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A simplified kinetic model for a full scale anaerobic wastewater treatment plant of a sugar factory under unsteady conditions

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ABSTRACT

A simplified time dependent mathematical model was developed for an industrial a full-scale two stage anaerobic wastewater treatment plant of a sugar factory under unsteady conditions. As an overall approach, a two-step (acidogenesis and methanogenesis) instantaneous mass balance was considered in the model. The reactor equations employed were based on continuous flow well-mixed conditions. Kinetic parameters related to acidogenic and methanogenic reactions were imported from literature studies. The kinetic model was used to simulate MLVSS (mixed liquor volatile suspended solids), VFA (volatile fatty acid) and COD (chemical oxygen demand) equivalent glucose concentrations in hydrolysis tank, and MLVSS, VFA and gas production in anaerobic tank by making use of data from the full-scale anaerobic methane production plant. The model satisfactorily predicted the measured variables in the hydrolysis tank, but prediction was poor for variables in the anaerobic tank. The model has limitations in anaerobic reactions, which are basically due to model kinetic parameters unspecific to sugar factory wastewater.

Keywords: Anaerobic treatment; Kinetic modeling; Sugar industry

1. Introduction

Anaerobic treatment of wastewaters is a widely accepted and proven technology. The anaerobic wastewater treatment process offers valuable advantages compared to the classical aerobic treatment [1,2]. It has a high capacity to degrade concentrated and difficult substrates producing less sludge, recovers energy from methane production and requires less energy in operation [3].

Anaerobic process is based on a complex chain of biochemical reactions through which the waste is first partially transformed into volatile fatty acids (VFAs) and then these VFA's are converted to acetic acid, hydrogen and carbondioxide which are the primary substrates for methanogenesis. The major drawback for the application of anaerobic processes in wastewater treatment is the complex, interdependent bacterial community with slow growth rate, which is highly sensitive to sudden changes in substrate composition, pH and temperature, and to certain toxic or inhibitory compounds. Slow growth rate means slow recovery after toxic shock or overloading and requires effective biomass retention [4]. Given this inherent complexity, the process is quite vulnerable to abrupt operating changes, which,

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†*This article is dedicated to the memory of Prof. Dr. Abdurrahman Tanyolaç (1954–2011), who passed away after the manuscript was written.*

if uncontrolled, may eventually lead to a total process failure. Therefore, much importance has been given to early failure detection so that in the event of a shock, a preemptive remedial action can be taken to bring the process back into its normal operation. Mathematical models can assist to the description of shock behavior in the design of safeguard control systems [5]. However, due to the complexity of the biological process, it is difficult to develop a true mathematical model reflecting the biological reality [6].

Modeling and simulation have been identified as useful tools for evaluating transient digester performance and control strategies. The dynamic modeling of anaerobic digestion has been an attractive research area during the last three decades. Models are usually based on material balances, empirical growth models, mass transport equations, ionic equilibrium equations and stoichiometric relations. Due to insufficient data in literature for anaerobic treatment, some parameter values of the models can only be used as estimates, therefore, such models are of semi-quantitative nature. One of the reasons for this insufficiency is experimentation consisting troublesome due to long retention times and extreme sensitivity of methanogenic bacteria to oxygenous atmosphere. Despite these parameter-associated uncertainties, the accuracy of the model can be sufficient to evaluate the performance of anaerobic digesters [7].

The growing interest in dynamical modeling of anaerobic treatment during previous years has resulted in the development of a variety of mathematical models for different anaerobic digestion processes. Andrews introduced the Haldene model to characterize growth inhibition that can emphasize the process instability [8]. A model with a single bacterial population was then proposed by Graef and Andrew [9]. Hill and Barth proposed three-stage process modeling [10]. The work of Mosey was a keystone in the development of more advanced models [11]. These main modeling studies have been extended and detailed by other authors to get closer to the complexity of the process [6,12]. More detailed simulation models have also been developed [13–16]. These detailed models require the simultaneous solution of mass balance equations for each individual substrate and bacterial population, yielding equations with numerous model parameters. Models proposed by Bernard et al. and Noykova et al. considered two main bacterial population to obtain simplicity in modeling approach [3,17]. The latest available model developed for the simulation of anaerobic treatment is the Anaerobic Digestion Model 1 (ADM 1) published in the IWA Scientific and Technical Report (No:13) [18].

In this study, a simplified kinetic model was developed for an industrial full scale two stage anaerobic wastewater treatment plant (ANAMET) of a sugar factory operating under unsteady conditions. Differential mass balance equations were simultaneously solved for sequential hydrolysis and anaerobic tanks to simulate the time dependent profiles of MLVSS, VFA and COD equivalent glucose concentrations. The process was simplified by considering two main bacterial populations and two main substrates in consecutive reactors. From this point of view, mass balance model consisting seven differential equations was derived and numerically solved.

2. Material and methods

2.1. Process layout

The sugar beet processing factory has an actual capacity of processing 8000 tones of beet per day. The source of the wastewater consists of two main streams; one is flume and washing water and the other is the wastewater from miscellaneous usages of water in the process. Water from soil settlement lagoons and miscellaneous use are balanced in the equalization basin. The wastewater from equalization basin is then pumped to the treatment plant for the removal of COD and nitrogenous compounds prior to reuse and discharging offsite. The wastewater from the sugar factory is treated by a full-scale Anaerobic Methane Production (ANAMET) type plant, which consists of sequential anaerobic and aerobic biological treatment units. Anaerobic unit includes hydrolysis and anaerobic tanks, both totally mixed reactors, and a lamella type sludge separation system. ANAMET plant is designed for a wastewater flow rate of 4680 $m^3\ d^{-1}$, having a COD load of 37,500 kg d^{-1}. When the data were collected, the ANAMET plant was operating in the third year of the treatment campaign of the sugar factory. Anaerobic unit treatment efficiency and total treatment efficiency of the plant based on COD were realized 97% and 99%, respectively, in the same operating period.

2.2. Analysis and measurements

COD, VFA and MLVSS analysis were carried out according to standard methods [19]. Volumetric wastewater flow rates were measured by electromagnetic flow meters (Danfoss MagFlo). Gas flow rate was measured by a Bailey Fischer Porter vortex flow-meter. Gas composition of the biogas was determined by an on-line Varian Micro GC. A programmable logic control (PLC)—SCADA system was used to control the anaerobic plant and, wastewater and gas flow rates were monitored online from TEOS 32 SCADA system.

2.3. Influent wastewater characteristics

Plant data of 192 d were used in the model. Every 2 h, samples were collected from various locations of the treatment plant to form daily composite samples for COD, VFA and MLVSS analysis. Every 5 min values of wastewater and gas flow rates and also CH_4 content of biogas values were sampled from TEOS 32 SCADA system to obtain average daily values. The ranges of wastewater characteristics used for the model are given in Table 1.

2.4. Kinetic model

2.4.1. Model assumptions and description

In practice, anaerobic digestion of organic matter is generally considered to be a two-stage process in which the acidogenic and methanogenic bacteria are in dynamic equilibrium. In two stage (often called two phase) digestion, the acidogenic stage is spatially separated from the methanogenic stage by using two consecutive reactors [20,21].

In this study, a simplified mathematical model based on fundamental approach of mass balance in the studies of Moletta et al., Hill and Bart, Kiely et al., and Havlic et al., was established [6,10,12,22]. For the kinetic model of the anaerobic treatment unit, following assumptions were made and system observations were stated for mass balance equations over the hydrolysis and anaerobic tanks.

Table 1
Wastewater characteristics of the sugar factory

Wastewater parameter	Minimum	Maximum	Average
COD_{inf} (mg l^{-1})	2152	22,458	6050
COD_{hyd} (mg l^{-1})	2592	16,324	6060
COD_{ana} (mg l^{-1})	117	492	242
VFA_{inf} (mg l^{-1})	80	7390	2644
VFA_{hyd} (mg l^{-1})	280	7700	3392
VFA_{ana} (mg l^{-1})	10	60	24
$MLVSS_{inf}$ (mg l^{-1})	26	1520	283
$MLVSS_{hyd}$ (mg l^{-1})	50	2050	489
$MLVSS_{ana}$ (mg l^{-1})	3700	10,350	5609
pH_{inf}	4.00	6.99	5.89
pH_{hyd}	3.92	6.77	5.66
pH_{ana}	6.76	7.25	6.99
Q_{inf} (m^3 d^{-1})	218	4856	3107
$Q_{(inf\text{-}bypass)}$ (m^3 d^{-1})	218	4768	3003
$Q_{anarecyle}$ (m^3 d^{-1})	754	7852	4631
Q_{gas} (m^3 d^{-1})	150	20,325	9458
CH_4 (%), v/v	57.68	71.59	65.95

1. Sugar factory wastewater contains high amounts of sucrose and other related carbohydrates. These organic materials are hydrolyzed approximately 60% in soil settlement lagoons and equalization basin prior to entering wastewater treatment unit. Organic matter in wastewater entering to anaerobic treatment plant is in dissolved form and wastewater does not contain inorganic and organic suspended solids.
2. The microbiology of anaerobic digestion is complicated, because it involves several bacterial groups, each performing a separate task of the overall degradation process. But the model in this study considers the overall conversion of organic matter to methane by mainly two groups of microbial population. It is also assumed that only acidogenic microorganisms are available in hydrolysis tank, but both acidogenic and methanogenic microorganisms are present in anaerobic tank.
3. In the first stage, that is in hydrolysis tank, dissolved organic material (glucose) is degraded to volatile fatty acids and CO_2 by acidogenic microorganisms. In the second stage, that is anaerobic tank, volatile fatty acids are converted to acetic acid, hydrogen and carbondioxide which are the primary substrates for methanogenesis forming CH_4.
4. Formation of volatile fatty acids from sugar is mainly accomplished in the hydrolysis tank. Nevertheless, it is assumed that unhydrolyzed glucose passed into the anaerobic tank is converted to volatile fatty acids and methane simultaneously in the anaerobic tank.
5. There are only glucose and volatile fatty acids in the influent wastewater, and wastewater contains only hydrolytic fermentative and acidogenic microorganisms. In anaerobic tank, methanogenic microorganisms are dominant but acidogenic microorganisms also exist to degrade unhydrolyzed glucose.
6. All biological conversion reactions involved in the model are performed in hydrolysis and anaerobic tanks. Lamella clarifier is used for sludge separation and due to little retention time, no biological conversion is assumed to occur in this unit.
7. Hydrolysis tank of 1170 m^3 is in completely homogenized state and wastewater is heated to 37 ± 2°C before entry to this tank. Anaerobic tank of 8,000 m^3 is also completely homogenized and wastewater is kept at 35 ± 2°C in this tank.
8. Hydrolysis and anaerobic tanks are operated under anaerobic conditions and dissolved oxygen concentration in these tanks is almost zero.

9. Biomass concentration is uniform in both hydrolysis and anaerobic tanks.
10. It is known that unionized acetic acid inhibits acetogenic and methanogenic microorganisms and in return methane production [5,6,12,22]. Hence, there is an inhibition effect of unionized acetic acid (HAc) in hydrolysis tank, due to high VFA concentration expressed as HAc. Similarly, unhydrolyzed glucose from hydrolysis tank is further hydrolyzed to VFA in anaerobic tank; therefore, inhibition effect of HAc may also exist in anaerobic tank.
11. The main source of nitrogen, ammonium (NH_4), also shows inhibition effect, above 200 g N m^{-3} [23]. In both tanks, no ammonium inhibition effect should be experienced because average influent NH_4–N concentration was determined as 11.9 as g N m^{-3}.
12. CH_4 solubility is almost zero in anaerobic tank, due to high ion concentration and elevated temperature.
13. The pollution content of wastewater was expressed in terms of glucose and VFA. VFA is a measured system variable. VFA equivalent COD (1 g HAc l^{-1} is equal to 1.066 g COD l^{-1}) was subtracted from the total influent COD and the rest of the pollution in terms of COD was converted into glucose equivalent (1 g of glucose has a COD value of 1.066 g) [6,23].

2.4.2. Model development

Unsteady state mass balance equations in terms of COD equivalent glucose, VFA, biomass and methane were set-up around hydrolysis and anaerobic tanks with above statements and assumptions. Matrix forms of mass balance equations for hydrolysis and anaerobic tank with explanatory equations for the parameters are presented in follow.

2.4.2.1. Mass balance equations for hydrolysis tank

$$\begin{bmatrix} \frac{dS_1}{dt} \\ \frac{dS_2}{dt} \\ \frac{dX_1}{dt} \end{bmatrix} = \begin{bmatrix} -D_1 & 0 & -\left(\frac{\mu_1}{Y_{H1}} + m_1\right) \\ 0 & -D_1 & \left(\frac{\mu_1}{Y_{A1}} + 0.83m_1\right) \\ 0 & 0 & (\mu_1 - k_d - D_1) \end{bmatrix} \times \begin{bmatrix} S_1 \\ S_2 \\ X_1 \end{bmatrix} + \begin{bmatrix} D_1 S_{1,\text{inf}} \\ D_1 S_{2,\text{inf}} \\ D_1 X_{1,\text{inf}} \end{bmatrix} \quad (1)$$

where

$$\mu_1 = \frac{\mu_{1,\max}}{1 + \frac{K_{S1}}{S_1} + \frac{A_{h1}}{K_{i,1}}} \quad (2)$$

$$A_{h1} = \frac{A_1 H_1^+}{K_e} \quad (3)$$

2.4.2.2. Mass balance equations for anaerobic tank

$$\begin{bmatrix} \frac{dS_3}{dt} \\ \frac{dS_4}{dt} \\ \frac{dX_2}{dt} \\ \frac{dX_3}{dt} \end{bmatrix} = \begin{bmatrix} D_2 & 0 & -\left(D_2 - \frac{1}{V_2}Q_R\right) & 0 & 0 & -\left(\frac{\mu_2}{Y_{h1}} + m_2\right) & 0 \\ 0 & D_2 & 0 & -\left(D_2 - \frac{1}{V_2}Q_R\right) & 0 & \left(\frac{\mu_2}{Y_{A1}} + 0.83m_2\right) & -\left(\frac{\mu_3}{Y_{m2}} + m_3\right) \\ 0 & 0 & 0 & 0 & D_2 & -\left(D_2 - \mu_2 + kd_1\right) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\left(D_2 - \mu_3 + kd_2\right) \end{bmatrix} \times \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ X_1 \\ X_2 \\ X_3 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ \frac{Q_R X_R X_2}{V_2(X_2 + X_3)} \\ \frac{Q_R X_R X_3}{V_2(X_2 + X_3)} \end{bmatrix} \quad (4)$$

where

$$\mu_2 = \frac{\mu_{2,\max}}{1 + \frac{K_{S3}}{S_3} + \frac{A_{h2}}{K_{i,2}}} \quad (5)$$

$$\mu_3 = \frac{\mu_{3,\max}}{1 + \frac{K_m}{A_{h2}} + \frac{A_{h2}}{K_{i,3}}} \quad (6)$$

$$A_{h2} = \frac{A_2\ H_2^+}{K_e} \quad (7)$$

and methane production rate from related mass balance equation:

$$CH_{4\text{Production rate}} = V_{mmax}\ X_3 \left[\frac{A_{h2}}{K_{CH4} + A_{h2}}\right]\left[\frac{K_{im}}{K_{im} + A_{h2}}\right] V_2 - \left(Q_{I,\text{inf}} - Q_{\text{bypass}}\right)[CH_4] \quad (8)$$

A schematic view of ANAMET treatment plant included model variables are given in Fig. 1.

2.4.3. Model solution

Eqs. (1)–(8) were solved simultaneously using the fourth order Runga–Kutta–Gill method [12]. Runga–Kutta–Gill integration algorithm was programmed in Q-Basic and applied in double precision throughout the calculations. In the program optimum step size for time was applied as 5.62 min for the time range of 192 d. The optimum time interval of 5.62 min (0.00390625 d) was found by halving the default step size until same output up to 16th digit was realized.

Kinetic parameters of microorganism growth and substrate consumption used in Eqs. (1)–(8) were imported from various lab-scale studies of literature. Kinetic parameters and related literature sources are presented in Table 2.

ANAMET biological wastewater treatment plant data (a total of 192 d) were used for kinetic modeling. Since numerical solution requires smaller step size of time than a day for accuracy, which is the period of data collection, all values of independent variables are to be represented as a function of time to facilitate a sound interpolation.

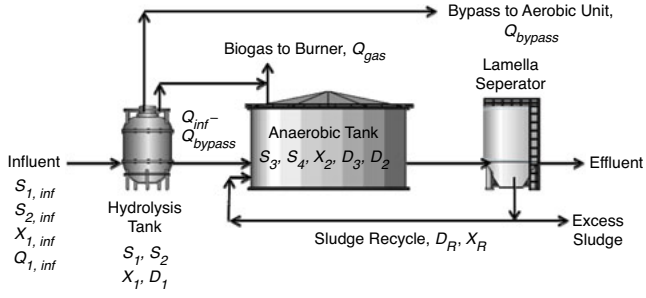

Fig. 1. A schematic view of ANAMET treatment plant.

Table 2
Kinetic parameters of microorganism growth and specific substrate consumption of the related literature

Parameter	Value	Literature
Y_{h1}	0.82 g g^{-1}	[6]
$\mu_{1,\max}$	1.5 d^{-1}	[6]
K_{S1}	260 g m^{-3}	[6]
K_e	1.728.10^{-05}	[6,12]
$K_{i,1}$	20 g m^{-3}	[6]
m_1	12.1 g g^{-1}	[6]
Y_{A1}	0.988	[6]
k_{d1}	0.025 d^{-1}	[22]
$\mu_{2,\max}$	1.5 d^{-1}	[6]
m_2	12.1	[6]
Y_{m2}	0.082	[12]
$\mu_{3,\max}$	0.6 d^{-1}	[12]
K_m	3 g m^{-3}	[6]
$K_{i,3}$	40 g m^{-3}	[6]
m_3	0	–
k_{d2}	0.04 d^{-1}	[22]
$V_{m\ max}$	0.5 g g^{-1}	[6]
K_{CH4}	20.8 g m^{-3}	[6]
K_{im}	5.72 g m^{-3}	[6]
$Y_{a/s}$	0.83	Calculated

For this purpose, sixth order polynomial equation fit was employed for the input variables ($Q_{1,inf}$, Q_{bypass}, Q_R, $S_{1,inf}$, $S_{2,inf}$, $X_{1,inf}$, X_R, pH_1 and pH_2) as a function of time using Excel 7.0 program. However, some of the variables did not correlate well in the constructed polynomial fit equations in the span of 192 d, resulting in poor correlation coefficients. Considering the fact that the use of these data functions with poor correlation coefficients in mass balance equations may produce erroneous results during the solution of the model algorithm, therefore this approach (i.e., the expression of each variable with a single data function for the whole 192-d data) was abandoned. Instead, 192-d data were divided into appropriate 12-, 16-, and 24-d time domains to improve the representation of the unsteady data, and individual sixth order polynomial regression was applied to each input variable data set of the model algorithm. The duration of each time domain was determined in accord with degree of fit to plant data.

By dividing a total of 192-d data of the wastewater treatment plant into 12-, 16- and 24-d sets, 16, 12 and 8 time domains were obtained, respectively. During polynomial regression of $Q_{1,inf}$, Q_{bypass}, Q_R, $S_{1,inf}$, $S_{2,inf}$, $X_{1,inf}$, X_R, pH_1 and pH_2 input variables as a function of time, a total of 144, 108 and 72 data functions were derived for 16, 12 and 8 time domains, respectively. In this case, the model algorithm was operated separately but sequentially with

the data functions derived from individual time domains. In the operation of model algorithm for each time domain, the resulting data from the previous time domain were inserted into the model algorithm as initial condition values for input variables in the present time domain.

During model operation, COD equivalent glucose concentration in anaerobic tank was found to go down to negative values in the calculations. Since a concentration value can be a minimum of zero and in order to prevent miscalculation of other variables in repetitive calculations, a control line was added to the model algorithm to assign the value of 10^{-06} mg l^{-1} to the variable when the calculated value was ≤0.

3. Result and discussion

A simplified kinetic model based on material balances at unsteady state was used to estimate MLVSS, VFA and COD equivalent glucose concentration in hydrolysis tank and MLVSS, VFA and gas production in anaerobic tank of a full-scale ANAMET plant. Except COD variable in anaerobic tank, other variables were simulated by the algorithm of the kinetic model.

3.1. Determination of optimum time domain for input data functions

The best correlation for data function was found in 16-d time domain based on correlation coefficients after plotting the real data and polynomial functions on the same scale as shown in Fig. 2(a)–(i).

At start-up prior to feeding of wastewater to treatment unit, the system was fed with molasses solution for biological acclimation/acceleration of microorganism propagation so that the start-up period could be shortened and sufficient amounts of biomass could be accumulated during treatment process. Consequently, as consistent with the literature [12], the data in first two time domains were not

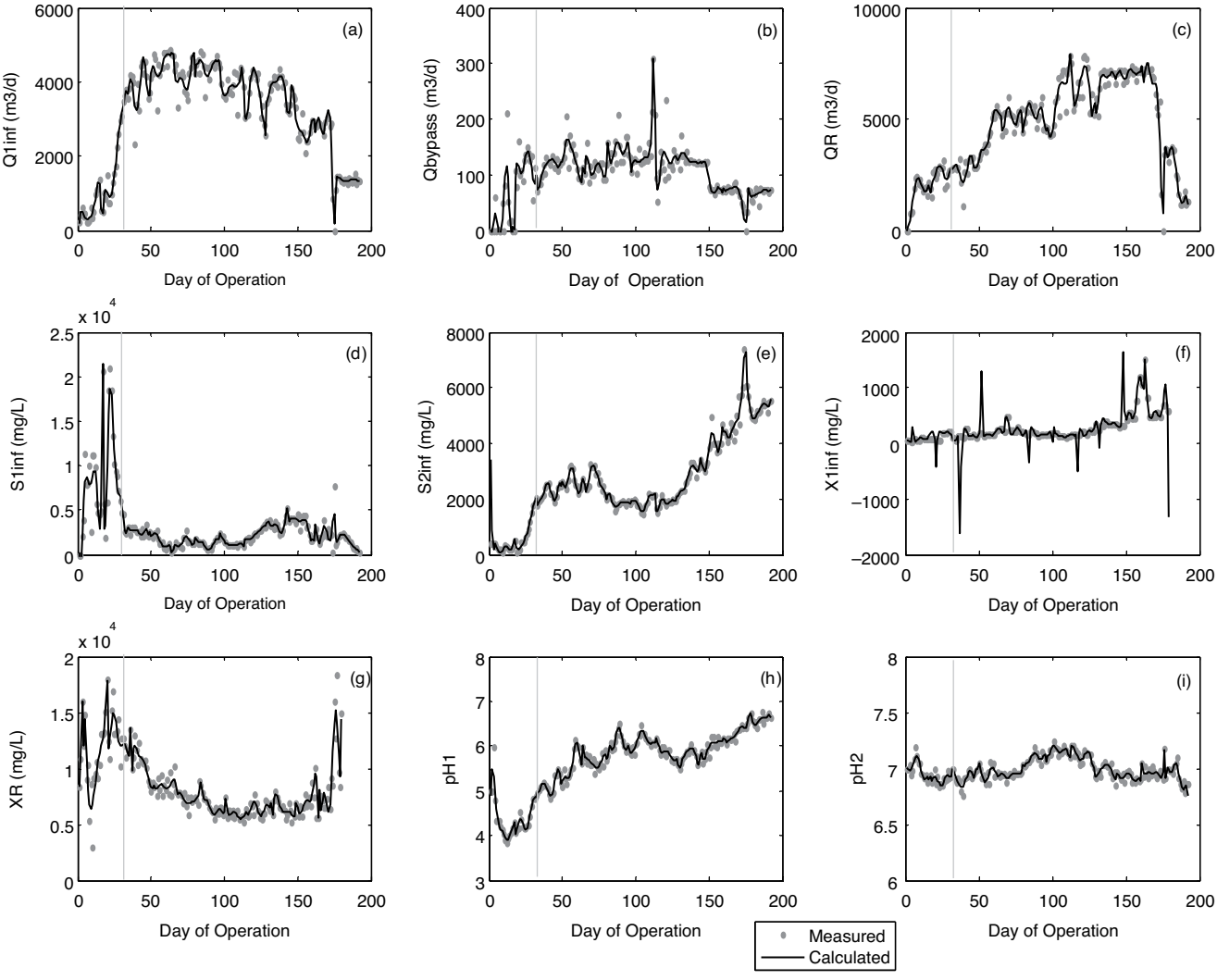

Fig. 2. $Q_{1,inf}$, Q_{bypass}, Q_R, $S_{1,inf}$, $S_{2,inf}$, $X_{1,inf}$, X_R, pH_1 and pH_2 values along with fitted polynomial functions of 16-d time domain.

Table 3
The initial condition values of input variables for each time domain used in model algorithm

16 d -time domain	S_1 (mg l^{-1})	S_2 (mg l^{-1})	S_3 (mg l^{-1})	S_4 (mg l^{-1})	X_1 (mg l^{-1})	X_2 (mg l^{-1})	X_3 (mg l^{-1})
3	2787	1880	182	20	114	1207	5893
4	2137	2824	1.11×10^{-06}	89	106	849	8957
5	9.99×10^{-07}	3114	9.99×10^{-07}	91	162	1003	9781
6	757	2758	1.45×10^{-05}	117	293	1159	10,203
7	1196	2311	9.99×10^{-07}	136	176	1092	8973
8	596	2663	9.99×10^{-07}	125	193	1160	11,209
9	2345	2728	9.99×10^{-07}	82	165	1044	11,594
10	3088	4381	9.99×10^{-06}	94	275	1516	13,926
11	40	5789	8.88×10^{-05}	69	319	1648	17,577
12	9.99×10^{-07}	26,742	9.99×10^{-07}	163	1170	2454	21,260

used in kinetic model due to the significant variations in system operation variables during molasses pre-feeding. Therefore, modeling studies were conducted using data starting from the third time domain. In this respect, in each simulation graph in figures starts from the operation day of 33. Table 3 shows the initial condition values of input variables for each time domain used in model solution.

3.2. Hydrolysis tank

Simulated and measured results of the MLVSS concentration in hydrolysis tank are presented in Fig. 3(a). The correlation coefficient between simulated and measured MLVSS concentrations in hydrolysis tank was found 0.6523. As seen from Fig. 3(a), during the operation, measured MLVSS concentration increased two times to 2000 mg l^{-1} and then decreased. First peak of MLVSS could not be simulated by the model solution, which fluctuated around 500 mg l^{-1}. Rather than due to weak prediction power of the model, there might be an external source of error such as unfiltered beet pulp particles in the fresh wastewater feed from equalization basin. Prior to entering to ANAMET, wastewater was heated in a plate heat exchanger, which was equipped with a basket type filter with screen size of 3 mm. That is, unpredicted rise of MLVSS in tank between 90 and 130 d can stem from the organic particles (beet pulp) having sizes smaller than 3 mm which may pass through the filter. After 130 d, model prediction of MLVSS concentration was consistent with the measured data and the model simulated the rising trend of MLVSS, although not the magnitude.

Simulated and measured results of the VFA concentration in hydrolysis tank are presented in Fig. 3(b). The correlation coefficient between simulated and measured VFA concentrations in the hydrolysis tank was found 0.7986. As seen in Fig. 3(b), except for 175–192 d data, the fitness of simulated and measured VFA concentrations in the hydrolysis tank is quite acceptable.

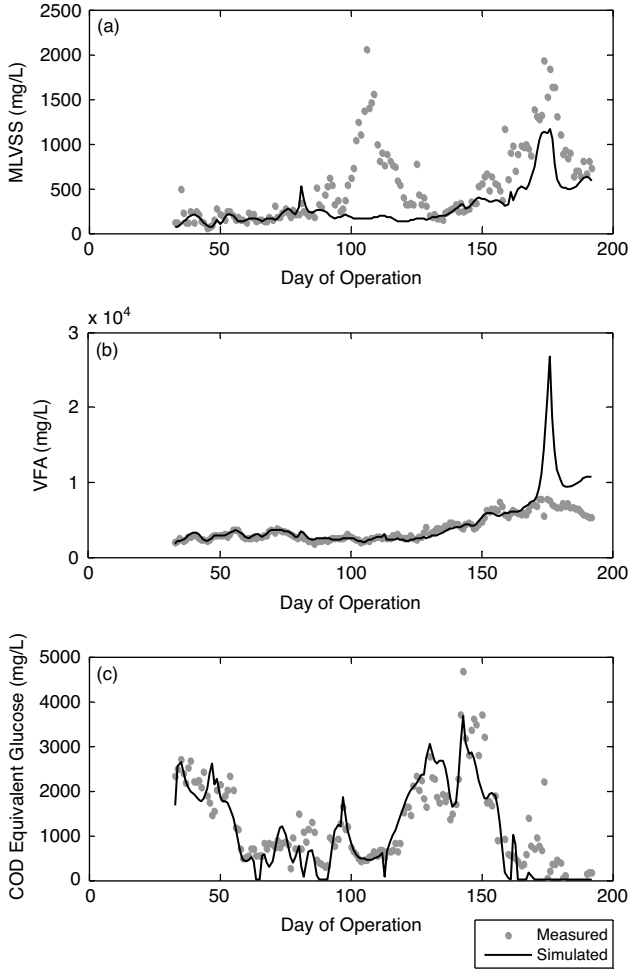

Fig. 3. Simulated and measured results of the MLVSS concentration (a) VFA concentration (b) and COD equivalent glucose concentration (c) versus time in hydrolysis tank.

Fig. 3(c) depicts simulated and measured COD equivalent glucose concentration results in the hydrolysis tank. The correlation coefficient between simulated

and measured COD equivalent glucose concentrations in hydrolysis tank was found 0.8584, denoting a fair prediction power. After 172 d, glucose concentrations were simulated as zero by the model, whereas average COD equivalent glucose concentration was measured approximately 559 mg l^{-1} between 172 and 183 d. Except last 3 d, between 184 and 189 d COD equivalent glucose concentrations were calculated about zero. This means that VFA equivalent COD concentration is approximately equal total COD concentration in hydrolysis tank. After the day of 160 in Fig. 3(a), MLVSS concentration increased more than the simulated results, while in Fig. 3(b) VFA concentration increased less than the simulated values. These results imply that glucose in hydrolysis tank was converted into VFA, and elevated MLVSS concentration (Fig. 3(a)) was not only due to organic particles escaped from the filter basket but also microorganism grown on this organic feed.

Except for unexpected peaks and drops due to operational problems, established model and kinetic parameters imported from the literature were found convenient for the prediction of MLVSS, VFA and COD equivalent glucose concentrations in hydrolysis tank.

3.3. Anaerobic tank

Simulated MLVSS (total of methanogenic and acidogenic microorganisms) and measured MLVSS concentration time profiles in anaerobic tank are presented in Fig. 4(a). Simulated methanogenic and acidogenic microorganism concentrations were summed up in daily basis to express the total MLVSS in anaerobic tank. In Fig. 4(a), MLVSS concentration was measured in the range 4000–8000 mg l^{-1}, while, simulated MLVSS concentrations were higher than measured. The correlation coefficient between simulated and measured MLVSS concentration in anaerobic tank was found 0.3174, denoting an unsatisfactory fit of the model. This result is most likely due to inappropriate kinetic parameters of literature related to yield factor $Y_{x/s}$ for acidogenic and methanogenic microorganisms in anaerobic tank as well as to data function of sludge recycle variable in model solution with a low correlation coefficient, as seen from Fig. 2(c) and (g). Moreover, due to lower VFA concentration observed in anaerobic tank than those of simulated (Fig. 4(b)), the inhibition effect of ionized acetic acid on acidogenic microorganisms considered in the model might have been negligible resulting in increased population of acidogenic culture in the anaerobic tank.

Simulated and measured results of the VFA concentration in anaerobic tank are depicted in Fig. 4(b). As seen from Fig. 4(b), measured VFA concentrations were obtained approximately 20–40 mg l^{-1} whereas simulated VFA concentrations were calculated in the range 60–180 mg l^{-1} resulting in a low correlation coefficient ($R = 0.1$) for model prediction to estimate VFA in anaerobic tank. As explained for MLVSS in Fig. 4(a), the amount of acidogenic microorganisms passing to anaerobic tank is more than anticipated by the model and has a higher kinetic activity.

Simulated glucose concentration were found zero in anaerobic tank indicating that unhydrolyzed glucose coming from the hydrolysis tank were totally converted to volatile fatty acids. For this reason glucose equivalent COD concentration was zero and comparison of simulated and measured COD concentrations was not performed. Nevertheless, semi-experimental COD concentrations were calculated by the summation of simulated VFA and analyzed NH_4^+–N in treated wastewater. Equivalent COD of 1 g HAc and 1 g NH_4^+–N were assumed 1.066 and 4.57 g O_2, respectively as stated Henze et al. and Grady et al. [23,24]. The model was aimed to simulate glucose equivalent COD, VFA and MLVSS for hydrolysis and anaerobic tank in a real scale industrial wastewater treatment plant. Moreover, influent average NH_4^+–N concentration analyzed as 11.9 g N m^{-3} indicated a low concentration; developed model considers that NH_4^+–N did not cause inhibition effect for growth kinetics of methanogenic bacteria. From these points of view, mass balance equation for NH_4^+–N was not performed.

Semi-experimental and measured COD concentrations in anaerobic tank are presented in Fig. 4(c). The correlation coefficient between semi experimental and measured COD concentration was found very low most likely due to high values of simulated VFA concentrations and unmatched kinetic parameters from literature.

Simulated and measured results of the biogas production are presented in Fig. 4(d). The correlation coefficient between simulated and measured biogas production was also found very low. But, simulated biogas production level corresponds well to the measured biogas production except ending periods of operation day.

There are numerous dynamic kinetic modeling of anaerobic digestion in literature, but only few were addressed to pilot and real scale applications. Bernard et al. applied dynamical modeling to the pilot plant anaerobic up flow fixed bed digester treating distillery vinasse [3]. They simplified the process by considering two main bacterial populations i.e., acidogenic and methanogenic bacteria and they assumed that anaerobic digestion can be described as a two-stage process. Biogas flow rate, COD, VFA and total VSS concentration were predicted quite well under steady state conditions. Blumensaat and Keller applied ADM1 modeling to the pilot scale two-stage sewage sludge digestion [25]. An iterative and heuristic method was applied to estimate the kinetic parameters for both thermophilic and mesophilic process stages. Simulated VFA components

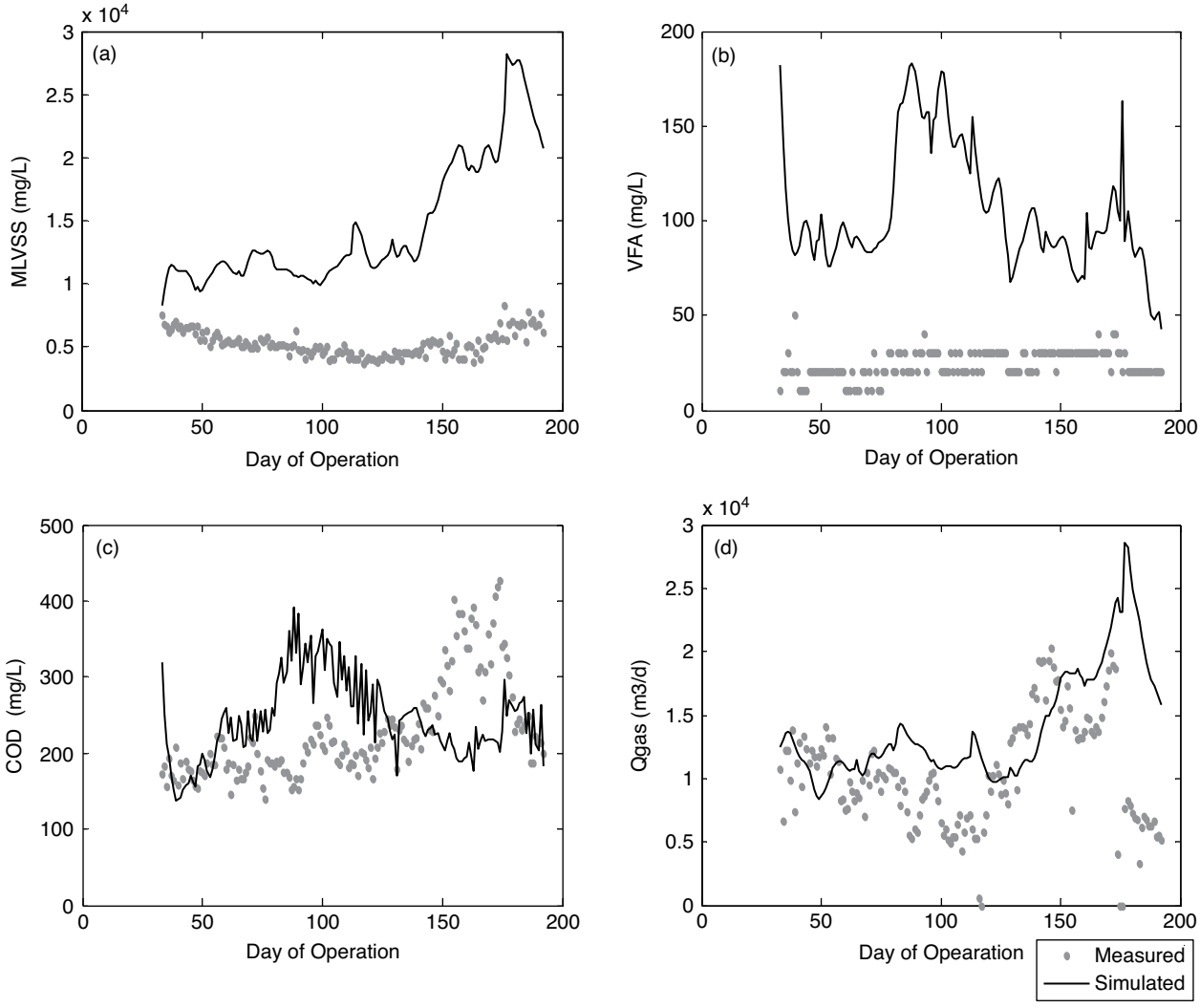

Fig. 4. Simulated and measured results of MLVSS concentration (a) VFA concentration (b) COD concentration (c) and biogas production (d) versus time profiles in anaerobic tank.

(acetate and propionate) and biogas production for thermophilic and mesophilic reactors were compared with experimental data. VFA production was predicted well in the first stage, but not in the second stage, and prediction of biogas production for thermophilic and mesophilic reactors was presented with some deviations. The authors pointed out that current understanding of modeling of anaerobic digestion was insufficient and good parameter estimation was crucially important for validation. Batstone and Keller also applied ADM1 to the case studies of contract work on industrial treatment plants [26]. First industrial plant has a mixed acidification reactor and methanogenic UASB reactor treating recycling paper mill wastewater where COD concentration entering to the latter was assumed to be monosaccaharides. The model simulated biogas flow rate quite well, but acetate concentration was simulated quite poor. The second industrial plant modeled was an anaerobic solids digester fed with solids and concentrated liquid streams from gelatine processing. Simulated results for acetate concentration and methane production under thermophilic and mesophilic conditions were in acceptable level. The authors indicated that high accuracy of all predictions is not required, as only a limited number of simulation outputs are of relevance, and the accuracy of these can be estimated quite well with some practical considerations. They also argued that using the model allowed a much better understanding of the governing process in full scale reactors and therefore making a good assessment of the possible impacts of operational modifications [26].

In this study, kinetic parameters used in mass balance equations were not obtained from the laboratory scale experiments rather imported from literature studies, but not specific to sugar factory wastewater and microorganisms in anaerobic plant since that data are

not available in literature. Moreover, the model was intended to predict the behavior of the treatment plant under unsteady conditions, in contrast to other studies of pilot and industrial scale operating at steady state. Nevertheless, in modeling studies of hydrolysis tank, kinetic parameters taken form literature fit the model satisfactorily and model simulations were in good agreement with measured results of the acidogenic microorganisms (MLVSS) concentration, VFA and COD equivalent glucose. However, modeling of anaerobic tank yielded poor simulation results most likely due to inappropriate kinetic parameters of anaerobic microorganisms taken from literature.

In conclusion, the kinetic model prediction power can be improved if the bio-kinetic parameters are determined through lab-scale experiments or obtained from application of parameter estimation and optimization techniques using plant data.

4. Conclusions

In this paper a simplified kinetic model describing the behavior of a sugar factory anaerobic wastewater treatment plant under unsteady conditions has been constructed and presented. The model is based on unsteady mass balance considerations and accounts for the main steps of the process. Kinetic parameters given in literature were used in this modeling study. The model predicted satisfactorily the behavior of hydrolysis tank variables, while prediction power dropped for anaerobic tank variables most likely due to imported kinetic parameters not specific to sugar factory wastewater and related culture.

The results indicate that model estimation power can be upgraded by using genuine kinetic parameters for sugar factory wastewater which can be obtained through laboratory study or parameter estimation and evaluation of the industrial plant data in operation.

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Symbols

$Q_{1,\text{inf}}$ — influent flow rate, $m^3\ d^{-1}$
Q_{bypass} — bypass flow rate, $m^3\ d^{-1}$
Q_{gas} — biogas flow rate, $m^3\ d^{-1}$
$S_{1,\text{inf}}$ — influent COD equivalent glucose concentration, mg l^{-1}
$S_{2,\text{inf}}$ — influent VFA concentration, mg l^{-1}
S_1 — COD equivalent glucose concentration in hydrolysis tank, mg l^{-1}
S_2 — VFA concentration in hydrolysis tank, mg l^{-1}
S_3 — COD equivalent glucose concentration in anaerobic tank, mg l^{-1}
S_4 — VFA concentration in anaerobic tank, mg l^{-1}
$X_{1,\text{inf}}$ — acidogenic microorganisms concentration in influent, mg l^{-1}
X_1 — acidogenic microorganisms concentration in hydrolysis tank, mg l^{-1}
X_2 — acidogenic microorganisms concentration in anaerobic tank, mg l^{-1}
X_3 — methanogenic microorganisms concentration in anaerobic tank, mg l^{-1}
X_R — microorganisms concentration of anaerobic tank sludge recycle, mg l^{-1}
D_1 — dilution rate in hydrolsis tank, d^{-1}
D_2 — dilution rate in anaerobic tank, d^{-1}
μ_1 — specific growth rate of acidogenic microorganism in hydrolysis tank, d^{-1}
μ_2 — specific growth rate of acidogenic microorganisms in anaerobic tank, d^{-1}
μ_3 — specific growth rate of methanogenic microorganisms in anaerobic tank, d^{-1}
$\mu_{1,\text{max}}$ — maximum specific growth rate of acidogenic microorganism in hydrolysis tank, d^{-1}
$\mu_{2,\text{max}}$ — maximum specific growth rate of acidogenic microorganisms in anaerobic tank, d^{-1}
$\mu_{3,\text{max}}$ — maximum specific growth rate of methanogenic microorganisms in anaerobic tank, d^{-1}
m_1 — maintanance constant of acidogenic microorganisms in hydroylsis tank, g glucose g $cell^{-1}$ d^{-1}
m_2 — maintanance constant of acidogenic microorganisms in anaerobic tank, g glucose g $cell^{-1}$ d^{-1}
m_3 — maintenance constant for methanogenic microorganisms in anaerobic tank, g acetic acid g $cell^{-1}$ d^{-1}
Y_{h1} — yield coefficient for acidogenic microorganisms on glucose, g cell produced g^{-1} glucose consumed
$Y_{a/s}$ — maximum growth yield of acidogenic microorganisms on glucose, 0.83 g g^{-1}
Y_{A1} — produced acidogenic microorganisms from 1 g VFA, g cell g^{-1} VFA $\left(\frac{Y_{h1}}{Y_{a/s}}\right)$
Y_{m2} — maximum growth yield of methanogenic microorganisms on acetic acid, g cell produced g^{-1} acetic acid consumed

k_{d1} — decay rate of acidogenic microorganisms, d^{-1}

k_{d2} — decay rate of methanogenic microorganisms, d^{-1}

K_{S1} — saturation constant of acidogenic microorganisms growth in hydrolysis tank, g l^{-1}

K_{S3} — saturation constant of acidogenic microorganisms growth in anaerobic tank, g l^{-1}

A_{h1} — unionized VFA concentration in hydrolysis tank, mg l^{-1}

A_{h2} — unionized VFA concentration in anaerobic tank, mg l^{-1}

$K_{i,1}$ — inhibition constant of acidogenic microorganisms growth in hydrolysis tank, g l^{-1}

$K_{i,2}$ — inhibition constant of acidogenic microorganisms growth in anaerobic tank, g l^{-1}

$K_{i,3}$ — inhibition constant of methanogenic microorganisms growth in anaerobic tank, g l^{-1}

A_1 — total VFA concentration in hydrolysis tank, mg l^{-1}

A_2 — total VFA concentration in anaerobic tank, mg l^{-1}

K_e — dissociation constant for acetic acid at 35°C

H_1^+ — hydrogen ion concentration in hydrolysis tank, mol l^{-1}

H_2^+ — hydrogen ion concentration in anaerobic tank, mol l^{-1}

K_m — saturation constant for methanogenic microorganisms growth, g l^{-1}

$V_{m\,max}$ — maximum methane production rate produced by 1 g methanogenic microorganisms, g CH_4 g $cell^{-1}$ d^{-1}

K_{CH4} — saturation constant of methane production, g l^{-1}

K_{im} — inhibition constant of acetic acid on methane production

V_2 — anaerobic tank volume, m^3

$[CH_4]$ — methane percentage in biogas, v/v %

COD — chemical oxygen demand, mg COD l^{-1}

VFA — volatile fatty acid, mg HAc l^{-1}

MLVSS — mixed liquor volatile suspended solids, mg l^{-1}

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