth of predators (red worms) was observed in all reactors (microscopic observations). The biggest predators population was in 15 d reactor followed by 10 d reactor, in 5 days reactor the amount of predators was

much lower than in older sludges (usually only few organisms were detected in observed sample).

6.1.2 Computed Mass Accumulation Coefficients.

Mass accumulation coefficients (Y, k_e) were computed from equation 2.10, based on the SBR influent and effluent substrate concentrations, and MLVSS concentrations.

By plotting experimental $1/t_s$ vs. $(S_o - S_e)/t_d/X_v$ data (each pair of values represented one reactor), coefficients Y and k_e were found as the slope and intercept of the fitted linear graph (eq 2.10, Fig. 6.1). Computed Y and k_e coefficients were equal to 0.368 and $-0.024\ d^{-1}$ respectively.

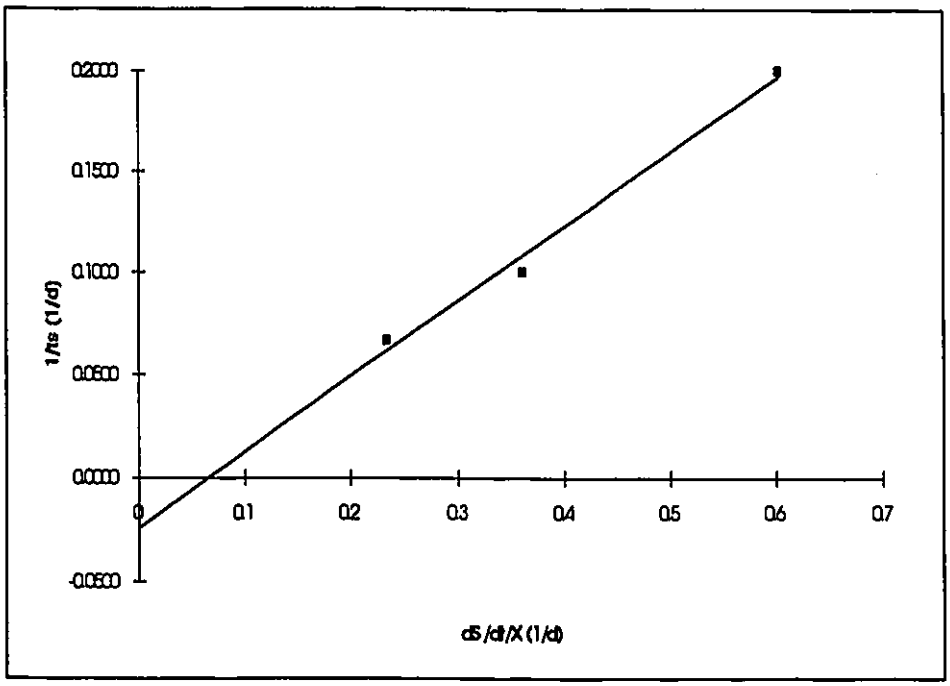

Figure 6.1 Mass accumulation coefficients

6.2 Batch Tests

6.2.1 Experimental Results

Detailed data from the batch phase of the experiment (TSS, VSS and COD for every test) are presented in Appendix B.

6.2.2 The Best Fitting Exponent n

The best fitting exponent n was found from computations on three sets of tests 2X, X and X/2 (Table 6.2). Sludge concentrations of 2X, X, and X/2 corresponded to two, one and one - half of the SBR MLVSS concentration.

Table 6.2 Description of sets of tests

2X	X	X/2	SRT	ITSC*
test #	test #	test #	d	mg COD/L
1	4	7	15	1000
2	5	8	15	500
3	6	-	15	250
10	13	16	10	1000
11	14	17	10	500
12	15	18	10	250
19	22	25	5	1000
20	23	26	5	500
21	24	27	5	250

*initial theoretical substrate concentration

6.2.3 Residual Substrate Concentration

The values of the residual substrate concentrations (S_r) for each tests, were defined according to the following three criteria. S_r should be either: a) equal to the lowest significant observed COD concentration in the test (S_{min}), b) approximately equal to $0.1S_0$ (S_0 = initial observed substrate concentration), because one tenth of the feed COD was a highly refractory compound, c) computed as the average of appropriate COD values at the end of the test. In all tests S_{min} was higher than $0.1S_0$, and S_r was either S_{min} (tests 1, 9, 11, 12, 14, 18, 19, 20, 21, 22, 23, 24, 26, 27), or $0.1S_0$ (tests 2, 3, 4, 5, 6, 7, 8, 10, 13, 15, 16, 17, 25), the criterion c) was not applied. The determination of S_r, as either S_{min} or $0.1S_0$,

depended on, which of those two values, had more support in the experimental data. In tests in which S_r was equal to S_{min}, S_{min} was clearly the lowest value obtained in this test. In tests in which S_r was equal to $0.1S_0$, S_{min} observed was not representing the lowest possible value of substrate concentration. This condition was indicated by the slope of the graph, and/or by the ratio of S_{min}/S_0, which was usually much higher than in tests with clearly defined minimum substrate concentrations. The set of S_r values used to compute results in this experiment are presented in Tables 6.3a-c.

To obtain kinetic coefficients reflecting kinetics of the utilization process in computations on individual tests, values of the actual S_r had to be closely approximated. However, the values of S_r did not affect the fundamental computations in this project, the value of the best fitting exponent n in the X^n expression, when the following conditions were fulfilled. The values of S_r, had to be set based on experimental data which extended to the end of the utilization process, or, if these data were not available, they had to be set at the level approximating the expected lowest substrate concentrations, according to the next best method (the influence of S_r on results is discussed in section 6.3.5). It was found, based on tests with clearly defined S_{min}, that setting S_r equal to $0.1S_0$ was the best method (Appendix F).

Table 6.3a Residual substrate concentrations, tests 1-9

test #	S(0)	0.1S(0)	S_{min}	S_r
	mg/L	mg/L	mg/L	mg/L
1	854	85	96	96
2	397	40	91	40
3	210	21	54	21
4	957	96	464	96
5	483	48	100	48
6	254	25	33	25
7	1064	106	620	106
8	538	54	93	54
9	266	27	36	36

Table 6.3b Residual substrate concentrations, tests 10-18

test #	S(0)	0.1S(0)	S_{min}	S_r
	mg/L	mg/L	mg/L	mg/L
10	665	66	77	66
11	304	30	40	40
12	150	15	26	26
13	793	79	81	79
14	364	36	36	36
15	154	15	24	24
16	750	75	242	75
17	429	43	64	43
18	140*	14	33	33

* Second observation at time 65 min is provided, S at time zero was not available.

Table 6.3c Residual substrate concentrations, tests 19-27

test #	S(0)	0.1S(0)	S_{min}	S_r
	mg/L	mg/L	mg/L	mg/L
19	796	80	131	131
20	417	42	97	97
21	224	22	47	47
22	734	73	179	179
23	438	44	134	134
24	233	23	80	80
25	762	76	268	76
26	391	39	87	87
27	243	24	80	80

6.2.4 Fitting Errors for Individual Tests

In addition to finding the best exponent n from sets of tests, and computing the degradation plots and errors for each test using the best fitting kinetic coefficients computed from sets, modified equations were fitted to each individual test separately. Those results were used to analyze influence of different values of S_r on kinetic coefficients computed from individual tests (section 6.3.5) and are listed in Appendix D.

6.2.5 Results Computed from Modified Monod Equation

6.2.5.1 The Best Fitting Exponent n

Kinetic coefficients and fitting error (E) for exponent n from 0 to 1 with increment 0.1 were computed for the following parameters of the initial DA; k from 100 to 12000 mg/L/d, and K_s from 5 to 700 mg/L; NK, NKS, SK, SKS equal to 11, 8, 2.25 and 1.75

respectively. Values of those coefficients were obtained based on trial runs on experimental data. Results are presented in Table 6.4.

Table 6.4 Kinetic coefficients and fitting error for 2X, X, and X/2 sets of tests (modified Monod equation)

n	2X			X			X/2		
	k^*	K_s	E	k^*	K_s	E	k^*	K_s	E
	mg/L/d	mg/L	mg/L	mg/L/d	mg/L	mg/L	mg/L/d	mg/L	mg/L
0	7797	349	23.17	2364	16.23	16.66	1772	33.00	8.72
0.1	3489	331	24.93	1108	10.04	18.31	914.1	28.43	9.01
0.2	1560	315	27.12	521.5	5.88	20.07	469.2	23.86	9.80
0.3	690.0	292	29.65	246.0	3.22	21.91	240.4	19.38	10.99
0.4	302.5	266	32.41	115.8	1.45	23.81	123.1	15.55	12.45
0.5	131.9	238	35.34	54.45	0.27	25.73	62.84	11.31	14.08
0.6	58.07	217	38.39	26.90	0.02	27.55	31.66	2.54	15.72
0.7	25.26	193	41.52	12.79	0.02	29.40	16.11	0.03	17.41
0.8	11.03	171	44.70	6.083	0.02	31.33	8.267	0.02	19.17
0.9	4.866	154	47.90	2.872	0.03	33.26	4.218	0.03	20.98
1	2.077	127	51.12	1.356	0.03	35.20	2.149	0.02	22.80

*$k = k_s X_s / X_v^n$, for $n = 0$ $k = k_s X_s$, $n = 1$ $k = k_s X_s / X_v$

The fitting errors in Table 6.4 show that the best fitting exponent n was equal to zero in each set (Table 6.4).

Fitting errors for sets of tests, computed from the modified Monod equation were plotted vs. exponent n on Fig. 6.2.

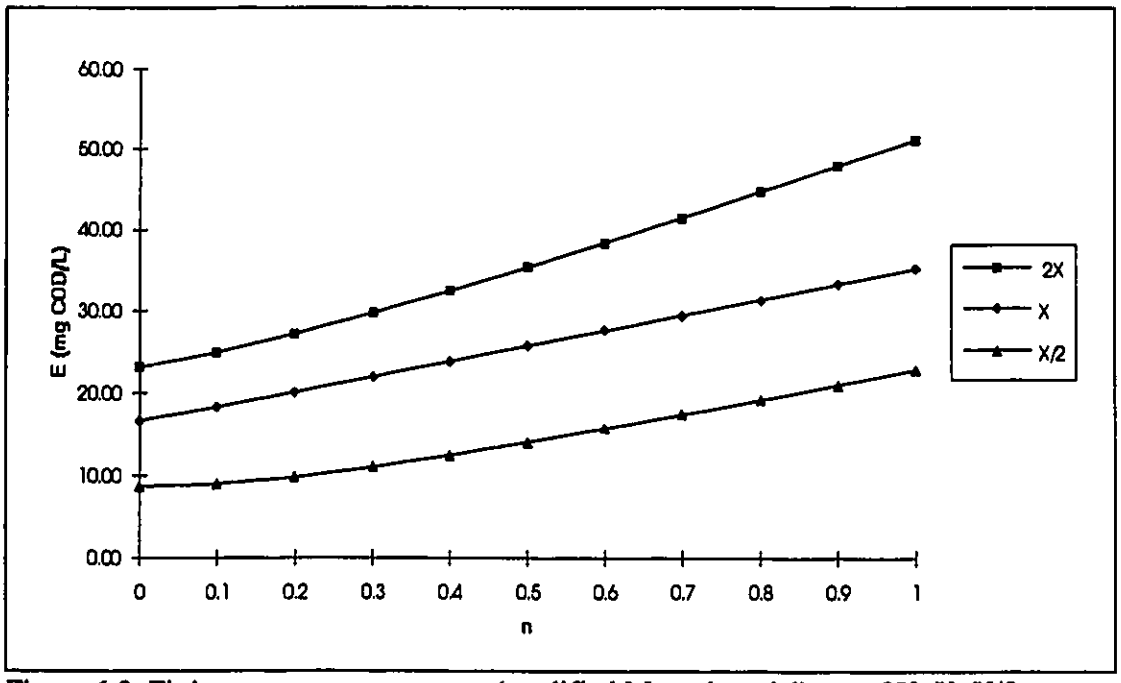

Figure 6.2 Fitting error vs. exponent n (modified Monod model), sets 2X, X, X/2

Improvement in fit when the modified Monod model (eq. 3.1) was applied instead of the Monod model (eqs. 2.1 and 2.2) to fit data in each set of tests is presented in Table 6.5.

Table 6.5 Improvement in fit for modified Monod model

Set	ER [%]*
2X	54.67
X	52.67
X/2	61.75

*ER = (E1-E0)/E1·100%, E0 = E at n = 0, E1 = E at n = 1

6.2.5.2 Fitting Error for Tests in Sets

Fitting errors for each test in a particular set, for the optimum exponent n and kinetic coefficients for this set are presented in Table 6.6.

Table 6.6 Fitting errors for tests for best fitting kinetic coefficients for sets 2X, X, X/2 (modified Monod model)

2X				X				X/2			
test	S_0*	S_{0c}**	EJ	test	S_0	S_{0c}	EJ	test	S_0	S_{0c}	EJ
#	mg/L	mg/L	mg/L	#	mg/L	mg/L	mg/L	#	mg/L	mg/L	mg/L
1	854	840	21.60	4	957	969	79.97	7	1064	1070	27.01
2	397	429	52.52	5	483	512	48.14	8	538	519	24.67
3	210	210	16.76	6	254	243	19.71	9	266	--	--
10	665	687	30.22	13	793	715	48.94	16	750	774	33.24
11	304	289	16.30	14	364	337	19.16	17	429	431	14.12
12	150	146	6.45	15	154	170	15.95	18	---	187	21.64
19	796	782	23.95	22	734	689	34.28	25	762	759	11.80
20	417	378	31.04	23	438	408	15.22	26	391	395	12.24
21	224	214	17.74	24	233	234	6.51	27	243	239	11.60

*initial observed substrate concentration
**initial substrate concentration computed from the best fitting curve

6.2.6 Results Computed from the Modified Linear Equation.

6.2.6.1 The Best Fitting Exponent n

Kinetic coefficients and fitting errors (E) for sets of tests were computed for the following parameters of the initial DA; k from 0 to 144 L/mg/d (for n = 0); NK and SK equal 11 and 1, respectively. Values of those coefficients were obtained based on trial runs on experimental data. Results are presented in Table 6.7.

Table 6.7 Kinetic coefficients and fitting errors for sets 2X, X, and X/2 (modified linear equation)

n	2X		X		X/2	
	k*	E	k	E	k	E
	L/mg/d	mg/L	L/mg/d	mg/L	L/mg/d	mg/L
0.0	11.32	16.28	6.426	32.83	3.470	29.18
0.1	5.205	17.16	3.083	34.45	1.782	30.17
0.2	2.390	18.27	1.475	36.10	0.9119	31.27
0.3	1.097	19.57	0.7048	37.75	0.4656	32.46
0.4	0.5022	21.01	0.3361	39.40	0.2367	33.73
0.5	0.2300	22.56	0.1601	41.04	0.1200	35.04
0.6	0.1052	24.19	0.07624	42.68	0.06062	36.38
0.7	0.04803	25.88	0.03624	44.30	0.03055	37.73
0.8	0.02193	27.61	0.01720	45.91	0.01533	39.07
0.9	0.009996	29.36	0.008134	47.49	0.007676	40.40
1.0	0.004551	31.12	0.003837	49.03	0.003826	41.70

*$k = k_n X_n / X_v^n$, for $n = 0$ $k = k_n X_n$, $n = 1$ $k = k_n X_n / X_v$

The fitting errors in Table 6.7 show that the best fitting exponent n was equal to zero in each set (Table 6.4).

Fitting error for sets of tests, computed from the modified linear equation is plotted against exponent n on Fig. 6.3.

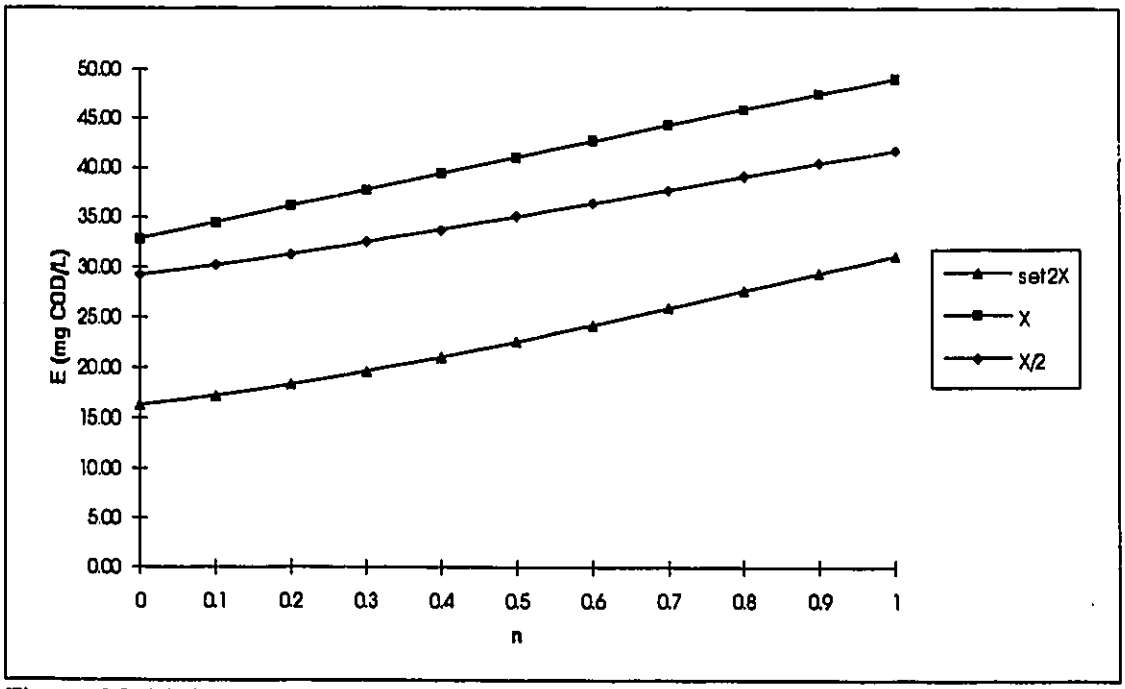

Figure 6.3 Fitting error vs. exponent n (modified linear equation), set 2X, X, X/2

The improvement in fit when the modified linear model (eq. 3.2) was applied instead of the linear model (eq. 2.3) to fit data in each set of tests is presented in Table 6.8.

Table 6.8 Improvement in fit for the modified linear model

Set	ER [%]*
2X	47.68
X	33.04
X/2	30.02

*ER = (E1-E0)/E1·100%, E0 = E at n = 0, E1 = E at n = 1

6.2.6.2 Fitting Errors For Tests in Sets

Fitting errors for each test in a particular set, for the optimum kinetic coefficients and exponent n for this set are presented in Table 6.9.

Table 6.9 Fitting error for tests for best fitting kinetic coefficients for set 2X, X, X/2 (modified linear equation)

2X				X				X/2			
test #	S_0* mg/L	S_{0c}** mg/L	EJ mg/L	test #	S_0 mg/L	S_{0c} mg/L	EJ mg/L	test #	S_0 mg/L	S_{0c} mg/L	EJ mg/L
1	854	794	36.67	4	957	958	144.44	7	1064	1067	105.89
2	397	376	27.25	5	483	438	18.34	8	538	422	83.96
3	210	176	20.36	6	254	176	65.25	9	266	--	--
10	665	635	36.84	13	793	710	58.44	16	750	720	50.44
11	304	225	30.57	14	364	247	57.50	17	429	323	61.31
12	150	101	17.76	15	154	89	34.28	18	---	95	41.19
19	796	692	32.29	22	734	528	60.31	25	762	702	29.24
20	417	260	45.57	23	438	218	59.90	26	391	241	57.99
21	224	150	28.13	24	233	112	43.92	27	243	102	45.19

*observed initial substrate concentration
**initial substrate concentration computed from the best fitting curve

6.2.7 Plots of Substrate Utilization Data and Fitted Modified Monod and Modified Linear Equations

Data obtained from substrate utilization tests and fitted modified Monod and modified linear equations with the best fitting kinetic coefficients and exponents n

computed from the sets of tests 2X, X, and X/2 are presented on Figs. 6.4, 6.5, and 6.6 respectively.

For the modified Monod equation good agreement was observed between experimental and computed substrate concentrations over time, for all individual tests when using the best k and K_s coefficients for the set. The agreement was not as good for the modified linear equation.

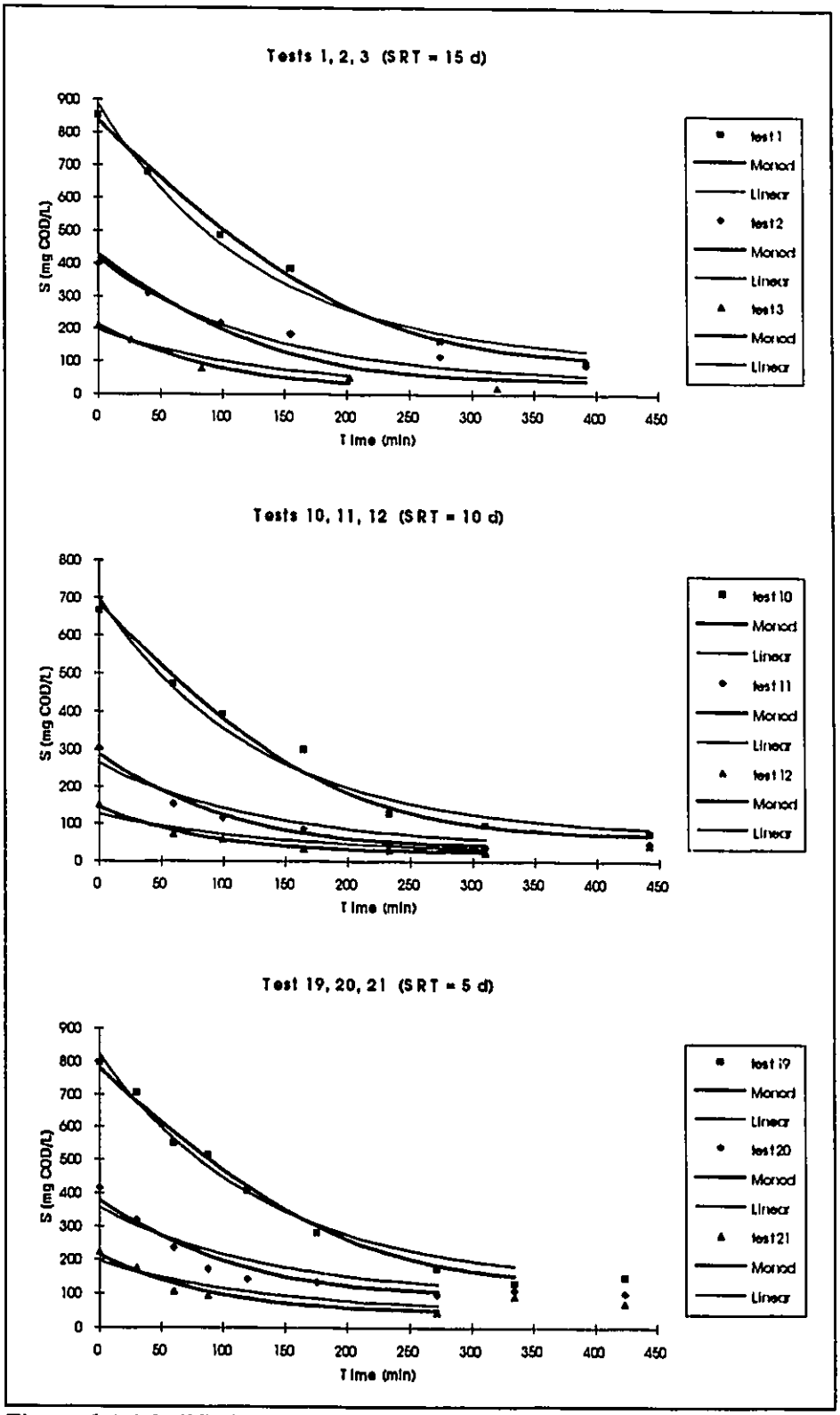

Figure 6.4 Modified Monod and linear equations fitted to tests from set 2X

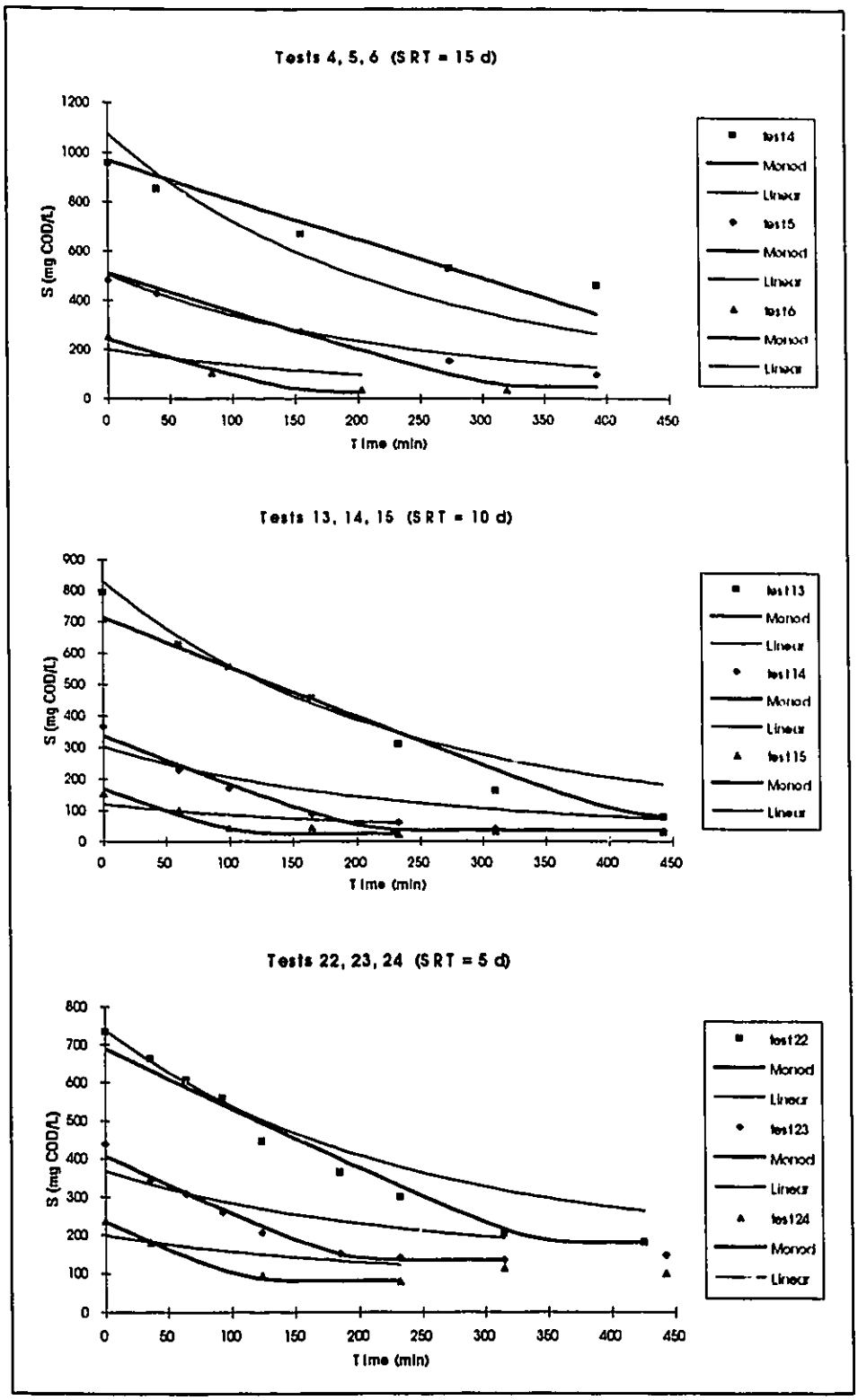

Figure 6.5 Modified Monod and linear equations fitted to tests from set X

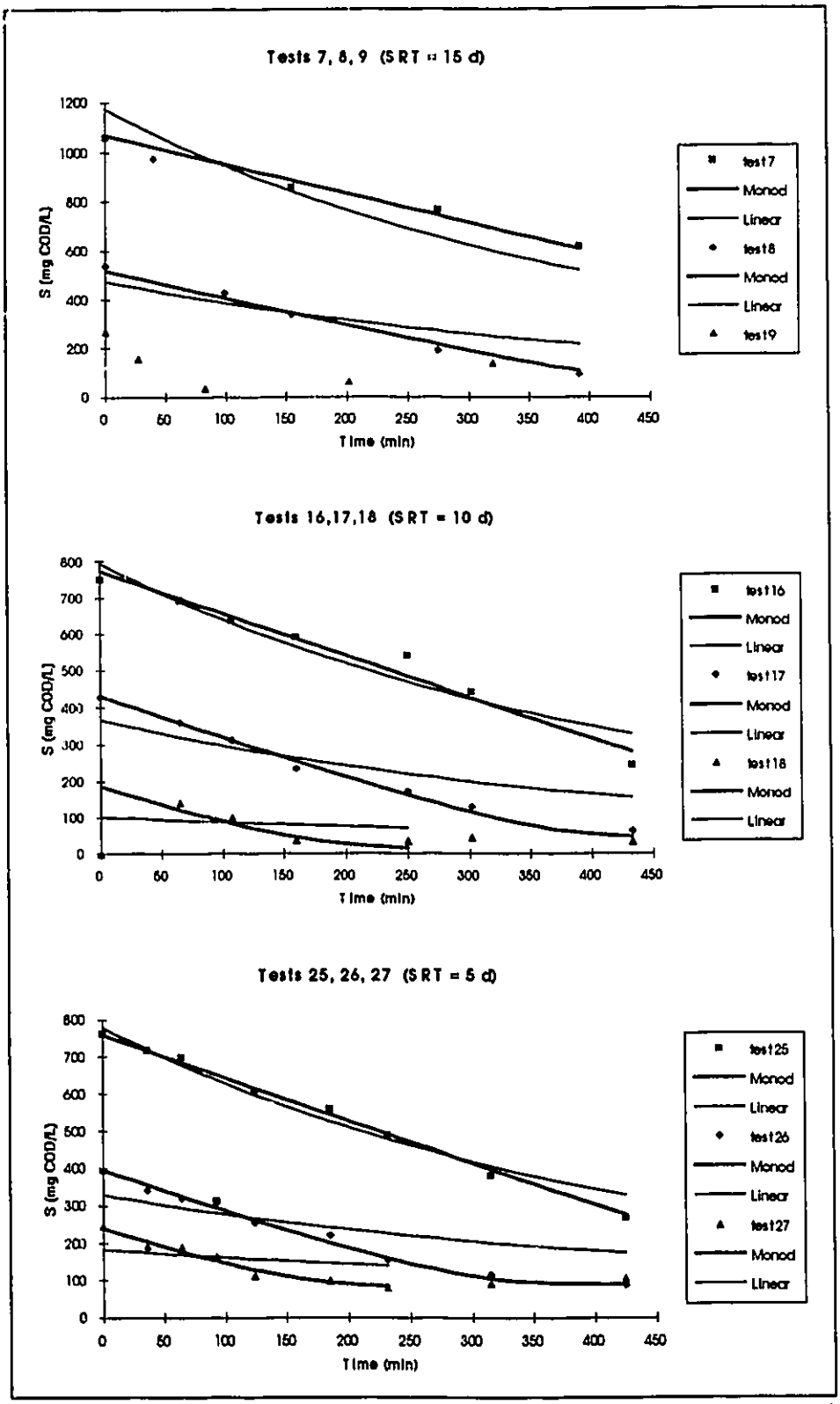

Figure 6.6 Modified Monod and linear equations fitted to tests from set X/2

6.3 Discussion

6.3.1 The Best Fitting Modified Monod and Linear Equations

Results obtained for sets of tests, confirmed the assumption that the expression AX_v^n is a better representation of active biomass concentration than the expression X_v, because the best fitting exponent n was equal to 0. The modified Monod and linear equations with n = 0, provided much better fit to the experimental data than the same equations with n = 1 (Tables 6.4 and 6.7, Figs. 6.2 and 6.3). For n = 1 the expression AX_v^n was reduced X_v, and the modified Monod and linear equations were reduced to eqs. 2.2, and 2.3, respectively.

According to the above results, the best fitting modified Monod and linear equations had the following form (eq. 6.1 and 6.2, respectively).

$$r_S = -\frac{kSX_v^0}{S+K_s} = -\frac{kS}{S+K_s}[mg/L/d] \tag{6.1}$$

$$r_S = -kSX_v^0 = -kS[mg/L/d] \tag{6.2}$$

Exponent n = 0 in the expression AX_v^n (A was embedded in coefficient k) indicated that active mass concentrations were very similar at different SRTs because dX_v^0/dt was equal to 0 (eq. 6.3).

$$AdX_v^n/dt_S = dX_a/dt_S \tag{6.3}$$

However, it was expected that the amount of active biomass will increase with increase in SRT, because the amount of sludge wasted per day decreases with increase in SRT. This results in increased amount of food (as a consequence of decayed bacteria) which is available to active mass.

Results obtained in this project, indicating constant amount of active biomass at all SRTs, may have been caused by the presence of predators feeding on sludge. Reactors

with 15 and 10 days SRT were the most affected, reactor with 5 days SRT was the least affected. This could cause the higher reduction in amount of active biomass in older sludges than in 5 days sludge, due to predation, resulting in active mass concentrations being approximately the same at all SRTs.

Results from the modified Monod equation (Table 6.4, Fig. 6.2) indicated that the values of fitting errors for n from 0 to 0.2 approximately, for set X/2, were very similar. The slopes of plots for sets 2X and X were almost uniform throughout the whole range of n values. In each set, differences between fitting error (E) computed for n between 0, and 0.2, were small in comparison to differences in E for n between 0 and 1 (in each set, the value of fitting errors computed for n = 0 were less than 50 percent of the value of fitting errors computed for n = 1). Thus, it could be assumed, that for practical purposes n from 0 to 0.2 range could be applied in this modified equation.

Similarly, for the modified linear equation, the differences in E computed for exponents 0 and 0.2 were small as compared to the differences in E for n between 0 and 1 (Table 6.7, Fig. 6.3). It could be assumed that n from 0 to 0.2 range could be applied in this modified equation.

The fitting errors for n = 0 in X and X/2 sets computed from the modified Monod model were lower than fitting errors computed from the modified linear model (Tables 6.4 and 6.7). The opposite results were obtained from set 2X. In this set residual mean square (RMS) computed from the modified linear equation (16.28 mg COD/L) was lower than RMS computed from the modified Monod equation (23.17 mg COD/L).

6.3.1.1 Comparison Between Exponent n Computed in This Project and from GE, CM and GR Models

The exponents n obtained from modified equations fitted to the theoretical data in computations on sludge models (Chapter 3), were in range higher (0.5 to 0.8) than n obtained from the experimental data in this study (0), and that obtained by Sun (1993)

(0.1). However, because the values of X_a and n computed from these models were model specific, and depended on sludge process conditions, they do not have to be matched by results obtained from this project (note the difference in X_a and n computed from CM and GR models for the same assumed conditions). Presumably the values of X_a and n computed from any of these models would be different for different substrates as well, because substrates which differ with respect to the biodegradation kinetics (and the percent of biodegradability) results in different concentrations and bacterial compositions of active mass. The main reason for performing computations on these models was to show that the expression AX_v^n with n less than 1 represents better the active biomass concentration (as computed from these models) than the expression X_v (for n = 1 AX_v^n = X_v).

6.3.2. The Evaluation of Fit

In addition to the criterion of fitting error, the determination which equation, modified Monod or modified linear, fitted better to the experimental data in each set of tests, was conducted based on visual evaluation of fitted S vs. t plots.

In set 2X, the value of fitting error computed from the modified linear equation was marginally lower than the value of fitting error computed from modified Monod equation, however from analysis of Figure 6.4 it can be concluded that the modified Monod equation was a better model for this data set. The best fitting modified linear equation overestimated the values of substrate concentration, for range of observed values below approximately 200 mg COD/L in almost all tests in this set. The slope of the fitted modified linear equation (dS/dt = utilization rate) for tests conducted for S_0 > 500 mg COD/L was clearly higher then the slope indicated by the experimental data, while in remaining tests the slope of fitted equation was significantly lower than the observed utilization rates.

In sets X and X/2 the best fitting modified Monod equation fitted the experimental data much better than the modified linear equation, in almost all tests (Figs. 6.5 and 6.6). In these tests the best fitting modified linear equation did not reflect neither the slope (dS/dt) nor the values of the observed substrate concentrations. This was reflected by significantly higher values of fitting errors computed from the modified linear equation than from the modified Monod equation in these sets of tests (Tables 6.4 and 6.7).

6.3.2.1 Statistical Analysis of Fit.

The accuracy of fit obtained from the least squares method can be evaluated from the plots of residuals vs. computed values (Draper and Smith, 1981). Any clear trend in this plot indicates a weakness of fit.

The plots of the residuals vs. computed substrate concentrations, computed from the modified Monod and linear equations, are presented on Figs. 6.7 and 6.8, respectively.

In all sets of tests residuals computed from the modified linear equation exhibited better defined trends and were in a wider range than residuals computed from the modified Monod equation (Figs. 6.7 and 6.8). The trend in plots of residuals computed from the modified linear equation was particularly visible in sets X and X/2.

Based on Figures 6.7 and 6.8 and the observations presented in section 6.3.2 it can be concluded that in each set of tests the modified Monod equation fitted the experimental data more accurately than the modified linear equation.

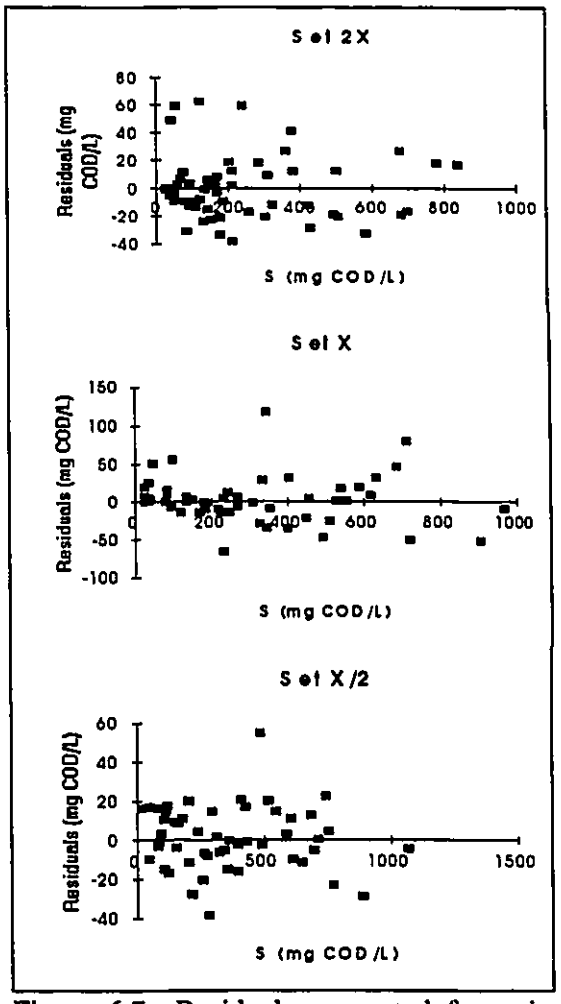

Figure 6.7 Residuals computed from the modified Monod equation for sets 2X, X, and X/2

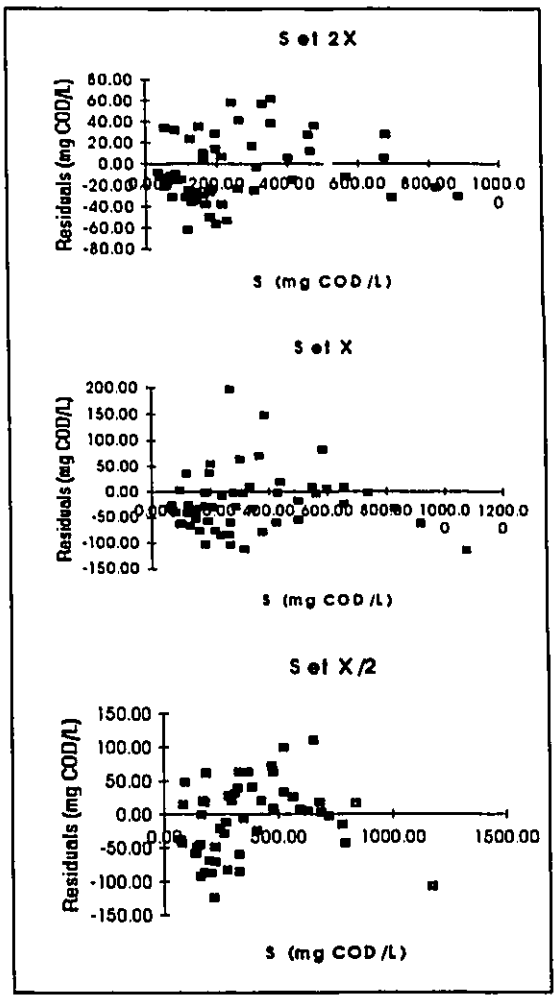

Figure 6.8 Residuals computed from the modified linear equation for sets 2X, X, and X/2

6.3.3 Kinetic Coefficients and Fitting Errors Computed from Individual Batch Tests

Kinetic coefficients computed from the modified Monod equation, from individual tests from set 2X, exhibited high variability (Table 6.10). For example, coefficients computed from tests 2, 3, 11, 12, and 20 were a number of times higher, than coefficients computed from other tests in this set (tests 1, 10, 19 and 21). True values of kinetic coefficients could not be determined based on the magnitude of fitting errors, because those errors were very similar in all tests in this set.

Table 6.10 Kinetic coefficients and fitting error from tests in set 2X (Monod equation, n = 0)

Test #	S_{ov} mg/L	k^* mg/L/d	K_s mg/L	EJ mg/L
1	843	8509	411	21.41
2	385	17620	1916	15.54
3	212	32931	1828	14.99
10	654	4928	157	23.58
11	303	30675	1518	10.76
12	151	28308	1257	4.79
19	801	8158	315	18.29
20	423	18957	695	10.46
21	229	6571	174	9.79

*$k = k_a X_a / X_v^n$, for $n = 0$ $k = k_a X_a$

It was assumed that the kinetic coefficients computed from sets of tests represented the actual sludge kinetics, because they were based on a much higher number of observations than coefficients computed from one test. Theoretically, coefficients computed from sets of tests and from individual tests should be the same. Kinetic coefficients k computed from tests 2, 3, 11, 12, and 20 were approximately 3 to 4 times higher than the k value of 7797 mg/L/d computed for the whole 2X set, coefficients K_s computed from those tests exhibited the same pattern (Table 6.10). Based on this, those coefficients were discarded. It was assumed that those results were caused by the fact that the experimental observations in tests 2, 3, 11, 12, and 20 covered only the lower part of the whole r_s range (from 0 to k). This was indicated by the initial r_s rates in those tests which were much lower than coefficient k for the whole 2X set, (Table 6.11). It was concluded that those experimental conditions combined with COD measurement errors could produce kinetic coefficients that were not representative of the actual process kinetic in those tests.

Table 6.11 Initial substrate utilization rates observed in tests 2, 3, 11, 12, 20

test #	time	S	initial r_s
	min.	mg/L	mg/L/d
2	0 - 40	397 - 311	3101
3	0 - 27	210 - 167	2297
11	0 - 60	304 - 154	3595
12	0 - 60	145 - 73	1849
20	0 - 30	417 - 320	4610

Coefficients k computed from the remaining tests in set 2X (tests 1, 10, 19 and 21) approximated well k computed from the whole set 2X (Table 6.10). Coefficients k from tests, in sets X and X/2 exhibited lower variability than in set 2X (Appendix D, Tables D2-D3).

To evaluate results from sets of tests and individual tests, the maximum substrate utilization rates (k) were computed directly from the experimental data from tests 7, 8, 16, and 25 (set X/2) in which the S vs. t plot was practically linear (Table 6.12). This linearity was caused by low sludge concentrations in those tests (set X/2), combined with high initial substrate concentrations. Those conditions resulted in microorganism limited substrate utilization (for a significant portion of the test), i.e. utilization at maximum r_s according to eq. 6.4 (which represents the reduction of equation 3.1 for $K_s << S$).

$$r_s = -kX^n \tag{6.4}$$

Table 6.12 Utilization rates computed directly from experimental data

Test #	VSS*	time	S	r_s
	mg/L	min.	mg/L	mg/L/d
7	1106	0 - 392	1064 - 620	1633
8	1009	0 - 392	538 - 93	1637
16	666	0 - 302	750 - 442	1469
25	432	0 - 425	762 - 268	1674

*X/2 set.

The maximum r_s computed from tests 7, 8, 16 and 25 (Table 6.12), were similar to coefficients k computed from other tests in set X/2 (tests 17, 18, 26, and 27, Appendix D, Table D3) and to k = 1772 mg/L/d computed from the whole set X/2 (Table 6.4), obtained using the nonlinear fitting method. Thus, it was concluded that those values of k were a close representation of the actual substrate utilization kinetics in this set of tests.

According to the same method, the analysis of kinetic coefficients computed from sets 2X, X and X/2 was conducted. If it was assumed that the amount of active mass in tests belonging to a particular set was directly proportional to the sludge dilution ratio and to the maximum substrate utilization rate for this set, then by knowing the average actual dilution ratios for sets (avg. ADR) and the value of k for one set, the value of k for other set could be determined (avg. ADR is equal to average ratio between average sludge concentrations in tests at a particular SRT and dilution rate (2X, X, X/2) defined as ADR and average sludge concentration in tests at the same SRT and at X dilution rate, Table 6.13). Comparison of dilution and k ratios between sets 2X, X and X/2 is presented in Table 6.13. Ratios r_1, r_2 and r_3 (in Table 6.13) were computed from the following equations:

r_1 = avg. ADR (from 2X or X set)/avg. ADR (from X/2 set)

r_2 = k (from 2X or X set)/k (from X/2 set)

$r_3 = r_2/r_1$

Table 6.13 Sludge dilution ratios and coefficients k for sets of tests

set	TDR	ADR				k	r_1	r_2	r_3
		15 d	10 d	5d	avg.	mg/L/d			
X/2	0.5	0.5459	0.5237	0.5374	0.5375	1772	1	1	1
X	1	1	1	1	1	2364	1.86	1.33	0.72
2X	2	1.8956	1.8099	1.9562	1.8815	7797	3.5	4.4	1.25

TDR-theoretical sludge dilution ratio (batch MLVSS/SBR MLVSS)

Based on r_3 ratio equal to 1.25 and 0.72, from sets 2X and X respectively (Table 6.13), it was assumed, that the actual average sludge dilution ratio (avg. ADR) in 2X and X sets was approximately directly proportional to the computed coefficient k from those sets. Thus, based on the assumption that the coefficient k computed from set X/2 represented a close approximation of the actual sludge kinetics (as it was concluded based on comparison to coefficients k computed directly from the experimental data from tests 7, 8, 16, and 25), the same assumptions were made about the coefficient k computed from sets 2X and X.

Summarizing, while fitting the modified Monod equation to data from one test, significant errors in computing coefficients k and K_s occurred, which were most likely caused by experimental errors in measuring substrate concentration (COD), and the fact that measurements were conducted over r_s range much smaller than whole range of substrate utilization rate. In this experiment, variability of results for tests conducted under these conditions was very high. In tests in which most of r_s range was covered by experimental data (sets X and X/2), the variability of computed kinetic coefficient was much lower (Appendix D, Table D1-D3).

The best fitting kinetic coefficients k (L/mg/d) computed from the modified linear equation from individual tests exhibited high variability in tests belonging to all sets of tests (Appendix D, Tables D4-D6).

6.3.4 Comparison Between Kinetic Coefficients Computed in This Project and Coefficients Found in Other Studies

One of the reasons why coefficients k or μ computed in different studies according to eqs. 2.1 or 2.2 have different values, is the fact that these coefficients represent maximum kinetic rates divided by X_v concentration (discussion of this topic was presented in Chapter 2). Thus, they exhibit variability due to the differences between X_v in those tests. This can be illustrated by the following example. To eliminate the variability of the

specific rates μ_s which was due to the division of μ by VSS concentration, coefficients μ_s obtained in Braha and Hafner's study were multiplied by corresponding VSS concentrations (X_0) to compute values of μ (Table 6.14, col. 5).

Table 6.14 Specific growth rates (Braha and Hafner, 1987)

SRT	S_0	X_0	μ_s	μ
[d]	[mg/L]	[g/L]	[1/d]	[g/L/d]
(1)*	(2)	(3)	(4)	(5)
11.4	277	5.88	0.400	2.352
9.3	281	4.31	0.482	2.077
8.0	319	4.19	0.500	2.095
6.4	296	4.02	0 568	2.283
4.9	281	3.68	0.776	2.856
4.0	273	5.02	0.548	2.751
3.6	228	3.88	0.383	1.486
		c_v(%)	25.15	20.21

It was found that the coefficient of variation (c_v) of μ set was lower than the c_v for the μ_s set (cols. 4 and 5, last row, Table 6.14). The difference between those coefficients of variation would be higher if differences in VSS concentrations between tests were larger (VSS concentrations from that experiment were similar (col. 3 Table 6.14)).

The purpose of this section is to compare only the ranges of kinetic coefficients μ_s and K_s computed in this study (Table 6.15) with ranges of those coefficients found in other studies.

Table 6.15 Specific kinetic rates for tests, set X

Test	VSS	S_0	k		μ_s	K_s
#	mg/L	mg COD/L	mg/L/d	h^{-1}	h^{-1}	mg/L
set X			2364	--	--	16
4	2121	933	7956	0.156	0.058	1823
5	2034	486	3862	0.079	0.029	296
6	1931	256	5454	0.118	0.043	159
13	1302	775	3089	0.099	0.036	27
14	1168	365	6376	0.227	0.084	264
15	1186	157	2813	0.099	0.036	70
22	843	742	3891	0.192	0.071	107
23	777	433	4130	0.222	0.082	94
24	732	234	3205	0.182	0.067	57

It was assumed that the values of kinetic coefficients in test no. 4 do not represent the actual kinetics of the utilization process in this test, because those values are much higher then kinetic coefficients conputed from other tests in this set and from the whole set X (see discussion for set 2X in section 6.3.3). Thus kinetic coefficients computed from test no. 4 were not compared to kinetic coefficients found in other studies.

Presented below are coefficients found in studies by Gaudy et al. (1967) (Table 6.16), Peil and Gaudy (1971) (Table 6.17), and quoted by Grady and Lim (1980) for heterogeneous populations (Table 6.18).

Table 6.16 Substrate utilization coefficients (Gaudy et al., 1967)

Dilution rate	μ_s	K_s	Y
h^{-1}	h^{-1}	mg/L	mg/mg
1/24	0.416	68	0.46
1/18	0.384	87	0.42
1/12	0.588	91	0.37
1/6	0.715	145	0.46
1/4	0.555	97	0.46
1/3	0.770	181	0.48
1/2	0.600	116	0.48
1/1.5	0.530	30	0.48

Table 6.17 Substrate utilization coefficients (Peil and Gaudy, 1971)

Substrate	Exp. no.	μ_s	K_s
		h^{-1}	mg/L
Glucose	1	0.49	29
Glucose	2	0.38	11
Lactose	1	0.53	55
Lactose	2	0.44	37
Lactose	3	0.21	--
Lactose	4	0.43	33
Sucrose	1	0.55	17
Sucrose	2	0.28	6
Sewage	1	0.49	41
Sewage	2	0.43	62

Table 6.18 Substrate utilization coefficients (Grady and Lim, 1980)

Substrate	μ_s	K_s	Basis for K_s
	h^{-1}	mg/L	
Glucose	0.31 - 0.77	11 - 181	COD
Glucose	0.69	26	COD
Skim milk	0.10	110	COD
Domestic Sewage	0.40	60	COD
Domestic sewage	0.46	55	COD
Domestic sewage	0.16	22	COD

The coefficients K_s obtained from most tests in this study were in the range of coefficients K_s obtained from other studies performed on different substrates. Coefficients μ_s (k/Y) computed in this study (Table 6.15) was in the range of this coefficient obtained for skim milk and domestic sewage (Table 6.18).

6.3.5 Influence of the Residual Substrate Concentration on Computed Coefficients

Computations of the best fitting kinetic coefficients and exponent n, were conducted for two additional sets of S_r, for the purpose of analyzing the influence of different values of the residual substrate concentration on the results.

In the first set (SR1) residual substrate concentrations were equal to S_{min}, and in the second set (SR2) S_r were equal to zero in all tests (in the modified Monod equation coefficients computed for sets SR1 and SR2 were indicated as k_1, K_{s1} and k_2, K_{s2}, respectively, k and K_s were the values computed for the actual S_r set (SRA)).

It had been observed that the values of the coefficient K_s computed from tests 7, 8, and 25 were strongly dependent on the S_r set used. Results from those tests and from test 16 for which K_s was equal to 0 are presented in Table 6.19.

Table 6.19 Kinetic coefficients and fitting errors computed from individual tests (SRA, SR1, and SR2 sets)

Test	k	$k_{(1)}$	$k_{(2)}$	K_S	$K_{S(1)}$	$K_{S(2)}$	E	$E_{(1)}$	$E_{(2)}$
#	mg/L/d	mg/L/d	mg/L/d	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
7	3622	1592	3308	919	0.01	894	21.82	23.05	2.13
8	2156	1861	2352	49	0.01	99	9.93	7.22	3.04
16	1626	1626	1625	0.0	0.01	0.0	31.00	31.00	5.09
25	1821	1735	1841	28	0.01	40	9.83	9.30	9.13

Coefficients K_s in tests 7, 8 and 25 for set SR1 were practically equal to 0, while for sets SRA and SR2 they were substantially higher. This was caused by the residual substrate concentrations in set SR1 (defined as S_{min} in all tests) which were higher than the actual S_r in those tests. Based on this it was concluded that the change of the S_r values (which is equivalent to arbitrarily repositioning the S vs. t plot with respect to the origin), in computation for individual tests, can force results which do not reflect the actual utilization kinetics.

In computations on the X/2 set of tests (containing tests 7, 8, 16 and 25) for SR1 set, small differences in the optimum n depended on which tests were included in this set (Table 6.20).

Table 6.20 Kinetic coefficients and fitting error from set X/2 (modified Monod equation, SR1 set)

n	X/2(1)*			X/2(2)**		
	$k_{(1)}$	$K_{s(1)}$	E	$k_{(1)}$	$K_{s(1)}$	E
	mg/L/d	mg/L	mg/L	mg/L/d	mg/L	mg/L
0	1764	20	10.89	1705	35	6.55
0.1	929.0	20	10.85	903.6	34	6.59
0.2	486.4	20	11.23	480.6	33	6.71
0.3	253.4	19	11.97	256.1	33	6.92
0.4	131.6	18	13.01	135.6	32	7.21
0.5	68.05	16	14.26	72.08	31	7.56
0.6	35.11	14	15.69	38.17	30	7.97
0.7	18.18	14	17.26	20.30	29	8.42
0.8	9.413	14	18.91	10.83	29	8.92
0.9	4.929	17	20.62	5.742	29	9.45
1	2.575	19	22.36	3.031	27	10.00

*tests 7, 8, 16, 17, 18, 25, 26, and 27
**tests 17, 18, 26, and 27

When computations were performed on this set containing all tests, the best n was equal to 0.1 (tests 7, 8, 16, 17, 18, 25, 26, and 27, Table 6.23, X/2(1) set). This would indicate a change in the amount of active biomass between tests, in set X/2, described according to eq. 6.5.

$$AdX_v^n/dt_S = dX_a/dt_S = dAX_v^{0.1}/dt_S \qquad (6.5)$$

However, if in sets 2X, and X, such a change was not indicated (n = 0, Table 6.4), theoretically there was no reason why it should occur in set X/2, because the ratios of X_v to X_a within each set of tests were constant (eq.6.6).

$$2X_v/2X_a = X_v/X_a = (X_v/2)/(X_a/2) \qquad (6.6)$$

It was observed that relatively high initial COD concentrations combined with low sludge concentrations in tests 7, 8, 16 and 25 (S_0 equal to 1064, 538, 750 and 762 mg COD/L, respectively, X/2 sludge concentration) caused the substrate utilization rate to be

microorganism limited in those tests in the observed r_s range (according to eq. 6.4 section 6.3.3).

When these tests were excluded from the X/2 set and computations were performed on remaining tests, the lowest fitting error (E) was obtained for n = 0 (Table 6.20, X/2(2) set). Thus, it was concluded that exponent n equal to 0.1 in set X/2, represented results skewed by experimental data from tests 7, 8, 16 and 25 which were reflecting only microorganism limited substrate utilization conditions (see section 6.3.3).

The change of S_r set from SRA to SR1 did not affect the value of the best fitting exponent n computed from sets of tests from the modified linear equation (Appendix E, Table E9, coefficient k for set SR1 was indicated as $k_{(1)}$). The kinetic coefficients k computed from individual tests showed a decrease with decrease in values of S_r (Appendix E, Tables E10-12).

CHAPTER 7

CONCLUSIONS

In this project the best fit to the experimental data was obtained from the following modified Monod and linear, substrate utilization rate equations (eqs. 6.1 and 6.2).

$$\text{(eq. 6.1)}\quad r_s = -\frac{kSX_v^0}{S+K_s} = -\frac{kS}{S+K_s}\ [\text{mg/L/d}]$$

$$\text{(eq. 6.2)}\quad r_s = -kSX_v^0 = -kS\ [\text{mg/L/d}]$$

At the conditions of constant X_v the above modified equations are equivalent to eqs. 2.2 and 2.3 respectively (see Chapter 3).

Based on the results obtained in this project the following other conclusions were derived.

1. Substrate utilization kinetics of sludge at different SRTs, cultivated at the same substrate organic loading rates were similar, for sludges with the same dilution ratio (within one set: 2X, X or X/2). This was indicated by computed exponent n equal to 0.

2. For data sets X and X/2 fitting errors computed from the modified Monod equation were lower than fitting errors computed from the modified linear equation, the opposite occurred in set 2X (Table 7.1).

Table 7.1 Fitting errors from modified Monod and linear models

Set	E, modified Monod model	E, modified linear model
2X	23.17	16.28
X	16.66	32.83
X/2	8.72	29.18

3. Based on the analysis of fitted plots and the distribution of residuals (section 6.3.2) it can be concluded that the modified Monod equation provided better fit to the experimental data than the modified linear equation, in all data sets.

4. The differences in average fitting error, computed from the modified Monod and linear models, for n between 0 and 0.2 were small in all sets (Tables 6.4 and 6.7), in comparison to differences in fitting error for n between 0 and 1.

5. Kinetic coefficients for individual tests computed from the modified Monod and linear equations were dependent on the residual substrate concentration. Values of coefficients k, K_s and n computed from sets of tests were marginally affected by the same conditions (section 6.3.5).

6. This modification can also be used for other models. The exponent n is a function of the wastewater and the model formulation.

CHAPTER 8

RECOMMENDATIONS FOR FUTURE RESEARCH

The best fitting value of exponent n in the modified substrate utilization models depends on the type of substrate and may be different depending on the range of SRT of the sludge tested. For those reasons it would be worthwhile to compile a table of exponents n to be used for the conditions of a particular waste and expected range of SRT. This could lead to the estimation of one general exponent n applicable to all SRTs. The example of such table is presented below (Table 8.1).

Table 8.1 Exponent n for different substrates and ranges of SRT

waste type	SRT range(d)							
	5-15	0-1	1-5	5-10	10-15	15-20	20-30	30-50
proteins	0.0-0.2*							
glucose								
...								
agricultural:								
...								
...								
domestic:								
...								
...								
industrial:								
...								
...								

*results from this project

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APPENDIX A SBR experimental data.

Table A.1 SS concentration (mg/L)

SS			
day	15 d	10 d	5 d
1	3353	2690	2178
2	3195	2528	1930
3	3172	2310	1684
4	3075	2156	1651
5	2885	2167	1466
6	2827	2004	1390
7	2670	1899	1349
8	2679	1760	1171
9	2567	1691	1074
10	2533	1593	908
11	2477	1645	998
12	2517	1662	878
13	2574	1569	863
14	2493	1584	942

Table A.2 Influent COD concentration (mg/L)

day	15 d	10 d	5 d
6	206.93	180.20	247.18
8	221.78	233.66	225.89
10	238.12	238.12	217.56
12	189.11	180.59	189.65
14	168.32	174.26	203.24

Table A.3 Effluent COD concentration (mg/L)

day	15 d	10 d	5 d
11	36.14	30.20	32.09
12	33.17	33.17	28.82
13	10.89	40.59	35.87
14	39.11	32.16	31.63

APPENDIX B Batch tests experimental data.

Table B.1 COD and SS vs. t, 15 days sludge, tests 1-9

Test	time	S	TSS	VSS	ISS	VSS/TSS
	min	mg COD/l	mg/l	mg/l	mg/l	
1	0	853.47	5255	4400	855	0.84
	40	681.19				
	99	488.12	4440	3545	895	0.80
	155	386.63	4465	3557	907	0.80
	274	165.35	4567	3645	922	0.80
	392	95.54				
				3787*		
2	0	397.03	4970	3927	1042	0.79
	40	310.89				
	99	218.81				
	155	186.14	4920	3892	1027	0.79
	274	114.85	4980	3947	1032	0.79
	392	91.09				
				3922		
3	0	209.90	4737	3717	1020	0.78
	27	166.83	4782	3797	985	0.79
	83	80.69	4937	3895	1042	0.79
	202	53.96	4930	3900	1030	0.79
	320	19.80				
				3828		
4	0	957.43	2580	2042	537	0.79
	40	853.47				
	99	87.13	2652	2115	537	0.80
	155	670.30	2702	2152	550	0.80
	274	530.69	2715	2175	540	0.80
	392	463.86				
				2121		
5	0	483.17	2515	1997	517	0.79
	40	426.73				
	99	738.61	2520	1997	522	0.79
	155	273.76	2590	2050	540	0.79
	274	153.47	2630	2090	540	0.79
	392	100.00				
				2034		
6	0	254.46	2337	1860	477	0.80
	27	426.73	2360	1862	497	0.79
	83	107.43	2480	1970	510	0.79
	202	33.17	2540	2030	510	0.80
	320	34.65				
				1931		
7	0	1064.36	1352	1075	277	0.79
	40	461.39				
	99	1477.23	1292	1030	262	0.80
	155	857.43	1400	1117	282	0.80
	274	768.32	1482	1200	282	0.81

	392	619.80		1106		
8	0	538.12	1262	1002	260	0.79
	40	976.24				
	99	426.73	919	832	86	0.91
	155	339.11	1327	1067	260	0.80
	274	189.11	1392	1135	257	0.82
	392	92.57		1009		
9	0	266.34	1205	947	257	0.79
	27	156.44				
	83	36.14	1042	775	267	0.74
	202	64.36	862	652	210	0.76
	320	137.13		792		

* average VSS concentration in a test

Table B.2 COD and SS vs. t, 10 days sludge, tests 10-19

Test	time	S	TSS	VSS	ISS	VSS/TSS
	min	mg COD/l	mg/l	mg/l	mg/l	
10	0	664.81	2097			
	60	473.65				
	100	393.76	2742	2088		0.76
	164	299.61				
	233	129.83	3075			
	310	97.02	3140			
	442	77.05		2088*		
11	0	303.87	3060	2300	760	0.75
	60	154.09				
	100	115.57	3115	2360	755	0.76
	164	87.04				
	233	44.24	3160	2365	795	0.75
	310	39.96	3145	2370	775	0.75
	442	49.95		2349		
12	0	149.81	2700	2035	665	0.75
	60	72.77				
	100	61.36	3082	2295	787	0.74
	164	32.83				
	233	29.98	2957	2212	745	0.75
	310	25.70	2940	2182	757	0.74
	442	42.82		2181		
13	0	793.19	1642			
	60	627.72				
	100	556.39	1585	1235	350	0.78
	164	459.38				
	233	311.00	1670	1292	377	0.77
	310	164.07	1757	1377	380	0.78
	442	81.33		1302		

14	0	363.79	1157	900	257	0.78
	60	229.69				
	100	174.06	1695			
	164	87.04				
	233	62.79	1682	1295	387	0.77
	310	39.96	1705	1307	397	0.77
	442	35.68				
				1168		
15	0	154.09	1360	1030	330	0.76
	60	99.88				
	100	44.24	1655	1250	405	0.76
	164	42.82				
	233	24.27	1685	1267	417	0.75
	310	32.83	1590	1197	392	0.75
	442	32.83				
				1186		
16	0	750.40	790	605	185	0.77
	65	693.34				
	108	636.27	820	625	195	0.76
	160	590.63				
	250	539.25	872	690	182	0.79
	302	442.25	950	745	205	0.78
	433	242.53				
				666		
17	0	429.41	815	607	207	0.75
	65	358.08				
	108	312.43	782	605	177	0.77
	160	233.97				
	250	171.20	785	615	170	0.78
	302	129.83	847	657	190	0.78
	433	64.21				
				621		
18	0	-2.83	677	527	150	0.78
	65	139.82				
	108	99.88	820	607	212	0.74
	160	35.68				
	250	32.83	907	697	210	0.77
	302	42.82	895	680	215	0.76
	433	32.83				
				628		

*average VSS concentration in a test

Table B.3 COD and SS vs. t, 5 days sludge, tests 20-27

Test	time	S	TSS	VSS	ISS	VSS/TSS
	min	mg COD/l	mg/l	mg/l	mg/l	
19	0	796.33	1572	1400	172	0.89
	30	705.95				
	60	550.59	1657	1457	200	0.88
	88	513.88				
	119	408.05	1692	1527	165	0.90
	175	280.95	1767	1590	177	0.90
	272	175.02	1750	1570	180	0.90
	334	131.24	1752	1565	187	0.89

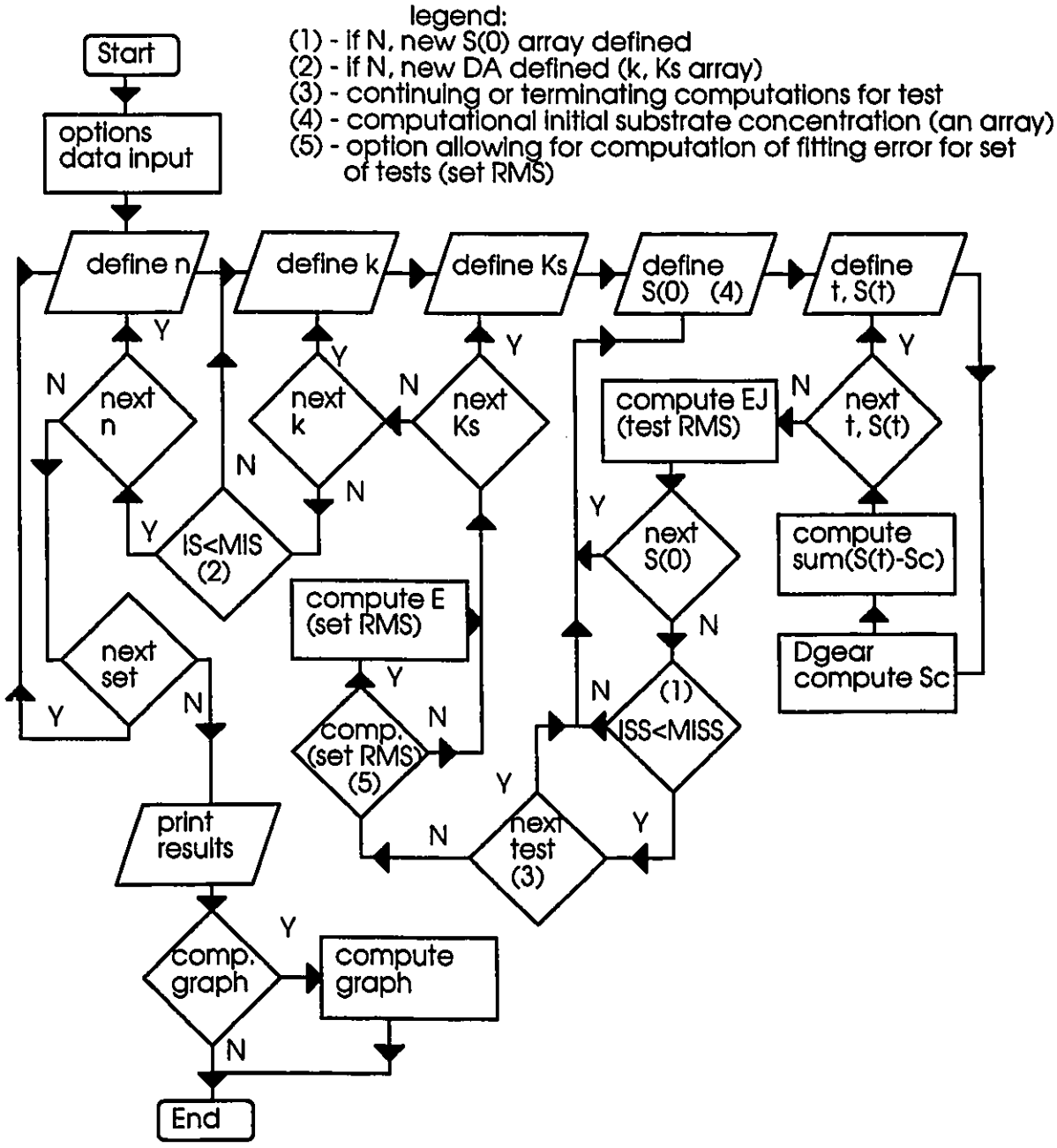
	424	148.19		1518*		
20	0	416.53	1587	1402	185	0.88
	30	320.49				
	60	237.17	1727	1530	197	0.89
	88	173.61				
	119	142.54	1642	1462	180	0.89
	175	134.07	1712	1507	205	0.88
	272	97.35	1670	1477	192	0.88
	334	110.06	1697	1515	182	0.89
	424	100.17		1482		
21	0	224.45	1772	1587	185	0.90
	30	175.02				
	60	105.82	1845	1635	210	0.89
	88	94.52				
	119	-7.16	1852	1642	210	0.89
	175	-7.16	1790	1582	207	0.88
	272	46.51	1810	1610	200	0.89
	334	91.70	1740	1550	190	0.89
	424	71.93		1601		
22	0	734.19	865	758	108	0.87
	36	663.58				
	64	607.09	1172	790	382	0.67
	93	559.07				
	124	446.09	955	830	125	0.86
	185	364.27				
	232	299.31	1002	880	122	0.88
	315	204.68	1095	955	140	0.87
	425	179.26		843		
23	0	437.71	807	707	100	0.88
	36	343.09				
	64	307.78	887	765	122	0.86
	93	259.76				
	124	207.51	917	790	127	0.86
	185	152.43				
	232	139.72	937	825	112	0.88
	315	134.07	947	797	150	0.84
	425	146.78		777		
24	0	235.75	760	682	77	0.90
	36	179.26				
	64	720.17				
	93	663.68				
	124	94.52	892	780	112	0.87
	185	148.19				
	232	80.40	870	740	130	0.85
	315	114.30	835	727	107	0.87
	425	100.17		732		
25	0	762.44	422	352	70	0.83

	36	717.24				
	64	697.47	455	380	75	0.84
	93	310.51				
	124	604.26	517	432	85	0.84
	185	557.76				
	232	487.14	577	485	92	0.84
	315	379.81	600	512	87	0.85
	425	268.24				
				432		
26	0	391.11	415	345	70	0.83
	36	340.26				
	64	317.67	447	390	57	0.87
	93	307.78				
	124	254.11	500	427	72	0.85
	185	220.22				
	232	153.84	552	462	90	0.84
	315	114.30	560	482	77	0.86
	425	87.46				
				422		
27	0	242.81	422	382	40	0.91
	36	191.97				
	64	187.74	435	385	50	0.89
	93	160.90				
	124	110.06	500	432	67	0.87
	185	97.35				
	232	80.40	500	432	67	0.86
	315	88.88	482	422	60	0.88
	425	103.00				
				411		

*average VSS concentration in a test

APPENDIX C Computer program.

C.1 Flowchart



C.2 Code

```
      PROGRAM MQ
C
      INTEGER N,METH,MITER,INDEX,IWK(2),IER,K,P,M
      REAL Y(2),WK(35),X,TOL,XEND,H,EXP,AK1,AK2,B1K,BK,AS1,AS2,B
     1     ,BS,Z1,Z2,ZIN,ZF,R1,R2,EI,YY
      EXTERNAL FCN,FCN1,DGFAR
      DIMENSION BRKS(8),BRN(50,27),A1F(50,27),A2F(50,27),DX(50),
     1     ,BXN(50),A3F(50),A4F(50),DXX(50),BMK(11),BMS(8),KG(100)
     2     ,ZZG(50,27),ZZS(50,27),BRN1(50,27),JNR1(3),JNR2(3)
     3     ,ATT(4,27),ATTL(3,27)
      COMMON D(40,27),EXP,BK,BS,JT,JF
      DOUBLE PRECISION R1A,RR,R2A,RX,X1,X2,X3,X4
C
      WRITE(*,1131)
      READ *,ID
       IF((ID.EQ.3).OR.(ID.EQ.4)) GO TO 911
      WRITE(*,1161)
      READ *,P
      WRITE(2,1111)
      WRITE(*,1105)
      WRITE(*,1120)
      READ *,JTF
      WRITE(*,1121)
      READ *,N1,N2,NP
      WRITE(*,1133)
      READ *,NR
       DO 3000 NRR=1,3
      WRITE(*,1122)NRR
      READ *,JNR1(NRR),JNR2(NRR)
3000 CONTINUE
      WRITE(*,1123)
      READ *,LP
      WRITE(*,1125)
      READ *,CTK,CTS
      WRITE(*,1126)
      READ *,LIM
C
      WRITE(*,1130)ID
      WRITE(2,1130)ID
      WRITE(*,1106)JTF,P,N1,N2,NP,NR,LP,CTK,CTS,LIM
      WRITE(2,1106)JTF,P,N1,N2,NP,NR,LP,CTK,CTS,LIM
      WRITE(*,1134)JNR1
      WRITE(2,1134)JNR1
      WRITE(*,1134)JNR2
      WRITE(2,1134)JNR2
C
      READ(1,*,END=800)D
C
  800 X1=D(36,1)
      X2=D(37,1)
      X3=D(38,1)
C
      NRR=1
 2000 J1=JNR1(NRR)
      J2=JNR2(NRR)
      JF=J2-J1+1
C
        DO 80 JT=1,JTF
       IF((JF.EQ.1).AND.(LP.EQ.0)) THEN
      WRITE(2,1010)D(1,JT)
      WRITE(*,1010)D(1,JT)
      WRITE(2,1011)
      WRITE(*,1011)
       END IF
       IF((JF.GT.1).AND.(LP.EQ.0)) THEN
      WRITE(2,1011)
      WRITE(*,1011)
       END IF
       IF(JF.EQ.1) THEN
      WRITE(2,1010)D(1,JT)
      WRITE(*,1010)D(1,JT)
       END IF
C
        DO 70 N1=N1,N2
      L=1
       IF(NF.EQ.0) THEN
      EXP=0
       ELSE
      EI=(N1-1)
      EXP=EI/NF
       END IF
      WRITE(2,1101)EXP
      WRITE(*,1101)EXP
      RR=1000000
      RX=1000000
C
       IF(JF.GT.1) THEN
      AK1=D(27,1)*200**(-EXP)
      AK2=D(28,1)*4000**(-EXP)
      X5=X2*2100**(-EXP)
       ELSE
      AK1=D(27,1)*D(25,JT)**(-EXP)
      AK2=D(28,1)*D(25,JT)**(-EXP)
      X5=X2*D(25,JT)**(-EXP)
       END IF
      AS1=D(30,1)
      AS2=D(31,1)
C
         IF(LP.EQ.0) THEN
        IF(JF.EQ.1) THEN
       IF(ID.EQ.1) THEN
      WRITE(2,1144)
      WRITE(*,1144)
       ELSE
      WRITE(2,1148)
      WRITE(*,1148)
       END IF
        ELSE
       IF(ID.EQ.1) THEN
      WRITE(2,1146)
      WRITE(*,1146)
       ELSE
      WRITE(2,1150)
      WRITE(*,1150)
       END IF
        END IF
         END IF
C
  200 B1K=(AK2-AK1)/(D(29,1)-1)
       IF(ID.GT.1) GO TO 201
      B2S=(AS2-AS1)/(D(32,1)-1)
C
  201    DO 60 KKI=1,D(29,1)
      BK=AK1+B1K*(KKI-1)
      BMK(KKI)=BK
C
         DO 50 KSI=1,D(32,1)
      RR1=1000000
      RX1=1000000
      BS=AS1+B2S*(KSI-1)
      BMS(KSI)=BS
      R2=0
C
       IF(JF.EQ.1) THEN
      Z1=(D(13,JT)-D(33,JT))*(100-D(23,1)/2)/100
      Z2=(D(13,JT)-D(33,JT))*(100+D(23,1)/2)/100
       END IF
C
      M=0
C
         DO 40 J=J1,J2
       IF(JF.GT.1) THEN
      Z1=(D(13,J)-D(33,J))*(100-D(23,1)/2)/100
      Z2=(D(13,J)-D(33,J))*(100+D(23,1)/2)/100
       END IF
      LZ=0
  100 ZIN=(Z2-Z1)/(D(24,1)-1)
C
       IF(JF.GT.1) THEN
      RR=1000000
      M=M+D(2,J)
       END IF
C
         DO 30 Z=1,D(34,1)
       IF(ID.EQ.1) THEN
      Y(1)=Z1+ZIN*(Z-1)
      ZF=Y(1)
       ELSE
      YY=Z1+ZIN*(Z-1)
      ZF=YY
       END IF
      N=1
      X=0.0
      TOL=.00001
      H=.00001
      METH=1
      MITER=0
      INDEX=1
      R1=0
       IF(JF.EQ.1) THEN
      Z4=D(2,JT)
       ELSE
```

```
      Z4=D(2,J)
       END IF
C
       DO 10 ZZ=1,Z4
       IF (JF.EQ.1) THEN
      K=D(ZZ+2,JT)
       ELSE
      K=D(ZZ+2,J)
       END IF
        IF (ID.EQ.1) THEN
      XEND=FLOAT(K)
      CALL DGEAR(N,FCN,FCNJ,X,H,Y,XEND,TOL,METH,MITER,
     1                ,INDEX,IWK,WK,IER)
      IF(IER.GT.128) GO TO 20
       IF (JF.EQ.1) THEN
      R1=R1+(Y(1)-(D(12+ZZ,JT)-D(33,JT)))**2
       ELSE
      R1=R1+(Y(1)-(D(12+ZZ,J)-D(33,J)))**2
       END IF
        ELSE
       IF (JF.EQ.1) THEN
      Y(1)=YY*2.71828183**(-BK/1440*D(25,JT)**EXP*K)
       ELSE
      Y(1)=YY*2.71828183**(-BK/1440*D(25,J)**EXP*K)
       END IF
       IF (JF.EQ.1) THEN
      R1=R1+(Y(1)-(D(12+ZZ,JT)-D(33,JT)))**2
       ELSE
      R1=R1+(Y(1)-(D(12+ZZ,J)-D(33,J)))**2
       END IF
        END IF
   10   CONTINUE
C
      R1A=(R1/(Z4-P))**0.5
C
C RMS FOR ONE TEST,ONE SET OF KK AND KS
C AND NUMBER OF INITIAL CONCENTRATIONS.
C
        IF (R1A.LE.RR) THEN
      RR=R1A
      BRN(N1,JT)=R1A
      BRN1(N1,J)=R1A
      ZZZ=ZF
      ZZG(N1,JT)=ZF
      ZZS(N1,J)=ZF
      A1=BS
      A1F(N1,JT)=BS
      A2=BK
      A2F(N1,JT)=BK
      DX(N1)=EXP
       ELSE
      RR=RR
      BRN(N1,JT)=BRN(N1,JT)
      BRN1(N1,J)=BRN1(N1,J)
      ZZZ=ZZZ
      ZZG(N1,JT)=ZZG(N1,JT)
      ZZS(N1,J)=ZZS(N1,J)
      A1=A1
      A1F(N1,JT)=A1F(N1,JT)
      A2=A2
      A2F(N1,JT)=A2F(N1,JT)
      DX(N1)=DX(N1)
       END IF
       IF (R1A.LE.RR1) THEN
      RR1=R1A
       ELSE
      RR1=RR1
       END IF
C
   30   CONTINUE
C
        IF (ZIN.GT.X1) THEN
      Z1=ZZZ-ZIN
      Z2=ZZZ+ZIN
      LZ=LZ+1
      GO TO 100
       END IF
      IF (JF.EQ.1)GO TO 40
C
      R2=R2+(RR**2)*(Z4-P)
C
   40   CONTINUE
C
      R2A=(R2/(M-P))**0.5

        IF (JF.EQ.1) THEN
      BRKS(KSI)=RR1
      GO TO 50
       ELSE
      BXKS(KSI)=RX1
       END IF
C
C MINIMUN RMS FOR A SET OF TESTS.
C
        IF (JF.EQ.1) THEN
      GO TO 50
       END IF
       IF (R2A.LE.RX) THEN
      RX=R2A
      BXN(NI)=R2A
      A3=BS
      A3F(NI)=BS
      A4=BK
      A4F(NI)=BK
      DXX(NI)=EXP
       ELSE
      RX=RX
      BXN(NI)=BXN(NI)
      A3=A3
      A3F(NI)=A3F(NI)
      A4=A4
      A4F(NI)=A4F(NI)
      DXX(NI)=DXX(NI)
       END IF
       IF (R2A.LE.RX1) THEN
      RX1=R2A
      BXKS(KSI)=R2A
       ELSE
      RX1=RX1
      BXKS(KSI)=BXKS(KSI)
       END IF
C
   50   CONTINUE
C
        IF ((KK1.EQ.1).AND.(LP.GT.0).AND.(L.LE.LP)) THEN
      WRITE(2,1100)L
      WRITE(*,1100)L
      WRITE(2,1102)BMS
      WRITE(*,1102)BMS
       END IF
C
        IF ((JF.EQ.1).AND.(LP.GT.0).AND.(L.LE.LP)) THEN
       IF (L.LT.3) THEN
      WRITE(2,1103)BK,BRKS
      WRITE(*,1103)BK,BRKS
       ELSE
      WRITE(2,1110)BK,BRKS
      WRITE(*,1110)BK,BRKS
       END IF
        END IF
C
        IF ((JF.GT.1).AND.(LP.GT.0).AND.(L.LE.LP)) THEN
       IF (L.LT.3) THEN
      WRITE(2,1103)BK,BXKS
      WRITE(*,1103)BK,BXKS
       ELSE
      WRITE(2,1110)BK,BXKS
      WRITE(*,1110)BK,BXKS
       END IF
        END IF
C
   60   CONTINUE
C
        IF (JF.GT.1)GO TO 300
C
       IF ((ID.EQ.1).OR.(ID.EQ.2)) THEN
      ZZZ1=ZZZ+D(33,JT)
       ELSE
      ZZZ1=ZZZ
       END IF
       IF (LP.GT.0) THEN
      WRITE(2,1100)L
      WRITE(*,1100)L
      WRITE(2,1012)
      WRITE(*,1012)
      WRITE(2,1112)EXP,ZZZ1,A2,A1,RR
      WRITE(*,1112)EXP,ZZZ1,A2,A1,RR
       ELSE
       IF (ID.EQ.1) THEN
      WRITE(2,1145)L,ZZZ1,A2,A1,RR
      WRITE(*,1145)L,ZZZ1,A2,A1,RR
       ELSE
      WRITE(2,1149)L,ZZZ1,A2,RR
      WRITE(*,1149)L,ZZZ1,A2,RR
       END IF
        END IF
C
        IF ((B1K.GT.X5).OR.(B2S.GT.X3)) THEN
C
      AK1=A2-CTK*B1K
```

```
      IF (AK1.LT.0) THEN
      AK1=0.0
       END IF
      AK2=A2+CTK*B1K
C
      AS1=A1-CTS*B2S
       IF (AS1.LT.0) THEN
      AS1=0.0
       END IF
      AS2=A1+CTS*B2S
C
      IF (L.EQ.LIM)GO TO 400
      L=L+1
      GO TO 200
C
        END IF
C
        IF (JF.EQ.1)GO TO 400
C
  300  IF (LP.GT.0) THEN
       WRITE(2,1100)L
       WRITE(*,1100)L
       WRITE(2,1011)
       WRITE(*,1011)
       WRITE(2,1000)EXP,A4,A3,RX
       WRITE(*,1000)EXP,A4,A3,RX
        ELSE
        IF (ID.EQ.1) THEN
       WRITE(2,1147)L,A4,A3,RX
       WRITE(*,1147)L,A4,A3,RX
        ELSE
       WRITE(2,1151)L,A4,RX
       WRITE(*,1151)L,A4,RX
        END IF
         END IF
C
        IF ((B1K.GT.X5).OR.(B2S.GT.X3)) THEN
C
      AK1=A4-CTK*B1K
       IF (AK1.LT.0) THEN
      AK1=0.0
       END IF
      AK2=A4+CTK*B1K
C
      AS1=A3-CTS*B2S
       IF (AS1.LT.0) THEN
      AS1=0.0
       END IF
      AS2=A3+CTS*B2S
C
      IF (L.EQ.LIM)GO TO 400
      L=L+1
      GO TO 200
C
        END IF
C
  400  IF (JF.EQ.1) THEN
       WRITE(2,1132)
       WRITE(*,1132)
       WRITE(2,1000)EXP,A2,A1,RR
       WRITE(*,1000)EXP,A2,A1,RR
        ELSE
       WRITE(2,1011)
       WRITE(*,1011)
       WRITE(2,1005)EXP,A4,A3,RX
       WRITE(*,1005)EXP,A4,A3,RX
        END IF
C
    70   CONTINUE
C
    80   CONTINUE
C
C SUMMARY OF RESULTS
C
       WRITE(2,1104)
       WRITE(*,1104)
        IF ((JF.EQ.1).AND.(ID.EQ.1)) THEN
       WRITE(2,1012)
       WRITE(*,1012)
        END IF
        IF ((JF.EQ.1).AND.(ID.EQ.2)) THEN
       WRITE(2,1142)
       WRITE(*,1142)
        END IF

       DO 910 JT=1,JTF
        IF ((JF.GT.1).AND.(ID.EQ.1)) THEN
       WRITE(2,1011)
       WRITE(*,1011)
        END IF
        IF ((JF.GT.1).AND.(ID.EQ.2)) THEN
       WRITE(2,1143)
       WRITE(*,1143)
        END IF
C
       DO 905 NI=N1,N2
         IF (ID.EQ.1) THEN
        IF (JF.EQ.1) THEN
       ZZ2=ZZG(NI,JT)+D(33,JT)
       WRITE(2,1112)DX(NI),ZZ2,A2F(NI,JT),A1F(NI,JT),BRN(NI,JT)
       WRITE(*,1112)DX(NI),ZZ2,A2F(NI,JT),A1F(NI,JT),BRN(NI,JT)
        ELSE
       WRITE(2,1000)DXX(NI),A4F(NI),A3F(NI),BXN(NI)
       WRITE(*,1000)DXX(NI),A4F(NI),A3F(NI),BXN(NI)
        END IF
         END IF
         IF (ID.EQ.2) THEN
        IF (JF.EQ.1) THEN
       ZZ2=ZZG(NI,JT)
       WRITE(2,1140)D(1,JT),DX(NI),ZZ2,A2F(NI,JT),BRN(NI,JT)
       WRITE(*,1140)D(1,JT),DX(NI),ZZ2,A2F(NI,JT),BRN(NI,JT)
        ELSE
       WRITE(2,1141)DXX(NI),A4F(NI),BXN(NI)
       WRITE(*,1141)DXX(NI),A4F(NI),BXN(NI)
        END IF
         END IF
  905 CONTINUE
  910 CONTINUE
C
       IF (JF.EQ.1)GO TO 900
C
       DO 906 J=J1,J2
       WRITE(2,1128)D(1,J)
       WRITE(*,1128)D(1,J)
       WRITE(2,1129)
       WRITE(*,1129)
       DO 907 NI=N1,N2
        IF (ID.EQ.1) THEN
       ZZ2=ZZS(NI,J)+D(33,J)
       WRITE(2,1127)DXX(NI),ZZ2,BRN1(NI,J)
       WRITE(*,1127)DXX(NI),ZZ2,BRN1(NI,J)
        END IF
        IF (ID.EQ.2) THEN
       ZZ2=ZZS(NI,J)
       WRITE(2,1127)DXX(NI),ZZ2,BRN1(NI,J)
       WRITE(*,1127)DXX(NI),ZZ2,BRN1(NI,J)
        END IF
  907 CONTINUE
  906 CONTINUE
C
       IF ((ID.NE.3).OR.(ID.NE.4)) GO TO 900
C
C GRAPH COMPUTATION FOR MONOD AND LINEAR EQUATIONS
C
  911 WRITE(*,1124)
       READ *,J1,J2
C
       WRITE(*,1134)J1
       WRITE(2,1134)J1
       WRITE(*,1134)J2
       WRITE(2,1134)J2
C
       READ(1,*,END=850)D
C
  850 READ(3,*,END=851)KG
  851  IF (ID.EQ.3) THEN
       READ(4,*,END=852)ATT
        ELSE
       READ(4,*,END=852)ATTL
        END IF
  852   DO 1060 J=J1,J2
       WRITE(2,1010)D(1,J)
       WRITE(*,1010)D(1,J)
C
       KIF=D(2,J)
       KXF=1
C
          DO 1061 KX=1,100
        IF (KG(KX).LT.D(2+KIF,J)) THEN
       KXF=KXF+1
        ELSE
       GO TO 990
        END IF
 1061 CONTINUE
  990  IF (ID.EQ.3) THEN
       WRITE(2,1101)ATT(1,J)
       WRITE(*,1101)ATT(1,J)
       EXP=ATT(1,J)
       BK=ATT(3,J)
       BS=ATT(4,J)
```

```
      ELSE
      WRITE(2,1101)ATTL(1,J)
      WRITE(*,1101)ATTL(1,J)
      EXP=ATTL(1,J)
      BK=ATTL(3,J)
       END IF
      WRITE(2,1108)
      WRITE(*,1108)
C
       IF (ID.EQ.3) THEN
      Y(1)=ATT(2,J)-D(33,J)
       ELSE
      YY=ATTL(2,J)
       END IF
      N=1
      X=0.0
      TOL= .00001
      H= .0000l
      METH=1
      MITER=0
      INDEX=1
C
        DO 1030 KZ=1,KXF
      K=KG(KZ)
       IF (ID.EQ.3) THEN
      XEND=FLOAT(K)
      CALL DGEAR(N,FCN,FCNJ,X,H,Y,XEND,TOL,METH,MITER
     1                ,INDEX,IWK,WK,IER)
      IF(IER.GT.128) GO TO 20
       ELSE
      Y(1)=YY*2.71828183**(-BK/1440*D(25,J)**EXP*K)
       END IF
       IF (ID.EQ.3) THEN
      YF=Y(1)+D(33,J)
       ELSE
      YF=Y(1)
       END IF
      WRITE(2,1109)KG(KZ),YF
      WRITE(*,*)KG(KZ),YF
 1030   CONTINUE
 1060   CONTINUE
C
  900  IF ((NR.GT.1).AND.(NRR.LT.NR)) THEN
      NRR=NRR+1
      GO TO 2000
       END IF
      STOP
   20   CONTINUE
C
C HANDLE IER.GT.128
C
      WRITE(2,*)TOL,N,Y(1),XEND,H,X,METH,MITER,IER,INDEX
      STOP
C
 1000 FORMAT(1X,F8.2,F12.4,F10.2,F12.5)
 1001 FORMAT(1X,F6.2,I5,3F10.2,F11.3)
 1002 FORMAT(1X,F6.2,2F10.2,F11.3)
 1004 FORMAT(1X,I6,3F8.2,I6,3F8.2)
 1005 FORMAT(1X,F8.2,F12.4,F10.2,F12.5)
 1006 FORMAT(1X,F6.2,I5,8F8.2)
 1010 FORMAT(1X,'TEST NO.=',F4.0)
 1011 FORMAT(1X,'EXPONENT    K      KS      E')
 1012 FORMAT(1X,'EXPONENT  Y(0)    K      KS      EP')
 1100 FORMAT(1X,'MATRIX NO.',I4)
 1101 FORMAT(1X,'EXPONENT =',F6.2)
 1102 FORMAT(6X,'K\KS',2X,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2)
 1103 FORMAT(1X,F10.4,1X,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2,F7.2)
 1104 FORMAT(1X,'RESULTS SUMMARY')
 1105 FORMAT(1X,'ENTER PARAMETERS:')
 1106 FORMAT(1X,'PARAMETERS:',7I4,2F6.2,I4)
 1107 FORMAT(1X,'GRAPH VARIABLES')
 1108 FORMAT(1X,9X,'X',6X,'Y')
 1109 FORMAT(1X,I10,F10.2)
 1110 FORMAT(1X,F10.4,1X,F7.3,F7.3,F7.3,F7.3,F7.3,F7.3,F7.3,F7.3)
 1111 FORMAT(1X,'PAR.:TS#,N1,N2,NF,TSET#,MAX,LG1,LG2,CTK,CTS,LIM')
 1112 FORMAT(1X,F8.2,F8.2,F12.4,F10.2,F12.5)
 1120 FORMAT(1X,'NO. OF TESTS (1-27):')
 1121 FORMAT(1X,'EXPONENT PAR.:N1(1),N2(11),NF(10):')
 1122 FORMAT(1X,'FIRST AND LAST TEST NO. IN A SET NO.:',I4)
 1123 FORMAT(1X,'NO. OF MATRIXES TO PRINT (0-LIM.):')
 1124 FORMAT(1X,'FIRST AND LAST TEST: J1, J2:')
 1125 FORMAT(1X,'ITERATION COEFFICIENTS, CTK(1-4.0),CTS(1-4.0):')
 1126 FORMAT(1X,'MAX. NO. OF MATRIXES TO COMPUTE (1-20):')
 1127 FORMAT(1X,F8.2,F10.2,F12.5)
 1128 FORMAT(1X,'TEST NO.',F4.0)
 1129 FORMAT(1X,'EXPONENT   Y(0)    EP')
 1130 FORMAT(1X,I6)
 1131 FORMAT(1X,'WRITE SET ID,(1-MONOD,2-LINEAR,3-MGRAPH,4-LGRAPH)',I6)
 1132 FORMAT(1X,'EXPONENT    K      KS      EP')
 1133 FORMAT(1X,'NO. OF RUNS(1-3):',I4)
 1134 FORMAT(1X,3H)
 1140 FORMAT(1X,I4.0,F8.2,F8.2,F12.6,F12.5)
 1141 FORMAT(1X,F8.2,F12.6,F12.5)
 1142 FORMAT(1X,'TEST   EXP.   Y(0)     K       EP')
 1143 FORMAT(1X,'EXPONENT     K       E')
 1144 FORMAT(1X,'AM NO.   Y(0)     K       KS       EP')
 1145 FORMAT(1X,I4,F10.2,F12.4,F10.2,F12.5)
 1146 FORMAT(1X,'AM NO.    K       KS       E')
 1147 FORMAT(1X,I4,F12.4,F10.2,F12.5)
 1148 FORMAT(1X,'AM NO.   Y(0)     K       EP')
 1149 FORMAT(1X,I4,F10.2,F12.6,F12.5)
 1150 FORMAT(1X,'AM NO.    K       E')
 1151 FORMAT(1X,I4,F12.6,F12.5)
 1160 FORMAT(1X,F6.3)
 1161 FORMAT(1X,'NO. OF PARAMETERS IN EQUATION')
      END
C
C
      SUBROUTINE FCN(N,X,Y,YPRIME)
      INTEGER N,J
      REAL Y(N),YPRIME(N),X,EXP,BK,BS
      COMMON D(40,27),EXP,BK,BS,JT,J,JF
C
       IF (JF.EQ.1) THEN
      YPRIME(1)=(Y(1)*BK/1440*D(25,JT)**EXP)/(Y(1)+BS)*(-1)
       ELSE
      YPRIME(1)=(Y(1)*BK/1440*D(25,J)**EXP)/(Y(1)+BS)*(-1)
       END IF
C
      RETURN
      END
C
C
      SUBROUTINE FCNJ(N,X,Y,PD)
      INTEGER N
      REAL Y(N),PD(N,N),X
      RETURN
      END
```

APPENDIX D The best fitting kinetic coefficients for individual tests.

D.1 Modified Monod Equation

Kinetic coefficients and fitting error (EJ) for each individual test, were computed for the following parameters of the initial DA; k from 100 to 24000 mg/L/d, and K_s from 5 to 1400 mg/L; NK, NKS, SK, SKS were equal to 22, 16, 4.5 and 3.5 respectively. Values of those coefficients were obtained based on trial runs on experimental data. Results are presented in Tables D1-D3.

Table D.1 Kinetic coefficients and fitting error from individual tests in set 2X (Monod equation, n = 0)

Test	S_c	k^*	K_s	EJ
#	mg/L	mg/L/d	mg/L	mg/L
1	843	8509	411	21.41
2	385	17620	1916	15.54
3	212	32931	1828	14.99
10	654	4928	157	23.58
11	303	30675	1518	10.76
12	151	28308	1257	4.79
19	801	8158	315	18.29
20	423	18957	695	10.46
21	229	6571	174	9.79

$^*k = k_a X_a / X_v^n$, for $n = 0$ $k = k_a X_a$.

Table D.2 Kinetic coefficients and fitting error from individual tests in set X (Monod equation, n = 0)

Test	S_c	k^*	K_s	EJ
#	mg/L	mg/L/d	mg/L	mg/L
4	933	7956	1823	29.57
5	486	3862	296	4.71
6	256	5454	159	0.04
13	775	3089	27	17.53
14	365	6376	264	5.81
15	157	2813	70	11.63
22	742	3891	107	14.56
23	433	4130	94	7.30
24	234	3205	57	0.21

Table D.3 Kinetic coefficients and fitting error from individual tests in set X/2 (Monod equation, n = 0)

Test	S_o	k^*	K_s	EJ
#	mg/L	mg/L/d	mg/L	mg/L
7	1062	3622	919	21.82
8	546	2156	49	9.93
9	270	6686	16	0.08
16	769	1626	0.00	31.00
17	433	2386	127	8.41
18	222	1739	2.3	5.46
25	765	1821	28	9.83
26	386	1628	31	10.66
27	241	1779	29	11.45

D.2 Modified Linear Equation

Kinetic coefficients and estimation error (EJ) for each individual test were computed for the following parameters of the initial DA; k from 0 to 144 L/mg/d, (for n = 0), NK and SK, equal to 11 and 1 respectively. The range of coefficient k was determined experimentally, and adjusted to cover all observed ranges of r_s in substrate utilization tests conducted in this study. Results are presented in Tables D4-D6.

Table D.4 Kinetic coefficients and fitting error tests 1-9 (modified linear equation, n = 0)

Test	S_o	k	EJ
#	mg/L	L/mg/d	mg/L
1	872	10.361	32.43
2	389	8.377	11.96
3	213	16.916	11.92
4	940	3.321	20.36
5	496	7.102	14.19
6	257	19.037	6.68
7	1066	2.178	19.40
8	568	6.414	39.22
9	277	42.817	17.07

Table D.5 Kinetic coefficients and fitting error tests 10-18 (modified linear equation, n = 0)

Test	S_o	k	EJ
#	mg/L	L/mg/d	mg/L
10	685	10.395	34.33
11	305	18.528	9.03
12	151	21.407	4.21
13	827	7.528	50.48
14	373	14.352	10.67
15	158	19.202	11.47
16	787	3.348	50.15
17	451	6.829	19.73
18	262	17.999	18.08

Table D.6 Kinetic coefficients and fitting error tests 19-27 (modified linear equation, n = 0)

Test	S_c	k	EJ
#	mg/L	L/mg/d	mg/L
19	831	11.806	31.55
20	426	21.529	10.56
21	232	22.834	9.47
22	779	9.281	35.03
23	449	16.137	14.89
24	238	22.611	7.75
25	789	3.721	27.44
26	408	8.215	21.62
27	249	15.009	14.72

APPENDIX E Computations for individual tests and sets of tests (SR1 and SR2 sets).

E.1 Modified Monod Equation, Computations for Individual Tests for SR1 and SR2

Table E.1 Kinetic coefficients and fitting error for SR1 set, tests from 2X set (modified Monod equation, n = 0)

Test	S_o	$k_{(1)}$	$K_{S(1)}$	EJ
#	mg/L	mg/L/d	mg/L	mg/L
1	844	8531	414	21.42
2	398	21470	1580	8.98
3	212	2567	10	0.13
10	653	4483	109	23.23
11	304	30649	1517	10.76
12	151	28304	1259	4.78
19	802	8171	316	18.28
20	424	19382	715	10.47
21	229	6671	179	9.80

Table E.2 Kinetic coefficients and fitting error for SR1 set, tests from X set (modified Monod equation, n = 0)

Test	S_o	$k_{(1)}$	$K_{S(1)}$	EJ
#	mg/L	mg/L/d	mg/L	mg/L
4	949	3869	153	13.03
5	484	2358	58	2.87
6	256	2750	9	0.07
13	776	3091	28	17.52
14	366	6410	266	5.80
15	157	2817	71	11.63
22	742	3889	108	14.56
23	434	4150	95	7.31
24	235	3254	59	0.23

Table E.3 Kinetic coefficients and fitting error for SR1 set, tests from X/2 set (modified Monod equation, n = 0)

Test	S_o	$k_{(1)}$	$K_{S(1)}$	EJ
#	mg/L	mg/L/d	mg/L	mg/L
7	1055	1592	0.01	23.05
8	544	1861	0.01	7.22
16	769	1626	0.01	31.00
17	431	2031	67	9.55
18	353	28901	1039	16.58
25	766	1735	0.01	9.30
26	387	1628	32	10.65
27	242	1790	29	11.44

Table E.4 Kinetic coefficients and fitting error for tests for SR2 set, tests 1-9 (modified Monod equation, n = 0)

Test	S_c	$k_{(2)}$	$K_{s(2)}$	EJ
#	[mg/L]	[mg/L/d]	[mg/L]	[mg/L]
1	845	20029	2008	15.79
2	376	14368	2008	20.53
3	207	27498	2009	16.43
4	930	7242	1902	28.78
5	487	7223	954	6.08
6	256	29468	1827	2.65
7	1060	3308	894	17.66
8	546	2352	99	9.65
9	271	16930	367	0.10

Table E.5 Kinetic coefficients and fitting error for tests for SR2 set, tests 10-18 (modified Monod equation, n = 0)

Test	S_c	$k_{(2)}$	$K_{s(2)}$	EJ
#	[mg/L]	[mg/L/d]	[mg/L]	[mg/L]
10	666	18987	1913	27.03
11	292	26752	2008	17.70
12	143	25252	2007	11.15
13	787	4644	286	19.81
14	362	24458	2008	13.10
15	155	27209	2001	11.56
16	769	1625	0.00	28.30
17	434	3319	325	7.59
18	268	27935	1771	13.33

Table E.6 Kinetic coefficients and fitting error for tests for SR2 set, tests 19-27 (modified Monod equation, n = 0)

Test	S_c	$k_{(2)}$	$K_{s(2)}$	EJ
#	[mg/L]	[mg/L/d]	[mg/L]	[mg/L]
19	797	20276	2008	20.31
20	395	24348	2009	31.06
21	220	28999	2005	19.12
22	744	13568	2007	22.49
23	416	15914	2009	23.43
24	225	17487	2009	16.77
25	765	1841	40	9.13
26	392	4577	630	12.24
27	241	15533	1989	11.31

E.2 Modified Monod Equation, Computations for 2X and X Sets of Tests (SR1 set)

Table E.7 Kinetic coefficients and fitting error for set 2X (modified Monod equation, SR1)

n	$k_{(1)}$	$K_{s(1)}$	E
	mg/L/d	mg/L	mg/L
0	6960	260	10.22
0.1	3131	249	11.06
0.2	1409	237	12.22
0.3	631.0	223	13.60
0.4	279.7	206	15.13
0.5	123.9	188	16.76
0.6	54.45	168	18.47
0.7	23.76	147	20.21
0.8	10.27	122	21.96
0.9	4.456	101	23.73
1	1.924	81	25.51

Table E.8 Kinetic coefficients and fitting error for set X (modified Monod equation, SR1)

n	$k_{(1)}$	$K_{s(1)}$	E
	mg/L/d	mg/L	mg/L
0	3613	97	8.20
0.1	1764	95	9.34
0.2	864.5	94	10.67
0.3	419.0	90	12.13
0.4	204.5	88	13.66
0.5	98.46	82	15.23
0.6	47.35	76	16.84
0.7	23.12	75	18.46
0.8	11.42	79	20.11
0.9	5.711	85	21.76
1	2.882	94	23.39

E.3 Modified Linear Equation, Computations for 2X, X and X/2 Sets (SR1 set)

Table E9 Kinetic coefficients and fitting errors for sets 2X, X, and X/2 (modified linear equation, SR1).

n	2X		X		X/2	
	k	E	k	E	k	E
	L/mg/d	mg/L	L/mg/d	mg/L	L/mg/d	mg/L
0	11.6988	16.59	9.1893	20.62	6.4162	23.70
0.1	5.3841	17.32	4.5060	20.97	3.3596	23.73
0.2	2.4762	18.31	2.2086	21.47	1.7579	23.93
0.3	1.1371	19.51	1.0824	22.12	0.9188	24.28
0.4	0.5218	20.88	0.5301	22.89	0.4794	24.78
0.5	0.2393	22.39	0.2594	23.76	0.2500	25.43
0.6	0.1100	24.01	0.1273	24.73	0.1302	26.19
0.7	0.0505	25.72	0.0625	25.78	0.0677	27.06
0.8	0.0231	27.49	0.0307	26.91	0.0351	28.01
0.9	0.0106	29.30	0.0150	28.09	0.0182	29.04
1	0.0049	31.15	0.0074	29.31	0.0095	30.13

E.4 Modified Linear Equation, Computations for Individual Tests (SR1 and SR2 set)

Table E10 Kinetic coefficients and fitting error from tests in set 2X (modified linear equation, SR1, and SR2).

Test #	SR1			SR2		
	S_e	$k_{(1)}$	$EJ_{(1)}$	S_e	$k_{(2)}$	$EJ_{(2)}$
	mg/L	L/mg/d	mg/L	mg/L	L/mg/d	mg/L
1	872	10.361	32.43	858	8.044	15.01
2	400	12.278	8.28	381	6.480	18.43
3	218	26.146	9.83	209	12.913	15.85
10	675	10.785	36.68	674	8.266	27.84
11	305	18.528	9.03	295	12.395	16.27
12	151	21.333	4.21	144	12.125	10.80
19	832	11.809	31.55	810	8.196	17.85
20	427	21.533	10.56	400	10.933	28.85
21	232	22.813	9.47	222	13.534	18.45

Table E11 Kinetic coefficients and fitting error in tests from set X (modified linear equation, SR1, and SR2).

Test #	SR1			SR2		
	S_e	$k_{(1)}$	$EJ_{(1)}$	S_e	$k_{(2)}$	$EJ_{(2)}$
	mg/L	L/mg/d	mg/L	mg/L	L/mg/d	mg/L
4	969	9.649	24.31	937	2.825	23.75
5	502	9.175	24.72	493	5.803	8.80
6	259	20.625	9.70	257	14.945	1.39
13	828	7.565	50.87	821	6.228	37.77
14	373	14.332	10.67	365	11.045	12.18
15	159	19.218	11.47	156	13.042	11.46
22	779	9.280	35.03	754	5.507	21.45
23	449	16.137	14.89	420	7.057	21.56
24	238	22.594	7.75	226	8.167	16.13

Table E12 Kinetic coefficients and fitting error from tests in set X/2 (modified linear equation, SR1, and SR2).

Test #	SR1			SR2		
	S_e	$k_{(1)}$	$EJ_{(1)}$	S_e	$k_{(2)}$	$EJ_{(2)}$
	mg/L	L/mg/d	mg/L	mg/L	L/mg/d	mg/L
7	1076	7.049	44.73	1066	1.901	18.61
8	569	7.336	46.16	566	5.420	31.94
16	791	4.963	61.10	786	2.912	47.20
17	453	7.548	23.61	447	5.662	13.96
18	224	15.119	21.64	234	12.239	15.12
25	799	6.111	43.80	787	3.203	23.95
26	408	8.215	21.62	399	5.225	13.41
27	250	15.021	14.72	242	7.240	11.23

APPENDIX F Residual substrate concentration (S_r) as 0.1S(0)

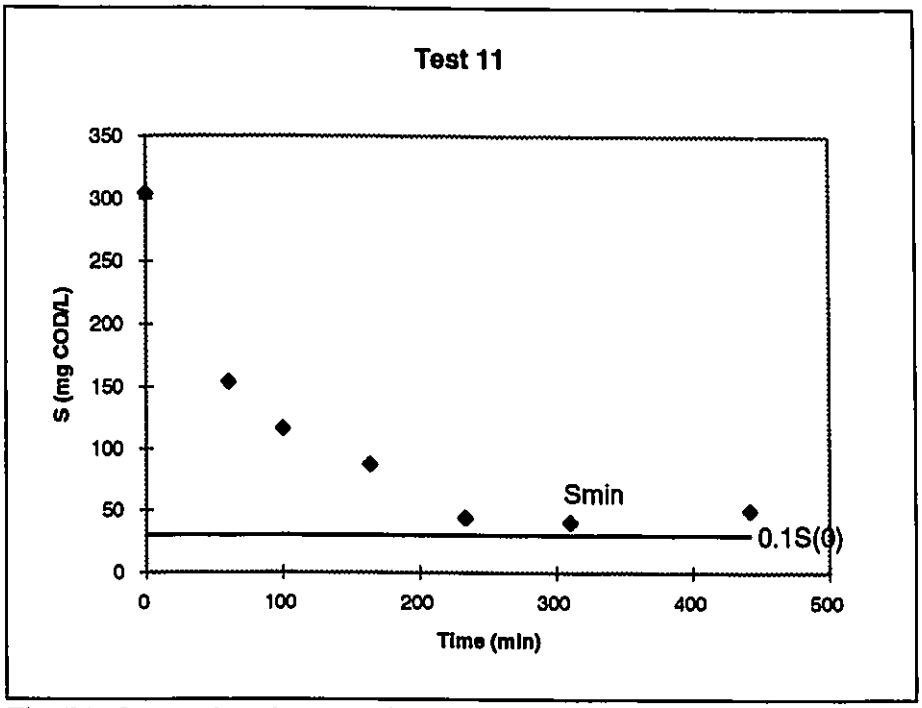


Fig. F1 Comparison between S_{min} and 0.1S(0) on the example of test 11