A STEADY-STATE MODULE FOR MODELING ANAEROBIC BIOFILM REACTORS

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***Abstract*— A steady state model of an anaerobic methanogenic biofilm reactor-module that accounts for the biological interactions of four microbial groups, ionic equilibrium in solution, gas-liquid transfer phenomena and biofilm processes is presented. The model consists of a continuous stirred tank reactor type that allocates an inert support material, whose specific surface is taken into account. The biofilm model assumes an homogeneous biofilm of uniform thickness and constant density with no mass transfer resistance. The biofilm detachment process rate is modeled as a second-order function on the biofilm thickness and a first-order function on the mass fraction of the fixed biomass concentration of each microbial group. The balance equations for non-active biomass in liquid and biofilm are included. The model predictions have been satisfactorily compared with steady state experimental data reported in literature from a one-phase methanogenic biofilm system treating an acetic acid-based synthetic effluent, and a two-phase system with combined suspended (acidogenic) and attached (methanogenic) microbial growth treating a food industry wastewater composed by two residual process streams.**

***Keywords*— Anaerobic digestion, biofilm reactor, steady state model, wastewater treatment.**

I. INTRODUCTION

Water contamination is one of the most serious environmental problems that the world is presently facing with. The former biological methods developed to clean wastewaters were the aerobic processes. However, these systems demand high-energy consumption for aeration and pumping, and generate a large amount of waste sludge for disposal. The increasing energy prices and decreasing available land for sludge disposal have motivated the use of the anaerobic process as an alternative. The anaerobic systems produce methane by recovering energy from waste. In addition, anaerobic microorganisms are quite resistant to toxics. However, they exhibit some drawbacks. The main disadvantage is the slow growth rate of the anaerobic microorganisms, which makes necessary to operate the conventional systems at long hydraulic retention times. This drawback has been overcome by accumulating large amount of active biomass within the bioreactor as attached or flocculated biomass. This generation of high-rate anaerobic processes is being successfully applied for treating industrial and municipal wastewaters. Nevertheless, there is a wide room for process optimization and for investigating aerobic-anaerobic hybrid processes. In this context, computer aided modeling, simulation and optimization are important tools to gain both insight into the anaerobic degradation process itself and skills to design, control and operate efficiently high-rate anaerobic processes and hybrid processes.

The aim of this paper is to present a model of a steady state reactor module of anaerobic attached biomass for application on wastewater treatment. Further usage of the model for design, optimization and system analysis is intended.

II. BACKGROUND

A. Kinetics of the anaerobic process

The substrate degradation scheme has generally been described through microorganism groups characteristic of each degradation stage that are present in major concentration in the biological community. The first unified kinetic model for substrate removal and microbial growth in anaerobic conditions was presented by Lawrence and McCarty (l969). This model is based on Monod-type kinetics for describing the removal of acetic, propionic and butyric acids, which are the main intermediates in anaerobic degradation. This model is one of the most widespread in anaerobic digestion and its biokinetic parameters have been used in many published models (Dalla Torre and Stephanopoulos, 1986; Droste and Kennedy, 1988). Andrews (1969), Graef and Andrews (1974) and Buhr and Andrews (1977) have only considered the acetic acid degradation stage by suspended acetoclastic bacteria, which was assumed as the limiting stage. Hill and Barth (1977) have included the hydrolysis and acidogenesis stages to compute the organic overload effect in the methane production rate. Kaspar and Wuhrmann (1978) have shown that the uptake rates and product distribution of some bacterial species are regulated by hydrogen gas. Mosey (1983) has developed a model to account for hydrogen gas and propionic and butyric acids produced in an anaerobic reactor degrading glucose. On growth inhibition, a feature of early models was to combine the inhibitory effects of volatile fatty acids and pH by using the inhibition model proposed by Andrews (1969). Kaspar and Wuhrmann (1978) and Denac (1986) have shown that acetogens rather than acetoclastic methanogens are inhibited by acetic acid. Angelidaki *et al*. (1993) included ammonia inhibition of the acetoclastic methanogenic

stage. Angelidaki *et al*. (1999) extended the organic waste characterization given in Angelidaki *et al*. (1993) defining the composition of a complex substrate (carbohydrates, lipids and proteins) subject to hydrolysis, and included non-competitive growth inhibition by long chain fatty acids (LCFA) in all degradation steps except for the LCFA acetogenic one, where a Haldane-type substrate inhibition was used. Kinetics of enzymatic hydrolytic steps is less known and first-order reaction rates on insoluble substrate concentration are usually assumed (Eastman and Ferguson, 1981; Pavlostathis *et al*., 1988; Angelidaki *et al*., 1999; Dalla Torre and Stephanopoulos, 1986). The specific hydrolysis rate has been assumed to be inhibited by VFA (Angelidaki *et al*., 1993, 1999) or as a function of free enzymes concentration (Huang, 1975; Dalla Torre and Stephanopoulos, 1986). Recently, Batstone *et al*. (2004) used the anaerobic digestion model ADM1 (Batstone *et al*., 2002) to study the influence of substrate kinetics on the microbial community structure in granular anaerobic biomass.

B. Anaerobic biofilms

Regarding kinetics in biofilms, Droste and Kennedy (1988) have assumed the same biokinetic constant values for microbial growth and substrate removal in the bulk liquid and biofilm in an anaerobic reactor model.

Although substrate utilization in biofilms has been traditionally modeled by coupling Fick's law of diffusion with Monod-type reaction kinetics, various studies (Droste and Kennedy, 1986; Williamson and McCarty, 1976a,b) have shown that diffusion limitations are less likely to occur in anaerobic biofilms. The model proposed by Henze and Harremoes (1983) predicts that mass transfer resistance may not be significant in methanogenic biofilms with thickness less than 1 mm. Speece (1983) pointed out that the production and utilization of volatile fatty acids and production of carbon dioxide in anaerobic conditions can cause changes in the local pH. Thus, some authors have modeled the pH variations within the biofilm (Szwerinski *et al.*, 1986; Siegrist and Gujer, 1987). De Beer *et al*. (1992) coupled Fickian diffusion with pH-dependent reaction kinetics to calculate the pH profiles within a methanogenic aggregate. Nevertheless, these models neglected the complex ionic equilibrium within the biofilm and ionic interactions in mass transfer. Suidan *et al.* (1994) developed a steady state model of methanogenic biofilms that accounts for mass transfer of neutral and ionic species, electroneutrality, gas production and pH changes within the biofilm, pH-dependent Monod-type kinetics and chemical equilibrium coupled to a continuous stirred tank reactor model fed with acetate as the sole carbon source.

The accumulation of biofilm is the net result of various processes such as adsorption, desorption, attachment, microbial growth and detachment (Characklis, 1990). Biofilm detachment, which is the main process that balances microbial growth, is the migration of cells and cell products from an existing biofilm into the bulk liquid. According to Bryers (1987), pieces of biofilm can be removed by erosion, sloughing, abrasion, predator grazing and human intervention. Erosion is the continuous removal of small biofilm particles and is presumed to be the result of shear forces exerted by moving fluid on the biofilm surface; whereas sloughing is the detachment of very large portions of a biofilm and is apparently a random and discrete process that mainly occurs in older and thicker biofilms or when environmental conditions change rapidly. Abrasion is caused by collisions of solid particles with the biofilm and it can be the dominant detachment process in fluidized bed reactors (Chang *et al.*, l991). Several expressions have been proposed for calculating the biofilm detachment rate. One commonly used detachment rate model assumes a first order dependence on the biofilm mass and thickness (Chang and Rittmann, 1988; Kreikenbohm and Stephen, 1985; Rittmann, 1982). Bakke *et al.* (1984) proposed a power law of the biofilm mass to model the detachment rate. Bryers (1984) and Characklis *et al.* (1990) assumed a second-order function of biofilm mass. Wanner and Gujer (1986) proposed a second order function of biofilm thickness to model the detachment of a multi-species biofilm. Shear stress has been explicitly incorporated into detachment rate expressions. Bakke *et al.* (1990) proposed a first-order dependence on shear stress. Rittmann (1982) suggested a fractional order in the fluid shear stress. However, Peyton and Characklis (1993) observed no significant influence of shear stress on the detachment rate in a roto-torque biofilm reactor with *Pseudomonas aeruginosa* and undefined mixed population biofilms. Speitel and DiGiano (1987), Chang *et al.* (l991), Peyton and Characklis (1993) incorporated the cell growth rate into the biofilm detachment rate expression. The simplest approximation to model an anaerobic fixed film reactor is to assume the same attachment and detachment rate coefficients for all microbial groups. There have been no studies providing evidence on differences between attachment and detachment rates for the groups of the anaerobic consortium (Droste and Kennedy, 1988).

Most biofilm models have considered constant biofilm density regardless of the substrate conditions or biofilm thickness (Rittmann and McCarty, 1980; Munier and Williamson, 1982). However, Hoehn and Ray (1973), Jewell (1985), Huang *et al.* (2000) and Abdul-Aziz and Asokelar (2000) found increased densities as thickness decreased. Bolte and Hill (1993) allow varying biofilm density according to substrate availability and mortality up to a maximum overall bacterial concentration.

III. ASSUMPTIONS. MODEL DERIVATION

The model development has been divided into five main modeling tasks: modeling of (a) the anaerobic degradation process, (b) the biofilm subsystem, (c) the reactor subsystem (reactor-module), (d) the gas phase subsystem, and (e) the ionic equilibrium in solution.

A. The anaerobic degradation process model

Four anaerobic microbial groups are considered in the

biosystem model: glucose fermenting acidogens, propionic acid degrading acetogens, butyric acid degrading acetogens and acetoclastic methanogens. After hydrolysis of complex substrates to simple sugars (glucose) and other short chain organics occurs, glucose degradation by pH-insensitive acidogenic bacteria to acetic, propionic and butyric acids is carried out. In the next step, slowly growing and pH-sensitive acetogens oxidize propionic and butyric acids to acetic acid. Subsequently, pH-sensitive and slowly growing acetoclastic methanogens reduce acetate to methane. Reduction of carbon dioxide to methane using hydrogen by relatively fast growing pH-sensitive autotrophic microorganisms is not considered separately in the model. The hydrogen-utilizing step is combined with butyric acid degrading acetogenic step to render an overall butyric acid degrading acetogenic reaction. The same assumption is considered for the propionic acid degrading acetogenic reaction. Despite of the combination of several steps causes loss of system information, it is not significant as the hydrogen utilization is relatively fast compared to oxidation of propionic and butyric acids (Angelidaki *et al.*, l993). Propionic and butyric acid-degrading microbial groups and acetoclastic methanogens are subjected to inhibition. Noncompetitive-type inhibition model is considered for both acetogenic steps and methanogenesis. Free ammonia and acetic acid are the growth inhibitors of methanogens and acetogens, respectively. A Michaelis pH inhibition function, normalized to give a value of 1.0 as center value, is included in the process rate expressions for these microbial groups. (Angelidaki *et al.*, l993).

The expressions for specific growth rates μ are listed below:

Acidogenic stage A

$$\mu_A = \mu_A^{\max} \frac{[Glc]}{K_{s_{Glc}} + [Glc]}. \quad (1)$$

Propionic acetogenic stage P

$$\mu_P = \Psi_{pH}\, \mu_P^{\max} \frac{[H\,\mathrm{Pr}]^T}{K_{s_{H\,\mathrm{Pr}}} + [H\,\mathrm{Pr}]^T} \frac{K^P_{inh_{HAc}}}{K^P_{inh_{HAc}} + [HAC]^T}. \quad (2)$$

Butyric acetogenic stage B

$$\mu_B = \Psi_{pH}\, \mu_B^{\max} \frac{[HBut]^T}{K_{s_{HBut}} + [HBut]^T} \frac{K^B_{inh_{HAc}}}{K^B_{inh_{HAc}} + [HAc]^T}. \quad (3)$$

Acetoclastic methanogenic stage M

$$\mu_M = \Psi_{pH}\, \mu_M^{\max} \frac{[HAc]^T}{K_{s_{HAc}} + [HAc]^T} \frac{K^M_{inh_{NH_3}}}{K^M_{inh_{NH_3}} + [NH_3{}_d]}. \quad (4)$$

pH inhibition function Ψ_{pH} of the specific growth rates

$$\Psi_{pH} = \frac{1 + 2 \cdot 10^{(0.5(pK_l - pK_h))}}{1 + 10^{(pH - pK_h)} + 10^{(pK_l - pH)}}. \quad (5)$$

where pK_h and pK_l are the upper and lower pH values at which Ψ_{pH} is 0.5.

Temperature dependence of the maximum specific growth rates μ^{max}

$$\mu_k^{\max} = \mu_k^{\max^{T^*}} 1.0718^{(T - T_k^*)},\ \mathrm{k} = \mathrm{A,P,B,M}, \quad (6)$$

where *k* refers to acidogens (A), propionic (P) and butyric (B) acetogens, acetoclastic methanogens (M) and the biological stages related. *T** is the reference temperature.

Temperature dependence of half-saturation constants:

$$Ks_{So} = Ks^{T^*}_{So}\, \omega_{So}^{(T^* - T)}, \quad (7)$$

where *So* refers to glucose (Glc), acetic (HAc), propionic (HPr) and butyric (HBut) acids.

$\omega_{Glc} = 1.072$; $\omega_{HBut} = 1.072$; $\omega_{HPr} = 1.291$; $\omega_{HAc} = 1.189$.

Temperature dependence of specific decay rates b_k

$$b_k = b_k^{T^*} 1.3496^{(T - T^*)}\ ;\ \mathrm{k} = \mathrm{A,P,B,M}. \quad (8)$$

B. The biofilm model

No mass transfer limitations in the biofilm and the same concentrations of substrates and products in the bulk liquid and biofilm are assumed. In addition, the same kinetic model and parameter values are assumed for each microbial group in the mixed liquid and biofilm. The model assumes a homogeneous biofilm of uniform thickness and constant density.

A second-order function on the biofilm thickness L_F and first-order function on the mass fraction of the fixed biomass concentration ($X^F{}_k/X^F{}_T$) of each microbial group *k* are proposed to model the biofilm detachment process rate r_{Ek} for an anaerobic multi-species biofilm reactor of volumen *V*:

$$r_{E_k} = V \cdot k_E^* \cdot L_F^2 \cdot \frac{X_k^F}{X_T^F}, \quad (9)$$

$$X_T^F = \sum_k \left(X_k^F + X_k^{F_{na}} \right)\ \ \mathrm{k} = \mathrm{A,P,B,M}, \quad (10)$$

where *na* refers to non-active biomass. The detachment rate coefficient k_E can be related to the specific surface A_S of the support material as follows. For a biofilm of thickness L_F, density ρ_F and volume V_F:

$$L_F = \frac{V_F}{A_S} = \frac{X_T^F}{\rho_F A_S}. \quad (11)$$

Then,
$$r_{E_k} = V \cdot \frac{k_E^*}{\rho_F^2 \cdot A_S^2} \cdot X_T^F \cdot X_k^F. \quad (12)$$

By defining
$$k_E = \frac{k_E^*}{\rho_F^2 \cdot A_S^2}, \quad (13)$$

the detachment rate expression becomes:

$$r_{E_k} = V \cdot k_E \cdot X_T^F \cdot X_k^F. \quad (14)$$

Thus, in the context of the model hypotheses, the parameter k_E is a specific system parameter (characteristic for each bioreactor) but $k_E{}^*$ is independent of the material support used.

The same detachment rate coefficient value is assumed for all microbial groups.

Since the support material consists of uniform size particles and biofilm growth modifies equally the apparent density of all particles, a complete mixing behav-

ior is assumed for the solid phase.

C. The reactor-module model

By coupling the biofilm model to the mass balance equations of a suspended biomass continuous stirred tank reactor model, a biofilm reactor model is derived, named the reactor-module model. The resulting equations system is of algebraic type.

In order to account for the total outlet chemical oxygen demand COD the balances for the nonactive (suspended and attached) biomass are included into the model.

For a volumetric flowrate Q, the mass balances for the chemical species are:

$$\frac{Q}{V}\left([So]_{in}^{T}-[So]^{T}\right)+\sum_{k}\lambda_{So}^{k}\frac{\mu_k}{Y_{So}^{k}}\left(X_k^S+X_k^F\right)=0\,, \quad (15)$$

[So] = [Glc], [HAc], [HPr], [HBut] ,

where $\lambda_{So}{}^{k}$=-1, +1 or 0, indicating whether *So* is a substrate, a product or does not participate in stage *k*, respectively.

The mass balances for the biological groups are:

Suspended active biomass X^S

$$\frac{Q}{V}\left(X_{k_{in}}^S-X_k^S\right)+\mu_k X_k^S-b_k X_k^S+k_E X_T^F X_k^F=0\,. (16)$$

k=A,P,B,M.

Attached active biomass X^F

$$\mu_k X_k^F-b_k X_k^F-k_E X_T^F X_k^F=0\,,\ \text{k = A,B,P,M.} \quad (17)$$

Suspended non-active biomass X^{Sna}

$$\frac{Q}{V}\left(X_{k_{in}}^{S_{na}}-X_k^{S_{na}}\right)+b_k X_k^S+k_E X_T^F X_k^{F_{na}}=0\,. (18)$$

k = A,B,P,M.

Attached non-active biomass X^{Fna}

$$b_k X_k^F-k_E X_T^F X_k^{F_{na}}=0\,,\ \text{k = A,B,P,M.} \quad (19)$$

Mass balance for carbonate system (inorganic carbon):

$$\frac{Q}{V}\left([H_2CO_3]_{in}^{T}-[H_2CO_3]^{T}\right)-K_{T_{CO_2}}\left([CO_{2_d}]-H_{CO_2}p_{CO_2}\right)$$

$$+\sum_{k}\lambda_{CO_2}^{k}\frac{\mu_k}{Y_{CO_2}^{k}}\left(X_k^S+X_k^F\right)=0$$

k = A,B,P,M, (20)

where CO_{2d} is the dissolved carbon dioxide. K_{TCO2} and Y^{k}_{CO2} are the CO_2 gas-liquid mass transfer coefficient and its yield coefficient in stage *k*, respectively.

Mass balance for ammonia-ammonium system

$$\frac{Q}{V}\left([NH_3]_{in}^{T}-[NH_3]^{T}\right)+\sum_{k}\lambda_{NH_4}^{k}\frac{\mu_k}{Y_{NH_4}^{k}}\left(X_k^S+X_k^F\right)=0\,,$$

k = A,B,P,M. (21)

D. The gas phase subsystem model

The three components considered in the gas phase are methane, carbon dioxide and water vapor. Since the anaerobic digestion process model combines the propionic and butyric acid degradation steps with the hydrogen-utilizing methanogenic step, the hydrogen cannot be computed. As the ammonia levels at the pH ranges of anaerobic reactors in operation are quite low, ammonia in the gas phase is not considered. Temperature dependence of the water vapor pressure is taken into account in the model. As the carbon dioxide solubility in water is 40 times higher than methane at pH 7 and 35°C (Hayes *et al.*, 1990), methane is considered to be insoluble in the liquid phase; consequently, methane production rate equals the liquid-gas transfer rate. The carbon dioxide liquid-gas transfer rate is modeled by a non-equilibrium driving force. Gases are assumed to obey the ideal gas law and to have the same temperature as the liquid phase. The headspace volume V_g is constant and assumed to be a fixed fraction γ of the liquid volume V. Based on these assumptions:

Carbon dioxide partial pressure p_{CO2}

$$-\frac{P_t}{V_g}s_v V T_{CO_2}-\frac{Q_g}{V_g}p_{CO_2}=0\ ;\quad V_g=\gamma\cdot V\ ; \quad (22)\text{-}(23)$$

$$T_{CO_2}=K_{T_{CO2}}\left([CO_{2_d}]-H_{CO_2}p_{CO_2}\right), \quad (24)$$

where P_t and Q_g are the total pressure and the gas volumetric flowrate, respectively.

Methane partial pressure p_{CH4}

$$-\frac{P_t}{V_g}s_v V P_{CH_4}^{*}-\frac{Q_g}{V_g}p_{CH_4}=0\,, \quad (25)$$

where:

$$Q_g=Q_{CH_4}+Q_{CO_2}+Q_{H_2O}\,, \quad (26)$$

$$Q_{CH_4}=P_t s_v\frac{V}{V_g}P_{CH_4}^{*}\,, \quad (27)$$

$$Q_{H_2O}=\frac{P_{V_{H_2O}}}{P_t-P_{V_{H_2O}}}\left(Q_{CO_2}+Q_{CH_4}\right), \quad (28)$$

$$P_{CH_4}^{*}=\sum_{k}\lambda_{CH_4}^{k}\frac{\mu_k}{Y_{CH_4}^{k}}\left(X_k^S+X_k^F\right),\ \text{k=A,B,P,M.} \quad (29)$$

Antoine's equation for water vapor pressure $P_{V\,H2O}$

$$P_{V_{H_2O}}=\frac{1.0}{760.0}10^{\left(8.07131-\frac{1730.63}{T+233.426}\right)}. \quad (30)$$

Temperature dependence of the molar volume s_v

$$s_v=22.4\cdot 1.008793^{(T-25)}. \quad (31)$$

Temperature dependence of CO_2 *Henry's constant* H_{CO2}

$$H_{CO_2}=A_{CO_2}^{H}+B_{CO_2}^{H}T+C_{CO_2}^{H}T^2+D_{CO_2}^{H}T^3\,. \quad (32)$$

E. The model of ionic equilibrium in solution

The components involved in the model of ionic equilibrium in solution are the following:

$$HAc\xleftrightarrow{K_{HAc}}Ac^{-}+H^{+}\,;\ H\,\mathrm{Pr}\xleftrightarrow{K_{H\,\mathrm{Pr}}}\mathrm{Pr}^{-}+H^{+}$$

$$HBut\xleftrightarrow{K_{HBut}}But^{-}+H^{+}$$

$$CO_2+H_2O\longleftrightarrow H_2CO_3\xleftrightarrow{K_{1H_2CO_3}}HCO_3^{-}+H^{+}$$

$$HCO_3^{-}\xleftrightarrow{K_{2H_2CO_3}}CO_3^{-2}+H^{+}$$

$$H_3PO_4 \xleftrightarrow{K_{1H_3PO_4}} H_2PO_4^- + H^+$$
$$H_2PO_4^- \xleftrightarrow{K_{2H_3PO_4}} HPO_4^{-2} + H^+$$
$$HPO_4^{-2} \xleftrightarrow{K_{3H_3PO_4}} PO_4^{-3} + H^+$$
$$NH_4^+ \xleftrightarrow{K_{NH_4^+}} NH_3 + H^+ ;\ H_2O \xleftrightarrow{K_w} OH^- + H^+$$
$$AH \longrightarrow A^- + H^+ ;\ COH \longrightarrow C^+ + OH^- .$$

The concentrations of ionic and non-dissociated species of each component are calculated as follows:

$$\left[H_pB\right]^T = \sum_{s=0}^{s=p} H_{p-s}B \,, \tag{33}$$

$$\left[H_{p-q}B\right] = \left[H_pB\right]^T \frac{\left[H^+\right]^{p-q}\prod_{i=1}^{i=q} K_i}{D_{(p)}} \,, \tag{34}$$

where:

$$D_{(p)} = \left[H^+\right]^p + \left[H^+\right]^{p-1}K_1 + \left[H^+\right]^{p-2}K_1K_2 + \cdots + \left[H^+\right]K_1K_2\cdots K_{p-1} + K_1K_2\cdots K_p \tag{35}$$

K_i is the *i*- acid dissociation constant and Π indicates the product of the dissociation constants K_i; p is the number of protons in the H_pB acid and q is the number of released protons; p-q is the amount of protons in the species considered. For a weak monoprotic acid *HB*

$$\left[HB\right]^T = \left[HB\right] + \left[B^-\right]; K_{HB} = \frac{[H^+][B^-]}{[HB]} \,, \tag{36)-(37}$$

$$\left[HB\right] = \left[HB\right]^T \frac{\left[H^+\right]}{\left[K_{HB}\right] + \left[H^+\right]} . \tag{38}$$

The overall *charge balance* (electroneutrality) becomes:

$$\left[H^+\right] = \left[H_2PO_4^{-1}\right] + 2\left[HPO_4^{-2}\right] + 3\left[PO_4^{-3}\right] + \left[HCO_3^{-1}\right] + 2\left[CO_3^{-2}\right] + \left[Ac^-\right] + \left[\mathrm{Pr}^-\right] + \left[But^-\right] + \left[A^-\right] + \left[OH^-\right] - \left[C^+\right] - \left[NH_4^+\right] \tag{39}$$

$$pH = -\log_{10}\left[H^+\right] \tag{40}$$

The optimal pH differs for each microbial group of the consortium. The model is able to manipulate the system pH by incorporating the concentration of "other anions" (A^-) and "other cations" (C^+) as chemical species.

Temperature dependence of dissociation constants K_i

Carbonic acid

$$-\log_{10} K_{1H_2CO_3} = A^{K_1}_{H_2CO_3} + B^{K_1}_{H_2CO_3}T + C^{K_1}_{H_2CO_3}T^2 \,, \tag{41}$$

$$-\log_{10} K_{2H_2CO_3} = A^{K_2}_{H_2CO_3} + B^{K_2}_{H_2CO_3}T + C^{K_2}_{H_2CO_3}T^2 \,. \tag{42}$$

Ammonium ion

$$-\log_{10} K_{NH_4^+} = A^{K_d}_{NH_4^+} + B^{K_d}_{NH_4^+}T + C^{K_d}_{NH_4^+}T^2 + D^{K_d}_{NH_4^+}T^3 \,. \tag{43}$$

Water dissociation constant K_w

$$-\log_{10} K_w = 4.771 + \frac{2747}{T + 273.15} \,. \tag{44}$$

Model parameters. The model parameters are biokinetic constants, parameters of the biofilm processes, thermodynamic properties, mass transfer coefficients, stoichiometric coefficients, physical properties of the support material, input stream specifications and bioreactor design data. The uncertainty in these parameters reported in literature varies for each case.

Table 1. Model parameters and correlation coefficients

Param.	Value	Unit	Param.	Value	Unit
$\mu_A^{\max 37}$	30	d^{-1}	Y^M_{HAc}	2.49	g mol^{-1}
$\mu_P^{\max 35}$	0.479	d^{-1}	$Y^M_{CO_2}$	2.63	g mol^{-1}
$\mu_B^{\max 35}$	0.389	d^{-1}	$Y^M_{CH_4}$	2.63	g mol^{-1}
$\mu_M^{\max 35}$	0.35	d^{-1}	P_t	1.0	atm
$K^{37}_{s_{Glc}}$	1.2e-4	mol L^{-1}	$K_{T_{CO_2}}$	100	d^{-1}
$K^{35}_{s_{HAc}}$	2.57e-3	mol L^{-1}	γ	0.2	
$K^{35}_{s_{H\,\mathrm{Pr}}}$	7.95e-4	mol L^{-1}	$A^H_{CO_2}$	0.0697	
K^{35}_{sHBut}	8.33e-5	mol L^{-1}	$B^H_{CO_2}$	-0.002	
b^{37}_A	6.1	d^{-1}	$C^H_{CO_2}$	2.56e-5	
b^{35}_P	0.02394	d^{-1}	$D^H_{CO_2}$	-1.2e-7	
b^{35}_B	0.027	d^{-1}	sv^o	22.4	L mol^{-1}
b^{35}_M	0.0154	d^{-1}	K_{HAc}	1.74e-5	
$K^P_{inh_{HAc}}$	0.05388	mol L^{-1}	$K_{H\,\mathrm{Pr}}$	1.29e-5	
$K^B_{inh_{HAc}}$	0.05388	mol L^{-1}	K_{HBut}	1.29e-5	
$K^M_{inh_{NH_3}}$	19.63e-3	mol L^{-1}	$K_{1H_3PO_4}$	5.9e-3	
Y_{NH_4}	113	g mol^{-1}	$K_{2H_3PO_4}$	6.17e-8	
Y^A_{glc}	12.6	g mol^{-1}	$K_{3H_3PO_4}$	4.8e-13	
Y^A_{HAc}	16.93	g mol^{-1}	$A^{K_d}_{NH_4^+}$	10.05	
$Y^A_{H\,\mathrm{Pr}}$	25.2	g mol^{-1}	$B^{K_d}_{NH_4^+}$	-0.0333	
Y^A_{HBut}	28.58	g mol^{-1}	$C^{K_d}_{NH_4^+}$	2.43e-5	
$Y^A_{CO_2}$	18.24	g mol^{-1}	$D^{K_d}_{NH_4^+}$	7.43e-7	
Y^P_{HAc}	7.5	g mol^{-1}	$A^{K_1}_{H_2CO_3}$	6.539	
$Y^P_{H\,\mathrm{Pr}}$	7.0	g mol^{-1}	$B^{K_1}_{H_2CO_3}$	-0.01	
$Y^P_{CO_2}$	43.62	g mol^{-1}	$C^{K_1}_{H_2CO_3}$	1.01e-4	
$Y^P_{CH_4}$	10.6	g mol^{-1}	$A^{K_2}_{H_2CO_3}$	10.619	
Y^B_{HAc}	3.9	g mol^{-1}	$B^{K_2}_{H_2CO_3}$	-0.014	
Y^B_{HBut}	7.38	g mol^{-1}	$C^{K_2}_{H_2CO_3}$	1.01e-4	
$Y^B_{CO_2}$	13.32	g mol^{-1}	k_E	See case studies 1 and 2	L g^{-1} d^{-1}
$Y^B_{CH_4}$	16.55	g mol^{-1}			

The parameters associated to the thermodynamic and physico-chemical properties (e.g. dissociation constants of acids and bases, Henry's Law constant and Antoine's coefficients) are well known and considered as uncertainty-free for the purposes of this work (Kolthoff et al., 1969; Weast and Melvin, 1980). The uncertainty in the parameter subset inherent to the biological system, which includes the maximum specific growth and death rates, half-saturation constants, yield coefficients and inhibition constants is quite important. So, a careful and extensive analysis of the experimental conditions under which they were estimated (reactor configuration, substrate type -real or synthetic-, presence of growth inhibitors, pure or mixed cultures, etc.) is required. As result of a bibliographic review on anaerobic digestion kinetics (Mussati, 2000), the biokinetic parameter values given by Angelidaki et al. (1993) and Lawrence and McCarty (1969) are selected for this work. Finally, for some model parameters there is little information. The parameters related to the biofilm model are included in this subset; specificaly, the detachment rate coefficient, which is here estimated for the case studies analyzed. The model parameters values and correlation coefficients are listed in Table 1.

IV. MODEL RESULTS

The model predictions have been compared with steady state experimental data reported in literature. Experimental data from one- and two-phase anaerobic systems and combined suspended-attached growth systems treating synthetic substrates and food industry wastewaters have been used for testing the model.

Case study I

The physical separation of the suspended growth of acidogens in completely mixed reactors and the fixed growth of methanogens has been investigated by several researchers. The opportunities for biomass recycle and retention, neutralization and optimal growth conditions for each microbial group are the main features of the two-phase systems. Schraewer and Karlstein (1988) dealt with such system for treating soluble substrates from a food processing industry. The wastewater consists of a mixture of process water and process waste streams (Table 2). The anaerobic degradation model proposed does not include the lactic acid degradation, which is present in the real influent considered. However, if low lactate concentrations are fed to an anaerobic bioreactor, very low lactate levels are detected in the outlet stream, indicating that lactate is easily degradable in such conditions. Clostridia convert lactate to acetate, propionate or butyrate as main products (Hippe *et al*., 1992; Zellner *et al*., 1994). The sulphate-reducing bacteria degrade lactate to acetate and form hydrogen sulfide. Therefore, there exist several metabolic paths for the methane production from lactate. Here, a complete and instantaneous conversion of lactate to a mixture of acetate and butyrate is supposed: 70% of the incoming lactic acid carbon is converted to acetate carbon and 30% to butyrate carbon. This assumption results in a higher acetate concentration than the resulting from mixing the process water and waste streams (Table 2). Operation data and design specifications are listed in Table 3. The detachment rate coefficient k_E=3.02e-3 L g^{-1} d^{-1} was estimated by a trial-and-error procedure since the physical properties of the inert support material (specific surface) are not reported. Tables 4 and 5 compare the simulated steady state results with experimental data for the acidogenic and the methanogenic reactors, respectively.

Table 2. Wastewater specifications

Parameter	Units	Process waste	Process water	Simulated waste
Q	m^3 d^{-1}	1182	818	2000
pH		5	6.5	5.5
COD	g L^{-1}	26	4	17
Sugars	g L^{-1}	3	0.8	3.4[(a)]
Acetic acid	g L^{-1}	2.8	0.2	3.3[(b)]
Lactic acid	g L^{-1}	7.5	-	†
Organic N	g L^{-1}	1.5	0.3	†
Sulphur	g L^{-1}	0.2	0.1	†
Phosphorous	g L^{-1}	0.4	0.1	0.28
Magnesium	g L^{-1}	0.1	<0.1	†
Dried matter	g L^{-1}	-	0.8	†
Butyric acid	g L^{-1}	-	-	1.13[(b)]
Ammonia-N	g L^{-1}	-	-	1.0[(c)]

(†) Components not included in the model; [(a)] As glucose; [(b)] Includes conversion of lactate to acetate and butyrate (see text); [(c)] Nitrogen.

Table 3. Input data for acidogenic and methanogenic reactors

Parameter	Units	Acidogenic R.	Methanogenic R.
V	m^3	2000	1000
Q_{in}	m^3d^{-1}	2000	2000
T	°C	37	37

Table 4. Model outputs and experimental data for acidogenic reactor

Parameter	Units	Exp. value	Predicted value
pH		5.8	5.8
Acetic acid	mmol L^{-1}	28	70[(a)] (28)
Propionic acid	mmol L^{-1}	8	10
N-butyric acid	mmol L^{-1}	29	22
I-butyric acid	mmol L^{-1}	1	†
N-valeric acid	mmol L^{-1}	13	(16.8)[(a)]
I-valeric acid	mmol L^{-1}	-	†
Lactic acid	mmol L^{-1}	0.5	†
Ammonia N	g L^{-1}	0.4	0.9
Organic N	g L^{-1}	0.2	

(†) Components not included in the model; [(a)] Since valerate is not included in the model, the equivalent valerate is computed (See text).

The difference between the acetate concentration predicted by the model and the experimental data for the acidogenic reactor (Table 4) can be explained by the measured amount of valerate present in the outlet stream, which is not included in the model.

Table 5. Model outputs and experimental data for methanogenic reactor

Parameter	Units	Exp. value	Pred. value
COD_{in}	g L^{-1}	-	14.9
COD loading rate	g $L^{-1}d^{-1}$	30	29.8
Biomass	g L^{-1}	20	18.4
COD_{out}	g L^{-1}	4.6	5.2
Reduced COD	%	75	65.1
pH		-	7.5

If the acetate concentration predicted in excess with respect to the experimental value (42 mmol L^{-1}) is converted to valerate on a carbon equivalent basis, 16.8 mmol L^{-1} of equivalent valerate is computed against 13 mmol L^{-1} measured experimentally. By accepting this consideration and taking into account that a two-stage combined system of (acidogenic) suspended and (methanogenic) attached growth treating a real effluent composed by two residual process streams is simulated, the model predictions are satisfactory.

Case study II

An acetic acid-based synthetic effluent is treated in a lab-scale anaerobic packed bed reactor (Radke and Aivasidis; 1989). The reactor specifications are listed in Table 6. As in *case study 1*, the detachment rate coefficient k_E=2.01e-2 L g^{-1} d^{-1} was estimated by a trial-and-error procedure since the specific surface of the support material is not reported.

Table 6. Reactor input data

Parameter	Units	Value
V	L	11.0
Residence time τ	d	0.46
COD_{in}	g L^{-1}	47.0
Org. loading rate	g L^{-1} d^{-1}	102.5

Table 7. Model outputs and experimental data

Parameter	Units	Exp. value	Predicted value
COD_{out}	g L^{-1}	7.0	6.97
Biomass X	g L^{-1}	12.44	12.51
Reduced COD	%	85	85.1
Reduced COD	$gL^{-1}d^{-1}$	87.1	87.34
Org. loading rate/X	$gg^{-1}d^{-1}$	8.2	8.19
Reduced COD/X	$gg^{-1}d^{-1}$	6.9	6.97
P_{biogas}/V	$LL^{-1}d^{-1}$	60.0	56.6
PH		-	6.7

The simulated steady state results are compared to experimental data in Table 7, where 6% deviation in the worst case and 1% in other ones are obtained. In this case only one degradation step (methanogenesis) is involved.

V. COMPUTATIONAL ASPECTS

The mathematical model was implemented and solved using the process modeling software tool gPROMS (Process Systems Enterprise Ltd., 2004). The models involved in case studies 1 and 2 consist of 272 and 125 model equations, respectively, and were both solved in less than 0.2 sec. of total CPU time.

VI. CONCLUSIONS

A steady state model of an anaerobic attached biomass reactor module for application on wastewater treatment was presented. Biological interactions of four microbial groups, ionic equilibrium in solution, gas-liquid transfer phenomena, biofilm processes, and a continuous stirred tank system were integrated in the reactor-module model.

The model predictions are satisfactory. Good concordance between model outputs and data from pilot and full-scale plants reported in literature were obtained. One-phase (methanogenic) biofilm system and two-phase (suspended acidogenic-attached methanogenic) system were satisfactorily simulated.

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