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Review

Kinetic Models for Anaerobic Fermentation Processes-A Review

Emmanuel Amagu Echiegu

Department of Agricultural and Bioresources Engineering, University of Nigeria, Nsukka, Nigeria

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E-mail: emmanuel.echiegu@unn.edu.ng

Abstract: A review of basic kinetic models describing the generation of biomass and utilization of substrates in anaerobic fermentation processes is presented as well as the stoichiometric and empirical models for the prediction of biogas production. The applications of these models to anaerobic reactor systems such as the CSTR, activated sludge, plug flow reactor, etc are also presented. These models are useful in the modeling of anaerobic digestion processes.

Keywords: Kinetic Models, Anaerobic Digestion, Microbial Growth, Substrate Utilization, CSTR, Plug Flow Reactors

Introduction

Anaerobic fermentation is a process which utilizes a group of anaerobic microorganisms for the stabilization of waste and biogas generation. The waste stabilization efficiency of the process is measured by the Chemical Oxygen Demand (COD) or the Volatile Solids (VS) reduction. Among other operating parameters such as temperature, loading rate, pH, etc this efficiency depends on the rate at which the microorganism is generated in the system which in turn depends on the rate of substrate utilization. A number of models have been developed to predict the performance of anaerobic reactors in terms of biomass generation rate, substrate utilization, organic solids reduction and hence waste stabilization as well as biogas production. Reviewed in the study are some of these basic models.

Microbial Growth

When a small number of viable bacterial cells are placed in a closed system containing excess nutrient supply and maintained in a suitable environmental condition, unrestricted growth of bacteria takes place. The generation time can vary from up to 80 days to less than 20 min depending on the specie. The increase in cell mass and bacterial population will continue until the nutrient is exhausted.

The growth of pure bacterial culture in a batch system measured by increased in bacterial population usually follows a pattern similar to the growth curve shown in Fig. 1. The curve is divided into six well defined phases as follows:

- Lag phase-represents the time required by the bacteria to acclimatize to the new environment. This phase is characterized by long generation time, zero growth rate and maximum rate of metabolic activity
- Acceleration phase-represents the end of adaptation period and the beginning of cell generation. It is characterized by decreasing generation time and increasing growth rate
- Exponential or logarithmic phase-characterized by minimal but constant generation time and maximum rate of substrate utilization (and biogas yield in the case of anaerobic digestion)
- Declining growth phase-occurs as a result of gradual decrease in substrate concentration as well as increased accumulation of toxic metabolites. The phase in characterized by increased generation time and decreased growth rate
- Stationary phase-in which the microbial population remains constant generally as a result of depletion of substrate, maximum physical crowding, higher concentration of toxic metabolites and/or balance between growth and death rate of biological cells
- Endogenous decay-in which death rate exceeds growth rate. The phase is characterized by endogenous metabolism and cell lysis and is usually the inverse of exponential growth phase

As noted by (Benefield and Randall, 1980), the growth cycle just described is not a basic property of the bacterial cells but rather a result of their interaction with a closed environment. In an open system such as continuous flow process, it is possible to maintain the cells in the exponential growth phase over a long period of time.

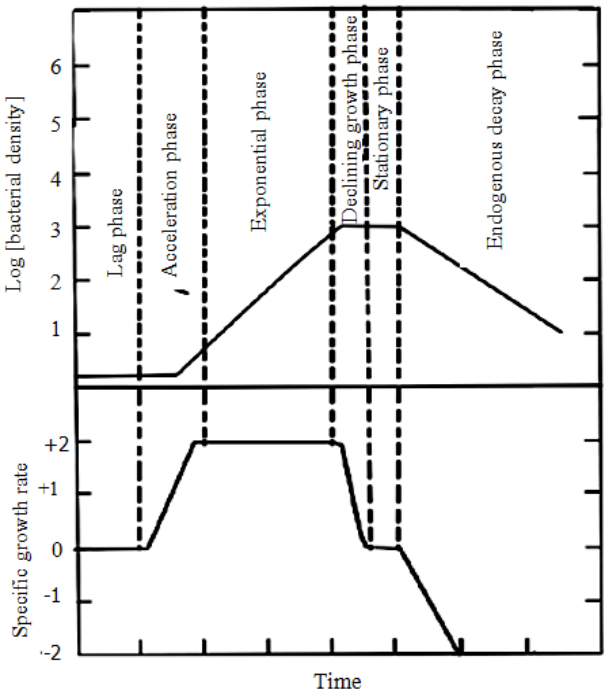

Fig. 1. Characteristic growth curve of microbial culture (Benefield and Randall, 1980)

The objective of anaerobic digestion and other waste stabilization processes from the kinetic point of view is to maintain the system in this phase.

Basic Kinetic Models for Microbial Growth and Substrate Utilization

The growth rate of a batch culture under the exponential phase is generally believed to follow the first order kinetic model i.e., the growth rate is proportional to the microbial mass in the system. Mathematically:

$$\frac{dX}{dt} = \mu X \tag{1}$$

Where:

$\frac{dX}{dt}$ = The bacterial growth rate (mg/L.s)
X = The bacterial cell concentration (mg/L) and
μ = The proportionally constant known as the Specific Growth Rate (s^{-1})

As long as there is no change in biomass composition and the food supply is not limited, the relationship holds. On the other hand, if any of the essential nutrients is present in limited quantity, it will be depleted first and growth will cease-the maximum growth rate attained being proportional to the initial concentration of the "growth limiting nutrient" in the substrate. Growth, however, does not increase indefinitely with the concentration of the growth limiting nutrient originally present in the substrate but reaches a maximum after which further increase in nutrient concentration does not result in any significant increase in growth rate. The relationship is illustrated in Fig. 2 (Grady and Lim, 1980).

A variety of empirical models describing this phenomenon has been presented. However, the models presented by (Monod, 1950; Contois, 1959) seem to enjoy the widest acceptance. These are respectively given as Equations 2 and 3:

$$\mu = \frac{\mu_m S}{K_s + S} \tag{2}$$

$$\mu = \frac{\mu_m S}{bX + S} \tag{3}$$

Where:

μ_m = The maximum specific growth rate (s^{-1})
S = The concentration of growth limiting substrate (mg/L)
K_s = The half velocity constant i.e., the substrate concentration at one half the maximum growth rate (Fig. 2) (mg/L), b kinetic parameter and X the biomass concentration in the system (mg/L). Combining Equations 1 and 2 yields:

$$\frac{dX}{dt} = \frac{\mu_m XS}{K_s + S} \tag{4}$$

Similarly, the rate of substrate utilization can be described as:

$$-\frac{dS}{dt} = \frac{kXS}{K_s + S} \tag{5}$$

where, $-\frac{dS}{dt}$ is the rate of substrate consumption (g/L.s), k maximum rate of substrate utilization (mg/L.s). Equation 5 shows that an increase in biomass concentration results in increased rate of substrate utilization. Defining *Growth Yield (Y)* as the ratio of biomass yield rate to substrate consumption rate, then:

$$Y = \frac{\left(\frac{dX}{dt}\right)}{\left(\frac{dS}{dt}\right)} \tag{6}$$

Or:

$$\frac{dX}{dt} = Y\frac{dS}{dt} \tag{7}$$

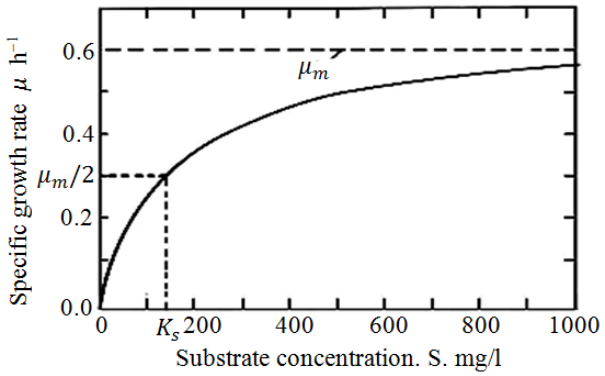

Fig. 2. Relationship between specific growth rate and concentration of growth limiting nutrient (Grady and Lim, 1980)

Expressing $\frac{dS}{dt}$ in terms of Y in Equation 6 and combining with (4) yields:

$$\frac{dS}{dt} = \frac{-\mu_m XS}{Y\left(K_s + S\right)} \tag{8}$$

which combined with Equation 5 yields:

$$k = \frac{-\mu_m}{Y} \tag{9}$$

Effects of Microbial Death and Endogenous Decay

A viable cell is one which will divide and form a colony on a favourable media. Under certain circumstances, this ability to subdivide is lost by cells. Such morbid cells can therefore not operate in the exponential phase and are committed to death. Some cells also fall prey to predators such as rotifers and protozoa. To account for the fact that a portion of the bacterial population present in a given biological system do not actually contribute to the activities therein, the effect of death, loss of viability and energy required for maintenance are often lumped together as *Endogenous Decay* with the assumption that the decrease in cell mass concentration is proportional to the biomass concentration in the system. Thus:

$$\frac{dX_d}{dt} = -k_d X \tag{10}$$

Where:

k_d = The death rate (endogenous decay) coefficient (s^{-1}) and

$\frac{dX_d}{dt}$ = The rate of decrease in cell mass concentration due to endogenous decay (mg/L.s). Thus the net bacterial growth rate is given by:

$$\frac{dX'}{dt} = \left(\mu - k_d\right)X = \left(\frac{\mu_m S}{K_s + S} - k_d\right)X = \mu' X \tag{11}$$

Where:

X' = Net cell mass concentration in the system (mg/L) and

μ' = The net specific growth rate $\left(\frac{\mu_m S}{K_s + S} - k_d\right)$ (s^{-1}).

Combining Equations 7 and 11 yields:

$$\frac{dX'}{dt} = Y\left(\frac{dS}{dt}\right) - k_d X \tag{12}$$

And substituting for $\mu_m = Y_k$ from Equation (9) in (11) gives:

$$\frac{dX'}{dt} = \left(\frac{YkS}{K_s + S} - k_d\right)X \tag{13}$$

The *Observed Yield* (net yield) may therefore be defined as:

$$Y' = \frac{\left(\frac{dX'}{dt}\right)}{\left(\frac{dS}{dt}\right)} \tag{14}$$

Effects of Temperature

Temperature affects the rate of biochemical reactions. Although many relationships have been proposed to account for the effects of temperature, the most widely accepted is the *van't Hoff's* relationship given by:

$$r_T = r_o[\theta]^{(T - T_o)} \tag{15}$$

Where:

r_T = The reaction rate (μ or k) at any given temperature T (°C)

$r_\circ$ = The reaction rate at a reference temperature T_o and

θ = The temperature activity coefficient

For most biochemical operations, the reference temperature is taken as 20°C (Metcalf and Eddy, 1978; 2003) and θ is determined as the antilog of the slope of the plot of $\log\left[\frac{r_T}{r_o}\right] vs (T - T_o)$.

The applications of the growth rate and substrate utilization models to various reactor systems are now discussed.

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Batch Reactors

Cell Mass Balance

$$\begin{bmatrix} \text{Net rate of} \\ \text{cell mass} \\ \text{accumulation} \\ \text{in the system} \end{bmatrix} = \begin{bmatrix} \text{Rate of} \\ \text{biomass} \\ \text{formation} \end{bmatrix}$$

That is:

$$\left[\frac{dX'}{dt}\right]_n V = \frac{dX'}{dt}V \tag{16}$$

where, $\left[\frac{dX'}{dt}\right]_n$ is the net rate of biomass accumulation (mg/L.s) ($=\mu' X$). Integrating between time, $t = 0$ and t:

$$\int_{X_o}^{X} \frac{dX'}{dt} = \mu' \int_0^t dt$$

Or:

$$X = X_o e^{\mu' t} \tag{17}$$

where, X_o is the initial biomass concentration at time $t = 0$ i.e., biomass concentration in the seed material (mg/L) and X is the biomass concentration in the reactor at time t from start.

Substrate Mass Balance

By methods similar to cell mass balance, the substrate concentration at time, t can be determined as:

$$S = S_o e^{-kt} \tag{18}$$

Where:

S_o = The initial substrate concentration (mg/L)

S = The substrate concentration in the reactor at time t from start (mg/L)

k = The substrate utilization rate (s^{-1}). Therefore the time required to achieve the desired effluent concentration is:

$$t = \frac{1}{k} \ln \ln \left[\frac{S_o}{S}\right] \tag{19}$$

Continued Stirred Tank Reactors (CSTR) with Simple Biomass and Substrate System

The system is shown schematically in Fig. 3 where Q is the liquid flow rate (L/s) and V is the volume of the reactor (L).

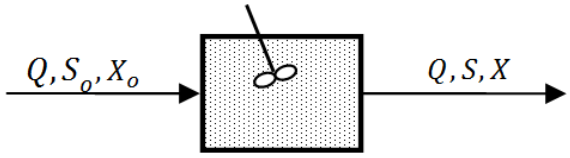

Fig. 3. Flow scheme for a CSTR

Cell Mass Balance

$$\begin{bmatrix} \text{Net rate of} \\ \text{cell mass} \\ \text{accumulation} \\ \text{in the system} \end{bmatrix} = \begin{bmatrix} \text{Inflow} \\ \text{rate} \\ \text{of} \\ \text{biomas} \end{bmatrix} - \begin{bmatrix} \text{Out } f \text{ low} \\ \text{rate} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{biomass} \\ \text{generation} \end{bmatrix}$$

That is:

$$\left[\frac{dX'}{dt}\right]_n V = QX_o - QX + \frac{dX'}{dt}V \tag{20}$$

where, X_o and X are influent and effluent cell mass concentration, respectively (mg/L) and $\left[\frac{dX'}{dt}\right]_n$ is the net rate of change of biomass concentration within the system (mg/L.s). Assuming that the influent biomass concentration is negligible and that steady state condition prevail, i.e., $\left[\frac{dX'}{dt}\right]_n = 0$ and combining Equation 11 and 20 and simplifying yields:

$$\frac{1}{\theta_h} = \frac{\mu_m' S}{K_s + S} - k_d = \mu' \tag{21}$$

Or:

$$\frac{1}{\theta_h} = \frac{YkS}{K_s + S} - k_d \tag{22}$$

where, θ_h is the hydraulic retention time = V/Q (days). Also the biological Solid Retention Time (SRT) is defined as:

$$\theta_c = \frac{X_T}{\left[\frac{dX}{dt}\right]_w} \tag{23}$$

Where:

θ_c = The solid retention time (d)

X_T = The total biomass in the system = VX (g) and

$\left[\frac{dX}{dt}\right]_w$ = The rate biomass wastage from the system = QX (g/L). Thus:

$$\theta_c = \frac{VX}{QX} = \theta_h = \frac{1}{\mu'} \tag{24}$$

Thus in a CSTR without cell mass recycle:

$$\theta_h = \theta_c \tag{25}$$

Substrate Mass Balance

$$\begin{bmatrix} Net\ rate\ of \\ substrate \\ accumulation \\ in\ the\ system \end{bmatrix} = \begin{bmatrix} Inflow \\ rate \\ of \\ substrate \end{bmatrix} - \begin{bmatrix} Out\ f\ low \\ rate \end{bmatrix} + \begin{bmatrix} Rate\ of \\ substrate \\ consumption \end{bmatrix}$$

Or:

$$\left[\frac{dS}{dt}\right]_n V = QS_o - QS + \frac{dS}{dt}V \tag{26}$$

where, S_o and S are influent and effluent substrate concentration, respectively (g/L) and $\left[\frac{dS}{dt}\right]_n$ is the net rate of change of substrate accumulation within the system (g/L.s). At steady state $\left[\frac{dS}{dt}\right]_n = 0$. Combining Equation 5 and 26, assuming steady state and simplifying yields:

$$\frac{S_o - S}{\theta_h} = \frac{kXS}{K_s + S} = \frac{dS}{dt} \tag{27}$$

Effluent Biomass and Substrate Concentration

From Equation 21:

$$\frac{S}{K_s + S} = \frac{1 + k_d\theta_h}{\mu_m\theta_h} \tag{28}$$

Substituting Equation 28 in 27 and solving for X while nothing that $\mu_m = Y_k$ yields:

$$X = \frac{Y(S_o - S)}{1 + k_d\theta_h} \tag{29}$$

Substituting for $\theta_c = \theta_h$ in Equation 22 and solving for S yields:

$$S = \frac{K_s\left[1 + k_d\theta_c\right]}{\theta_c\left(Yk - k_d\right) - 1} \tag{30}$$

Various parameters have been used to approximate biological solids concentration (X). These include: The dry weight of suspended matter present in the system i.e., total suspended solids (Thimann, 1955; Echiegu, 1992; Echiegu and Ghaly, 1993; Ghaly and Echiegu, 1993; Echiegu and Ghaly, 2014), the quantity of cellular constituents such as carbon, nitrogen and phosphorus (Agardy *et al.*, 1963; Lawrence and McCarty, 1969), DNA content (Agardy *et al.*, 1963), ATP content (Holm-Hansen and Both, 1966) and number of living cells per unit volume. However the most widely accepted parameter for the approximation of active biomass concentration is Volatile Suspended Solids (VSS) (Stewart, 1958; Andrew *et al.*, 1964; Lawrence and McCarty, 1969; Toerien *et al.*, 1967; Metcalf and Eddy, 1978; 2003) as the use of most of the other parameters has some inherent problems (Preterious, 1969).

Substrate concentration is usually measured as total dissolved solids, BOD or COD. Where any particular nutrient is considered as rate-limiting and is being investigated, its concentration can also be used as the limiting substrate concentration *S.* Generally, however, for anaerobic digestion of animal waste, COD is used as an estimate of the substrate content of the feedstock.

Other Design Parameters

Although the effluent solids and substrate concentrations can be determined from Equation 29 and 30 respectively, the kinetic constants are often difficult to determine. This fact has led to the development of other more useful parameters.

Specific Substrate Utilization (U)

This is defined as the amount of substrate utilized by a given quantity of microbial cells per given time, i.e.,:

$$U = \frac{\left(\frac{dS}{dt}\right)}{X} = \frac{S_o - S}{X\theta_c} \tag{31}$$

Dividing Equation 12 by X and using the definition of θ_c and U from Equation 23 and 31, respectively yields:

$$\frac{1}{\theta_c} = YU - k_d \tag{32}$$

Substituting for $\frac{dS}{dt} = UX$ from (31) and $\frac{dX'}{dt}$ from (12) in (14) and rearranging yields:

$$Y' = \frac{YU - k_d}{U} \tag{33}$$

and substituting for U from Equation (32) in (33) yields:

$$Y' = \frac{Y}{1 + \theta_c k_d} \tag{34}$$

Equating 21 and 32 and solving for S while nothing that $\mu_m = Y_k$ gives:

$$S = \frac{UK_s}{k - U} \tag{35}$$

Food to Micro-Organism (F/M) Ratio

This is defined as:

$$F/M = \frac{S_o}{\theta_h X} \tag{36}$$

Efficiency of the Process (η)

This is defined as:

$$\eta = \frac{100(S_o - S)}{S_o} \tag{37}$$

Combining (36) and (37) with (31) gives:

$$U = \frac{\eta(F/M)}{100} \tag{38}$$

Efficiency is a function of the microbial cell population in and the SRT of the system. The relationship between efficiency (η) and SRT (θ_c) is shown in Fig. 4. The figure indicates that for any given substrate and operating conditions, there exist an optimum retention time beyond which little added benefit in treatment efficiency is obtained. At higher SRT, the effect of temperature becomes negligible (Parkin and Owen, 1986). The effect of SRT on temperature and treatment efficiency is shown in Fig. 5.

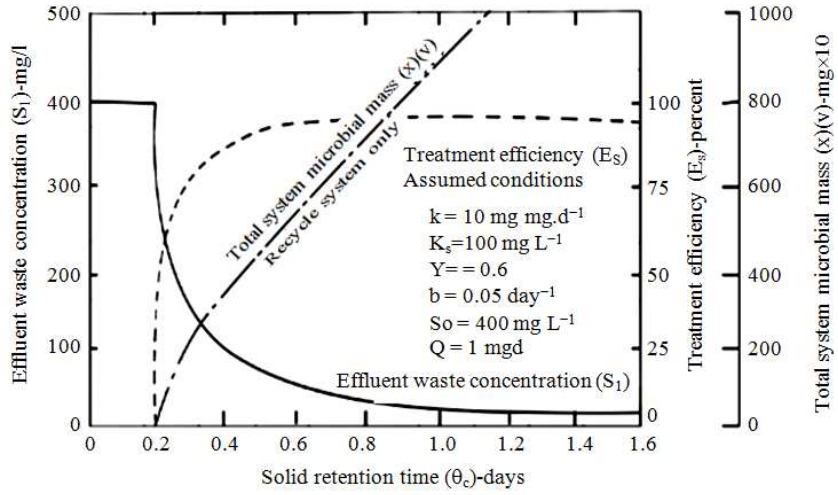

Fig. 4. Steady-state relationship between specific treatment efficiency, effluent substrate concentration, total biomass concentration and SRT (Lawrence and McCarty, 1969)

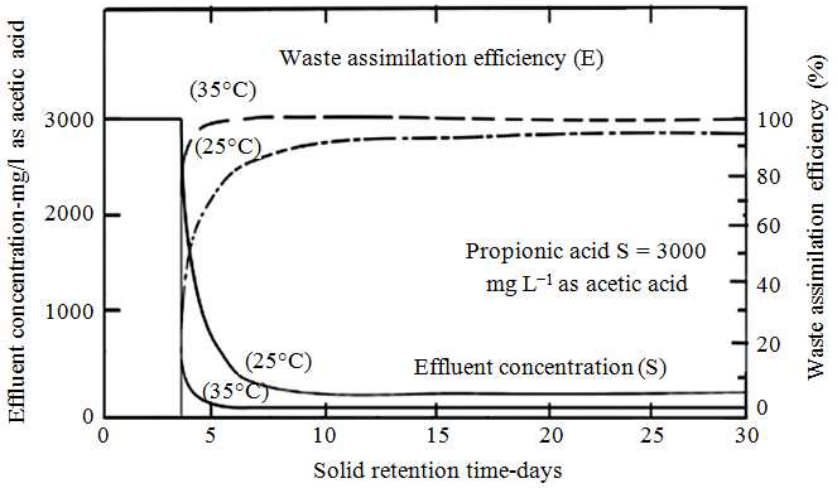

Fig. 5. Effect of SRT on temperature and steady-state treatment efficiency (Lawrence and McCarty, 1969)

Determination of Kinetic Parameters

Dividing Equation 27 by X, taking the inverse and linearizing while noting that for a CSTR $\theta_c \cong \theta_h$ yields:

$$\frac{X\theta_h}{S_o - S} = \frac{1}{U} = \left(\frac{K_s}{k}\right)\left(\frac{1}{S}\right) + \frac{1}{k} \tag{39}$$

By conducting a laboratory experiment on a waste sample of known substrate (COD) concentration (S_o), determining the effluent substrate (S) and biomass (X) concentrations for various retention times (θ_h) and carrying out a plot of ($1/U$) Vs ($1/S$), the maximum substrate utilization rate (k) is determined as the reciprocal of the intercept of the plot while the half velocity constant (K_s) is determined as the product of k and the slope of the plot (Fig. 6).

Also by plotting ($1/\theta_h$) Vs U (Equation 32), the growth yield (Y) is determined as the slope while the endogenous decay coefficient (k_d) is determined as the intercept of the plot (Fig. 6). Values of kinetic constants for simple substrates as compiled by Mossey (1983) are shown in Table 1.

Concept of Microbial Washout and Safety Factor

At a detention time equal to or less than the minimum detention time, the influent and effluent substrate concentrations are equal. Thus from Equation 22:

$$\theta_c^{\min} = \left[\frac{YkS_o}{K_s + S_o} - k_d\right]^{-1} \tag{40}$$

and where $K_s << S_o$:

$$\theta_c^{\lim} = \left[Yk - k_d\right]^{-1} \tag{41}$$

Where:

$\theta_c^{\min}$ = Minimum solid retention time (days)

$\theta_c^{\lim}$ = The limiting SRT (i.e., bacterial generation time)

If a particular treatment efficiency (η) is desired, the appropriate detention time to use is given by:

$$\theta_c^d = \left[\frac{Yk(1-\eta)S_o}{K_s + (1-E)S_o} - k_d\right]^{-1} \tag{42}$$

Where:

θ_c^d = The design detention time and

η = The desired treatment efficiency (decimal)

The ratio of deign to minimum detention time equals the Safety Factor (SF), i.e.,:

$$SF = \frac{\theta_c^d}{\theta_c^{\min}} \tag{43}$$

and ranges from 2.5 to 10 (Lawrence and McCarty, 1970; Lawrence, 1971).

Table 1. Values of kinetic constants[a]

Substrate	Temp (°C)	Y (mg/mg.d)	K (mg/mg.d)	K_s (mg/L)	K_d (d^{-1})
Acetate	35	0.040	8.10	154	0.019
	30	0.054	4.80	333	0.037
	25	0.050	4.70	869	0.011
Propionate	35	0.042	9.60	32	0.010
	25	0.051	9.80	613	0.040
Butyrate	35	0.047	15.60	5	0.027
Long chain	35	0.120	6.67	680	0.015
fatty acid	25	0.120	4.65	1270	0.015
	20	0.120	3.85	1580	0.015
Glucose	37	0.173	30.00	23	0.800

[a]Mossey (1983)

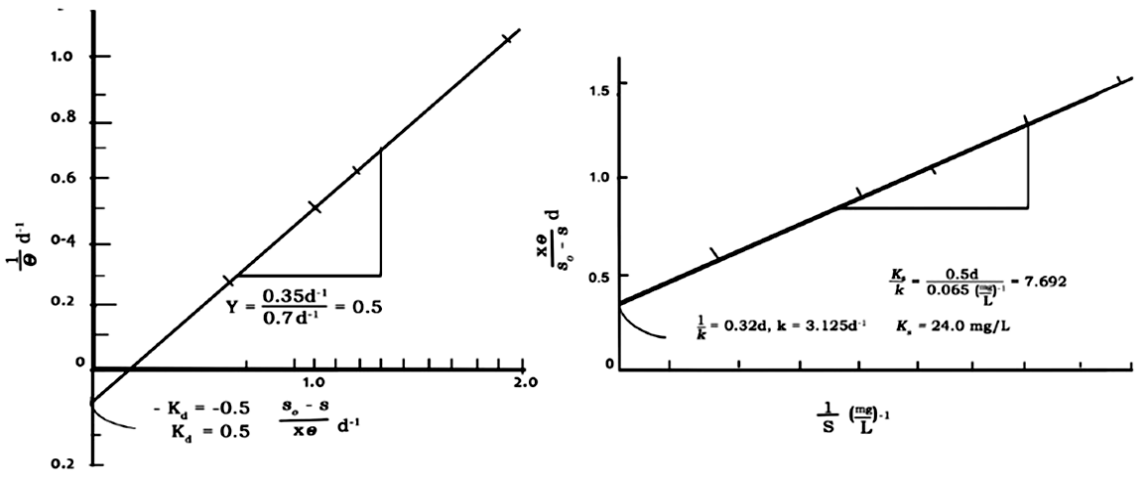

Fig. 6. Determination of kinetic parameters (Metcalf and Eddy, 1978)

Anaerobic Contact Process

The anaerobic contact reactor is shown schematically in Fig. 7. Referring to the figure, Let:

Q = Influent flow rate of substrate into the reactor (m^3/d)
S_o = Reactor influent substrate concentration (kg/m^3)
X_o = Reactor influent biomass concentration (kg/m^3)
S_1 = Effluent (or biomass separator influent) substrate concentration (kg/m^3)
X_1 = Effluent (or biomass separator influent) biomass concentration (kg/m^3)
q_r = Flow rate of recycle liquid (m^3/d)
X_r = Biomass concentration of recycle solids (kg/m^3)
q_w = Wastage rate from the recycle line (m^3/d) and
X = Final effluent biomass concentration (kg/m^3)

Therefore the effluent flow rate from the reactor equals (Q+q_r) which in turn equals the influent flow rate into the separator. The effluent flow rate from the separator equals (Q–q_w) assuming there is no substrate utilization in the separator, the influent substrate concentration into the separator (S_i) equals the effluent concentration from the separator (S) which in turn equals the substrate concentration in the recycle line and from the definition of SRT:

$$\theta_c = \frac{Total\ cell\ mass\ content\ of\ the\ reactor}{rate\ of\ cell\ mass\ wastage\ from\ the\ reactor} \tag{44}$$

That is:

$$\theta_c = \frac{VX_1}{(Q-q_w)X + q_w X_r} \tag{44a}$$

Cell Mass Balance

Accumulation=Inflow-Outflow+Net growth.
That is:

$$V\left[\frac{dX'}{dt}\right]_n = QX_o - \left[q_w X_r + (Q-q_w)X\right] + V\frac{dX'}{dt} \tag{45}$$

At steady state and assuming no cell concentration in the influent:

$$V\frac{dX'}{dt} = q_w X_r + (Q-q_w)X \tag{46}$$

Substituting for $\frac{dX'}{dt}$ from (13) and simplifying yields:

$$\frac{YKS_1}{K_s + S_1} - k_d = \frac{q_w X_r + (Q-q_w)X}{VX_1} = \frac{1}{\theta_c} \tag{47}$$

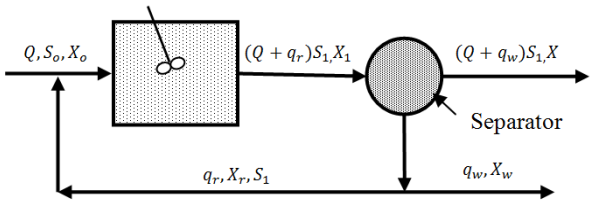

Fig. 7. Flow scheme of anaerobic contact process

which is the same as for CSTR.

Also carrying out the mass balance about the reactor alone at steady state yields:

$$QX_o + q_r X_r + V\frac{dX'}{dt} - (Q-q_r)X_1 = 0 \tag{48}$$

Assuming that there are no biological cells in the influent and substituting values for $\frac{dX'}{dt}$ and simplifying yields:

$$\frac{1}{\theta_c} = \frac{1}{\theta_h}\left[1 + r - r\left(\frac{X_r}{X_1}\right)\right] \tag{49}$$

where, θ_h is V/T equals to the HRT and r equals q_r/Q equals to the recycle ratio. Equation 49 shows that the SRT is a function of the ratio $\left(\frac{X_r}{X_1}\right)$ which in turn is a function of the settling characteristics of the biomass and the efficiency of the biomass separation unit. At a separation efficiency of approximately 100%, the maximum solid concentration in the recycle line is given by:

$$(X_r)^{\max} = \frac{10^6}{SVI} \tag{50}$$

where, SVI is sludge volume index. Note also that is a function of the recycle ratio which implies that SRT can be controlled by controlling wastage of biomass (i.e., varying q_w) from the system.

Substrate Mass Balance

Substrate mass balance about the reactor alone yields (in word) Accumulation=Inflow+Recycle-Outflow-Consumption.

Or mathematically:

$$V\left[\frac{dS_1}{dt}\right]_n = QS_o + q_r S_1 - (Q+q_r)S_1 - V\frac{dS_1}{dt} \tag{51}$$

Substituting for $\left[\frac{dS_1}{dt}\right]$ from (5) at steady state and simplifying yields:

$$\frac{KX_1S_1}{K_s+S_1}=\frac{S_o-S_1}{\theta_h} \tag{52}$$

Effluent Biomass and Substrate Concentration

Substituting for $\frac{KS_1}{K_s+S_1}$ from Equation 47 in 52 and solving for X_1 yields:

$$X_1=\frac{Y\theta_c(S_o-S_1)}{\theta_h(1+\theta_c k_d)} \tag{53}$$

The final effluent biomass concentration is determined by solving for X in Equation 47, i.e.,:

$$X=\frac{(\theta_h-\theta_c wC)X_1}{\theta_c(1-w)} \tag{54}$$

where, $w=\frac{q_w}{Q}$ is the wastage ratio and $C=\frac{X_r}{X_i}$ and the final effluent substrate concentration is got by solving for S_1 in Equation 47, i.e.,:

$$S_1=\frac{K_s(1+\theta_c k_d)}{\theta_c(Yk-k_d)-1} \tag{55}$$

which is the same for a CSTR. The minimum and design detention time can also be determined as for a CSTR (Equations 40 and 42).

Plug Flow Reactors

Plug Flow Reactor with Simple Substrate and Microbe System

Plug flow reactor models assumes that there is no lateral dispersion. i.e., biomass and substrate concentration at any given cross-section is constant. However, there is both a biomass and substrate concentration gradient along a time and hence along the length axis of the reactor. Thus substrate concentration decreases while biomass concentration increases as the waste moves along the length of the reactor from the influent to the effluent end.

Lawrence and McCarty (1970) have pointed out that because of interdependence between substrate removal and microbial growth, it is not possible to obtain explicit analytical solution for the system. They however noted, as operated in practice, there is usually very little difference between influent and effluent biomass concentration of the reactor and suggested the use of average value for biological cell concentration $\left(\bar{X}\right)$ within the reactor to simplify the analysis. (This assumption is most valid in a reactor with $\frac{\theta_c}{\theta_h}>5.0$).

Microbial Cell Mass Balance

Consider an elemental volume of reactor (*dV*) of length (*dL*) (Fig. 8) Accumulation=Inflow-Outflow+Generation.

Referring to Fig. 8:

$$dV\frac{d}{dt}\left[\frac{\left(\bar{X}-\frac{\partial\bar{X}}{\partial L}dL\right)+\bar{X}}{2}\right]$$
$$=Q\left[\bar{X}-\frac{\partial\bar{X}}{\partial L}dL\right]-Q\bar{X}+dV\mu'\left[\frac{\left(\bar{X}-\frac{\partial\bar{X}}{\partial L}dL\right)+\bar{X}}{2}\right]a \tag{56}$$

Assuming steady state, neglecting second order terms and simplifying yields:

$$v\frac{d\bar{X}}{dt}=\frac{d\bar{X}}{dt}-\mu'\bar{X} \tag{57}$$

where, ν is the velocity. The elemental volume under consideration is analogous to a CSTR moving along a time axis. Therefore combining Equation 12 and 21 with (57) and substituting for $\frac{dS_1}{dt}=\frac{S_o-S_1}{\theta_h}$ gives:

$$\frac{Y\left(S_o-S_1\right)}{\theta_h\bar{X}}-k_d=\frac{1}{\theta_c} \tag{58}$$

Substrate Mass Balance

Substrate balance about the element of the reactor of volume *dV*:

$$dV\frac{d}{dt}\left[\frac{S+\left(S-\frac{\partial S}{\partial L}dL\right)}{2}\right]$$
$$=QS+Q\left[S-\frac{\partial S}{\partial L}dL\right]-KdV\left[\frac{S+\left(S-\frac{\partial S}{\partial L}dL\right)}{2}\right] \tag{59}$$

where, *K* is substrate utilization coefficient (compare with μ'). Substituting for $K=\frac{k\bar{X}}{K_s+S}$, assuming steady state, neglecting second order terms and integrating gives:

$$K_s\ln\left(\frac{S_o}{S}\right)+\left(S_o-S_1\right)=\frac{L}{v}=k\bar{X}\theta_h \tag{60}$$

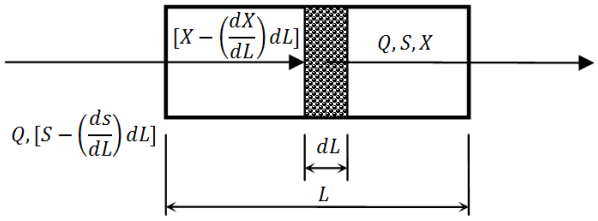

Fig. 8. Definition sketch for plug flow reactor

where, L is length of reactor and v flow velocity. Substituting for (S_o-S_1) from Equation 58 in 60 and solving for $\bar{X}$ yields:

$$X_1 = \frac{YK_s\theta_c(\ln\ln S_o - \ln\ln S)}{\theta_h(Yk - k_d) - 1} \tag{61}$$

And solving for $\bar{X}\theta_h$ from Equation 60 and substituting in (58) yields:

$$\frac{1}{\theta_c} = \frac{YK(S_o - S_1)}{K_s \ln\ln\left(\frac{S_o}{S}\right) + (S_o - S_1)} - k_d \tag{62}$$

Equation 61 and 62 give effluent biomass concentration and retention time respectively. The effluent substrate concentration can be calculated from:

$$S = S_o e^{-k\theta_h} \tag{63}$$

which is obtained from direct integration of Equation 59 without substituting for the value of $K = \frac{k\bar{X}}{K_s + S}$. K can be obtained experimentally in the laboratory.

Plug Flow with Recycle

The microbial mass balance around the entire system (Fig. 9) is similar to the anaerobic contact process except that the cell mass concentration in the reactor is replaced by the average biomass concentration $(\bar{X})$ as suggested by Lawrence and McCarty (1970). The resultant equation is identical to Equation 58, i.e.,:

$$\frac{1}{\theta_c} = \frac{YQ(S_o - S_1)}{\bar{X}V} - k_d \tag{64}$$

Also carrying out substrate mass balance similar to that of plug flow without recycle results, after integrating and simplifying, to:

$$K_s \ln\left(\frac{S_o}{S}\right) + (S_i - S_1) = k\bar{X}\theta_h \tag{65}$$

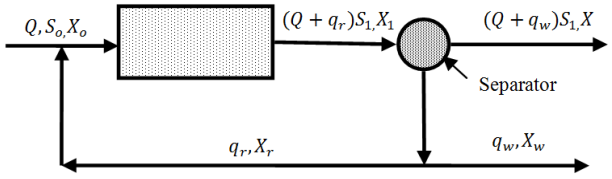

Fig. 9. Schematics of plug flow reactor with recycle

where, S_i is the substrate concentration after mixing the influent substrate stream with the recycle stream, i.e., $S_i = \frac{QS_o + q_rS_1}{Q + q_r}$ and $\theta_h = \frac{V}{Q + q_r}$.

Substituting the values of θ_h and S_i in Equation 65, solving for $\bar{X}V$ and substituting in (64) gives:

$$\frac{1}{\theta_c} = \frac{Yk(S_o - S_1)}{(S_o - S_1) + (1+r)K_s \ln K_s \ln\left[\frac{(rS_1 + S_o)}{(1+r)S_1}\right]} - k_d \tag{66}$$

$$\lim_{(r\to 0)} (1+r)\ln\left[\frac{(rS_1 + S_o)}{(1+r)S_1}\right] = \ln\left[\frac{S_o}{S_1}\right] \tag{66a}$$

The approximation is usually sufficient when $r < 1.0$ (Lawrence and McCarty, 1970). When this applies, Equation 66 reduces to (61).

Also substituting for $\theta_h = \frac{V}{Q + q_r}$ in (64) and (65) and for (S_o-S_1) from (64) and S_i in (65) and solving for $\bar{X}$ yields:

$$\bar{X} = \frac{Y\theta_c(1+r)K_s \ln\left[\frac{(rS_1 + S_o)}{(1+r)S_1}\right]}{\theta_h\left[\theta_c(Yk - k_d) - 1\right]} \tag{67}$$

Plug Flow with Dispersion

Plug flow as assumed in the analysis of CSTR and piston flow as assumed in that of plug flow are ideal situation which are seldom observed in practice. In real situations, intermediate amount of mixing generally occur. To account for such effects, Wehner and Wilhem (1956) proposed a dispersion model which approaches complete mixing when the degree of dispersion approaches infinity and converts to plug flow where there is no dispersion. The model is given in Equation 68:

$$\frac{S_o}{S} = \frac{4ae^{\left(\frac{1}{2}d\right)}}{(1+a)^2 e^{\left(\frac{a}{2}d\right)} - (1-a)^2 e^{\left(-\frac{a}{2}d\right)}} \tag{68}$$

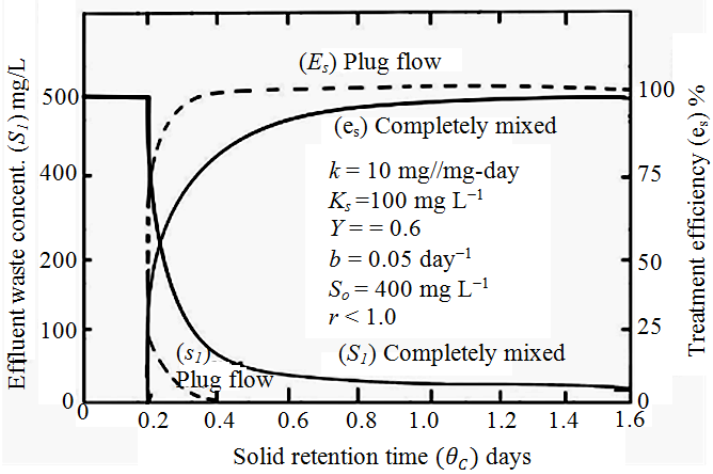

Fig. 10. Comparison of steady-state treatment efficiency and effluent substrate concentration of a plug flow reactor and a CSTR (Lawrence and McCarty, 1970)

where, $a = (1 + 4K\theta_h d)^2$; $d = \frac{D}{vL} = \frac{D\theta_h}{L^2}$ = dispersion factor ; D is the axial dispersion coefficient (m^2/s); v is the fluid velocity (m/s); L is the characteristic length of travel of path of typical particle in the reactor (m) and K is the substrate utilization coefficient (s^{-1}). The second term in Equation 68 is small and when neglected an approximate form of (68) is:

$$\frac{S_o}{S} = \frac{4ae^{\left[\frac{(1-a)}{2}d\right]}}{(1+a)^2} \text{ valid for d} \le 2 \qquad (69)$$

Comparison of Plug Flow with CSTR

Although both the plug flow and the CSTR may have the same minimum SRT for a given waste sample, true plug flow are generally more efficient than the complete mix system (Lawrence and McCarty, 1970; Metcalf and Eddy, 1978). This is illustrated in Fig. 10. However plug flow reactors have the disadvantage of being less stable under toxic or shock load conditions as such loads are concentrated at one end and not dispersed immediately as in complete mix systems. Furthermore there is a considerable evidence to indicate that in practice, true plug flow conditions do not actually occur as there is always a high degree of back-mixing in the system. The net result is that, in actual practice, the difference between the two systems are usually not significant so that the equations for CSTR may be applied to plug flow reactor with only a conservative result being yielded.

Kinetics of Digestion of Complex Wastes

The kinetic relationships so far developed refer to anaerobic digestion of simple substrates involving single microbe specie. Where complex wastes such as animal manure are involved, the rate-limiting models developed by (O'Rourke, 1968) and described in detail by (McCarty, 1964) are generally employed. O'Rourke (1968) working with primary sludge consisting essentially of fatty acids (lipids), propionic acid acetic acids found that the anaerobic digestion kinetics of complex wastes could be described by the kinetics of the breakdown of the individual components of the waste with the resultant effluent a contribution from the decomposition of the various components.

The values of the kinetic parameters Y, k and k_d (measured in terms of mg/L COD) for the conversion of the various short chain volatile acids to methane have been found to be essentially equal at a given temperature (O'Rourke, 1968) and for different wastes, the parameters also do not vary to a significant extent for most engineering purposes (Lawrence and McCarty, 1970). The half velocity coefficient K_s however do vary over a wide range of different substrates. It also varies with substrate concentration and together with k, the maximum substrate utilization rate, it varies with temperature (O'Rourke, 1968; Lawrence and McCarty, 1969; Lawrence, 1971). When it is assumed that Y, k and k_d are equal for all short chain acids of concern, the kinetic relationships already developed for simple substrates may be adapted for complex wastes by replacing K_s by:

$$K_s = \sum_{i=1}^{n} K_{s_i} \qquad (70)$$

where, K_{si} is the K_s for component i and n is the number of components.

Thus the effluent substrate concentration of a CSTR without recycle S_o, for example, will be given by:

$$S_c = \frac{k_L(1+k_d\theta_c)}{\theta_c(Yk-k_d)-1} \quad (71)$$

K_s value at any given temperature can be determined with reference to a known temperature by using the formula developed for acetic acid by (Lawrence and McCarty, 1969), i.e.,:

$$\log\left[\frac{K_{s_2}}{K_{s_1}}\right] = 6980\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \quad (72)$$

where, K_s is the half velocity coefficient at temperature T_i.

Flocculent Bed and Fixed Film Reactors

These include the Up-flow Anaerobic Sludge Blanket (UASB), Down-flow Stationary Fixed Film (DSFF), Suspended Particles Attached Growth Reactors (SPAG) and the No-mix energy efficient reactors as well as the Anaerobic Filter (AF). A model developed by (Bolte and Hills, 1985) can be applied for the analysis of any of these retained biomass reactors where SRT>>HRT or where the relationship between the SRT and HRT can be precisely determined (empirically or otherwise).

A microbial mass and substrate balance about a CSTR without recycle can be expressed as:

$$\frac{dX}{dt} = \left(\mu' - \frac{1}{\theta_c}\right)X \quad (73)$$

$$\frac{dS}{dt} = \frac{S_o - S}{\theta_h} - \frac{\mu' X}{Y} \quad (74)$$

where, $\mu' = (\mu - k_d)$. Under steady state, Equation 73 and 74 reduce respectively to:

$$\mu - k_d = \frac{1}{\theta_c} \quad (75)$$

and:

$$\frac{S_o - S}{\theta_h} - \frac{\mu X}{Y} \quad (76)$$

One of the kinetic models used to describe the relationship between microbial growth and the concentration of growth-limiting substrate as has been presented earlier (Equation 3) is given by (Contois, 1959) as:

$$\mu = \frac{\mu_m S}{bX + S} \quad (77)$$

Combining (75), (76) and (77) and simplifying yields:

$$\frac{S}{S_o} = \frac{K}{\mu_m\theta_h + K - \frac{\theta_h}{\theta_c}(1+k_d\theta_h)} \quad (78)$$

where, $K = Yb$ is a dimensionless parameter. Thus it is evident that substrate removal efficiency depends on the ratio $\frac{\theta_h}{\theta_c}$. In a completely mixed reactor, $\theta_c = \theta_h$ so that (78) reduces to:

$$\frac{S}{S_o} = \frac{K}{\theta_h(\mu_m - k_d) + K - 1} \quad (79)$$

In the flocculent and attached film reactors $\theta_c >> \theta_h$ (Young and McCarty, 1968), as the SRT becomes large at short HRT (< 5 days), the ratio $\frac{\theta_h}{\theta_c}$ tends to zero so that for flocculent and attached film reactors Equation 78 reduces to:

$$\frac{S}{S_o} = \frac{K}{\mu_m\theta_h + K} \quad (80)$$

Since the assumption $\theta_c >> \theta_h$, is valid for most flocculent and attached film reactor, Equation 80 can be used to estimate the substrate removal efficiency of flocculent and attached film reactors and in any case, Equation 80 will represent the maximum performance to be expected from any flocculent or attached film process for a given vale of θ_h, μ_m and K. In the case of attached film processes, it should be noted that the model (Equation 78) removes the capability to distinguish between different media characteristics in predicting the performance of a given reactor configuration since these characteristics would be reflected in the θ_c term. If θ_c the SRT is known for a given reactor configuration, Equation 78 can be used directly to predict precisely the substrate removal efficiency. Also from the definition of efficiency (Equation 37), it can be shown by combining (37) and (80) that the efficiency (η) can be given by:

$$\eta = 100\left[1 - \left(\frac{K}{\mu_m\theta_h + K}\right)\right] \quad (81)$$

The dimensionless parameter, K have been used as an indicator of the level of inhibition present in the reactor system (Hill, 1982; Hashimoto and Robinson, 1984) with high values usually indicating high levels of inhibition. K can be determined using a CSTR to determine values for plotting the linearized form of Equation 79, i.e.,:

$$\frac{S}{S_o} = \theta_h\left(\frac{\mu_m + K}{K}\right) + \frac{K-1}{K} \quad (82)$$

The intercept equals $\frac{K-1}{K}$. The value of K for swine waste can be determined from a relationship given by (Hashimoto and Robinson, 1984), i.e.,:

$$K = 0.6 + 0.0206e^{0.051S_o} \quad (83)$$

In addition to the Bolte and Hills (1985) model presented above, the following model proposed by Metcalf and Eddy (1978) for the analysis of trickling filter can be adapted for Down-flow Stationary Fixed Film (DSFF) Reactors and anaerobic reactors operated in downward mode:

$$\frac{S}{S_o} = e^{-\left[(fhk_o)\frac{WZ}{Q}\right]} \quad (84)$$

where, f is proportionality factor (= E/S), E is effectiveness factor $0 \le E \le 1$, S is effluent substrate concentration (mg BOD/L), S_o is the overall influent substrate concentration including recycled fraction if provided (mg BOD/L), h is the thickness of slime layer (m), k_o is the maximum reaction rate (d^{-1}), WZ is the surface area of filter media (m^2) and Q the volumetric flow rate (m^3/d).

The equation was developed by carrying out a mass balance about an elemental volume of slime layer (attached film) of thickness h attached to a media surface of area WdZ. The relationship developed by (Atkinson *et al*., 1974) to describe the rate of heat flux of organic materials into the slime layer, assuming that diffusion into the slime layer controls the rate of reaction and that there is no concentration gradient across the liquid, i.e.,:

$$\frac{dS}{dt} = \frac{Ehk_o\overline{S}}{K_s + S} \quad (85)$$

Where:

$\overline{S}$ = Average BOD concentration in the bulk liquid in volume of element and

K_s = The half velocity constant

The term (fhk_o) can be condensed into a constant and determined as a slope of a plot of $log\left(\frac{S}{S_o}\right) vs \left(\frac{WZ}{Q}\right)$. Other similar models that have been proposed and which can be utilized in the analysis of DSFF reactors include that of (Eckenfelder, 2000; Bruce and Merkens, 1973) which are given respectively in Equation 86 and 87:

$$\frac{S}{S_o} = \exp-\left[KZS_a^m\left(\frac{A}{Q}\right)^n\right] \quad (86)$$

$$\frac{S}{S_o} = \exp-\left[K_T S_a^c Q_v^{-b}\right] \quad (87)$$

where, K, K_T are observed removal coefficient (m/d), S_a is specific surface area ($=A_s/V$) (m^2/m^3), A_s surface area of media (m^2), V volume of reactor (m^3), Q volumetric flow rate (m^3/d), Q_v specific volume flow rate (m^3/m^3/d), A cross-sectional area of filter (m^2) and m, n, b, c are empirical constants.

Dynamic Models

In the models so far presented, steady state conditions were assumed to simplify the set of non-linear differential equations that results from cell and substrate mass balances. The steady-state models which were before the advent of analog-digital computer simulations, however, cannot be used to predict process performance during start-up and other transient operating conditions. The Monod type models that described the relationship between growth rate and substrate utilization also implies growth rate continues to increase asymptotically with increase in substrate concentration. It has long been known that as the substrate increases beyond certain level, substrate inhibition sets in. Monod type models cannot therefore predict the inhibitory effects of high levels of substrate concentration. Dynamic models, on the other hand, can be used to make such predictions.

Quite a good number of models have been proposed to account for inhibition due to various parameters. Mossey (1983) suggested the introduction of a factor, I (known as pH inhibition factor) into the Monod model to account for the effects of extremes of pH. The proposed model is shown in Equation 88:

$$\frac{dS}{dt} = \frac{KIXS}{K_s + S} \quad (88)$$

where, I is the pH inhibition factor which takes the value of 1.0 at the optimum pH range of 6-8 and progressively reduces to 0.1 at pH range of 8-9.5 or falls from 6 to 4.5 to account for the fact that the rate of bacterial metabolism decreases to 1/10 of its normal value at these pH extremes.

Mossey (1983) also suggested the modeling of bactericidal effects of extremes of acidity and alkalinity by varying the value of decay coefficient k_d in the yield equation given in (89):

$$\frac{dX}{dt} = Y\frac{dS}{dt} - k_d X \quad (89)$$

Allowing it to rise from its normal value of 0.02 (for acetoclastic bacteria at 35°C) up to 1.0 at pH values below 3.0 and above 11.0 to stimulate rapid death of these bacteria. However, the most widely accepted inhibition models are those developed by Andrews and Hill and Barth (Andrews, 1968; 1969; Andrews, 1971; Graef and Andrews, 1973; Hill and Barth, 1977). To predict the dynamic behaviour of anaerobic reactors under the inhibitory effects of high substrate concentration Andrews (1968) adopted Haldane (1965) enzyme inhibition function to modify Monod's equation as follows:

$$\mu = \frac{\mu_m}{\left[1+\left(\frac{K_s}{S}\right)+\left(\frac{S}{K_i}\right)\right]} \tag{90}$$

where, K_i is the inhibition constant which is numerically equal to the maximum substrate concentration at $\mu = \frac{1}{2}\mu_m$ in the presence of inhibition and K_s is the saturation (half velocity) constant, i.e., the minimum concentration at which $\mu = \frac{1}{2}\mu_m$ in the absence of inhibition. These are illustrated in Fig. 11. As can be seen from the figure, K_i equals infinity in the absence of inhibition, thus reducing Equation 90 to that of Monod. One of the effects of inhibition as can be seen from the figure is to reduce the maximum specific growth rate. For a given value of K_i less than infinity, the maximum attainable (μ_m) is obtained by setting the first derivative of Equation 90 equal to zero, thus (Equation 91):

$$\bar{\mu}_m = \frac{\mu_m}{\left[1+2\left(\frac{K_s}{K_I}\right)^{0.5}\right]} \tag{91}$$

where, $\bar{\mu}_m$ is the maximum specific growth rate in the presence of inhibition (d^{-1}). The substrate concentration at this growth rate is given by:

$$\hat{S} = (K_s K_i)^{0.5} \tag{92}$$

where, $\hat{S}$ is the substrate concentration at maximum specific growth attainable in the presence of inhibition (mg/L). To account for the effect of inhibition-causing un-ionized volatile acids and hence pH (since the degree of ionization is a function of pH), Equation 90 was modified by Andrews (1969) as follows:

$$\mu = \frac{\mu_m}{\left[1+\left(\frac{K_s K_a}{[S][H^+]}\right)+\left(\frac{[S][H^+]}{K_i K_a}\right)\right]} \tag{93}$$

where, $[H^+]$ is hydrogen ion concentration and $[S]$ is the total substrate concentration ≈ ionized acid concentration at pH ≥ 6.0 and K_a is the ionization constant ($10^{4\text{-}5}$ for acetic acid). The toxic loading effect was accommodated in the model by assuming that the rate of organism kill is first order with respect to the concentration of toxic agents as defined in Equation 94 (Andrews and Graef, 1971):

$$\frac{dX_T}{dt} = k_T X_T \tag{94}$$

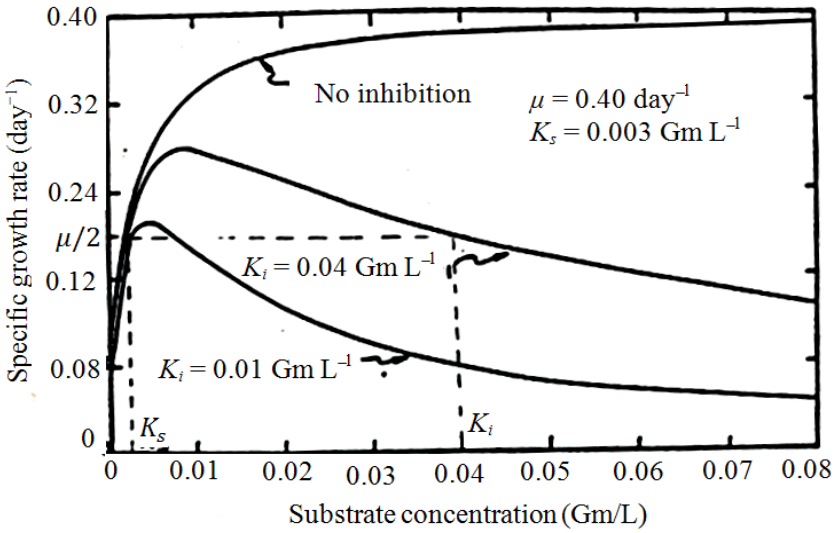

Fig. 11. Substrate inhibition function (Andrews, 1969)

where, $\frac{dX_T}{dt}$ is the rate of organism kill, k_T toxicity rate coefficient (mg/L.s) and S_T the concentration of toxic materials (mg/L). To account for mass transfer and accumulation in the liquid and gaseous phase for such materials as carbon dioxide, bi-carbonate and cations Andrews (1971) has since expanded the original model.

The dynamic model was further modified by (Hill and Barth, 1977) to account for inhibition due to high levels of free ammonia by adding a term to growth rate equation used by Andrews (1969), i.e.,:

$$\mu = \frac{\mu_m}{\left[1+\left(\frac{K_s K_a}{[S][H^+]}\right)+\left(\frac{[S][H^+]}{K_l K_a}\right)+\left(\frac{[NH_3]}{K_{NH_3}}\right)\right]} \quad (95)$$

where, $[NH_3]$ is the concentration of un-ionzed ammonia (mg/L) and K_{NH3} inhibition coefficient for free ammonia. The modified dynamic model was used to predict the dynamic responses during the digestion of poultry and swine manure to within 10% of the actual field data for the parameter of volatile acids (Hill and Barth, 1977).

The developed growth rate models are combined with the biomass and substrate mass balance equations and solved. Although the standard method of solution has been the use of computer simulations (Andrews, 1969; Fox and Rice, 1969) have shown that analytical solutions are possible and fairly easy. Obviously improvement will continue to be made on the existing dynamic models as well as the development of new ones. The development of a comprehensive model of the anaerobic digestion process of farm animal wastes will obviously be a breakthrough.

Kinetics of Biogas Production

Stoichiometric Model

The amount of biogas (methane and carbon dioxide) that can be produced from a waste of known chemical composition can be estimated from the stoichiometry of the overall anaerobic reaction involved. Bushwell and Muchler (1952) presented a simplified general formula for anaerobic conversion of typical substrate of the form $C_nH_aO_b$ to methane and carbon dioxide, i.e.,:

$$C_nH_aO_b+\left(n-\frac{a}{4}-\frac{b}{2}\right)H_2O\rightarrow\left(\frac{n}{2}-\frac{a}{8}-\frac{b}{4}\right)CO_2 +\left(\frac{n}{2}-\frac{a}{8}-\frac{b}{4}\right)CH_4 \quad (96)$$

For waste of the form $C_nH_aO_bN_c$ such as protein, Peavy *et al.* (1985) gave the formula:

$$C_nH_aO_bN_c +\left(n-\frac{a}{4}-\frac{b}{2}+\frac{3c}{4}\right)H_2O\rightarrow\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)CH_4 +\left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}+\frac{3c}{8}\right)CO_2+cNH_3 \quad (97)$$

The above stoichiometric relationships do into take into account that fact that a portion of the substrate is converted into cells. It is therefore the theoretical maximum yield.

Empirical Models

The rate of methane production can also be estimated by calculating the methane equivalent of the net COD reduction, i.e., total COD minus COD converted to biomass. The relevant equation is given by (Kugleman and Jerris, 1981; Benefield and Randall, 1980) as follows:

$$\gamma = \gamma_o\left[\Delta S - 1.42\Delta X\right] \quad (98)$$

where, γ is methane production rate (L/d), γ_o litters of methane produced per gram COD at STP (= 0.35 L/g COD at STP), ΔS the ultimate COD removal rate (g/d) [= $Q(S_o-S_1)$], Q the influent flow rate (L/d), (S_o-S_1) the COD reduction (g/L), ΔX the daily biomass production (g cell/ultimate BOD/d) and 1.42 the ultimate BOD per gram cell.

In terms of volume per unit volume of reactor, methane production rate can be estimated using the relationship developed by Chen and Hashimoto (1978), i.e.,:

$$\gamma_v = \frac{\beta_o S_o}{\theta_h}\left[1-\left(\frac{K}{\mu_m\theta_h - 1 + K}\right)\right] \quad (99)$$

where, γ_v is the volumetric methane yield (LCH_4/L of reactor vol/d), β_o ultimate methane yield (L/g VS added as HRT tends to infinity), S_o the influent total volatile solids concentration, θ_h the hydraulic retention time (d), K the kinetic parameter (dimensionless) and μ_m the maximum specific growth rate (d^{-1}).

For a given loading rate $\frac{S_o}{\theta_h}$, the volumetric methane production rate depends on the ultimate methane yield β_o which is a function of the type and biodegradability of the material. It also depends on the kinetic parameters μ_m the maximum specific growth rate and the kinetic parameter, K. The maximum growth rate, as has already been pointed out, is a function of temperature. K is a function of both the influent VS concentration and waste type. The maximum methane production is obtained by taking the derivative of γ_v with respect to θ_h and equating to zero, i.e.,:

$$\gamma_{v_{max}} = \frac{\beta_o S_o \mu_m}{\left(1+K^{-\frac{1}{2}}\right)^2} \quad (100)$$

Table 2. Ultimate methane yield for livestock waste[a]

Specie	Ration	Temp (°C)	(L CH_4/g VS)
Beef	18% silage	55.0	0.35-0.38
	20% roughage	60.0	0.280000
Dairy	58-68% silage	32.5	0.240000
	72% Roughage	60.0	0.170000

[a]Hashimoto *et al*. (1981)

Which occurs at $\theta_h = \frac{1+K^{-\frac{1}{2}}}{\mu_m}$. The ultimate methane yield, β_o is determined by plotting the steady-state methane yield (L/g VS added) $vs\frac{1}{\theta_h}$ and determining by extrapolation the methane yield corresponding to $\frac{1}{\theta_h}=0$. It can also be determined by incubating a known amount of substrate until a negligible amount of methane is produced (Hashimoto *et al.*, 1981). Typical values of ultimate methane yield for beef and dairy waste is given in Table 2.

Finally when it is desired to estimate biogas yield per mass of volatile solids added, the model developed by (Singh, 1977; Singh and Shulte, 1984) can be used, i.e.,:

$$\gamma = \gamma_m\left[1-e^{-k(t-\theta_c^m)}\right] \quad (101)$$

where, γ is gas production at STP per unit VS added (m^3/kg VS), γ_m the total gas produced at infinite time, i.e., the maximum produceable amount of biogas during digestion (m^3/kg VS added), k the reaction rate constant (d^{-1}), θ_c^m the washout time (minimum SRT) at the given temperature, t the time required for complete conversion of substrate into biogas and end products at a given temperature. Where γ_m, k and θ_c^m are known at one temperature T_1, methane yield, γ_{T2} at another temperature T_2 can be estimated by applying temperature correction factor as follows (Schulte *et al*., 1979):

$$\gamma_{T_2} = \gamma_m\theta_{h_1}^{(T_2-T_1)}\left[1-e^{-\left\{k\left(t-\theta_c^m\right)\theta_{h_2}^{(T_2-T_1)}\right\}}\right] \quad (102)$$

Conclusion

Presented in this review are the various basic kinetic models that have been developed for describing the generation of biomass and utilization of substrates in anaerobic fermentation processes. The stoichiometric and empirical models for the prediction of biogas production are also presented. The models are very simple and implementable and can be useful in the optimization and design of anaerobic reactors.

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