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Anaerobic Digestion Model to Enhance Treatment of Brewery Wastewater for Biogas Production Using UASB Reactor

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Abstract Biogas produced from an upflow anaerobic sludge blanket (UASB) reactor is a clean and an environmentally friendly by-product that could be used to meet partial energy needs. In this study, a modified methane generation model (MMGM) was developed on the basis of mass balance principles to predict and increase methane production rate in a UASB reactor during anaerobic fermentation of brewery wastewater. Model coefficients were determined using the data collected from a full-scale reactor. The results showed that the composition of wastewater and operational conditions of the reactor strongly influence the kinetics of the digestion process. Simulation of the reactor process using the model was used to predict the effect of organic loading rate and temperature on methane production with an optimum methane production at 29 °C and 8.26 g COD/L/day. Methane production rate increased from 0.29 to 1.46 L CH_4/g COD, when the loading rate was increased from 2.0 to 8.26 g COD/L/day. The results showed the applicability of MMGM to predict usable methane component of biogas produced during anaerobic digestion of brewery wastewater. This study would help industries to predict and increase the generation of renewable energy by improving methane production from a UASB reactor. To the best of our knowledge, MMGM is the first reported developed model that could serve as a predictive tool for brewery wastewater treatment plant available in the literature.

Keywords Bio-kinetic · Brewery wastewater · Methane generation model · Upflow anaerobic sludge blanket reactor · Volumetric methane production

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Abbreviations

B	Actual volume of methane produced (in litres) per gram of COD (substrate) added to the reactor at S.T.P.
NH_3	Ammonia
AD	Anaerobic digestion
CO_2	Carbon dioxide
COD	Chemical oxygen demand
X_e	Concentration of biomass in the effluent (g/L)
X_i	Concentration of biomass in the influent (g/L)
X_r	Concentration of biomass in the reactor (g/L)
S	Concentration of substrate (g COD/L)
S_r	Concentration of substrate in the reactor (g/L)
b	Dimensionless kinetic parameter
S_e	Effluent substrate concentration (g/L)
K_d	Endogenous decay coefficient (/day)
K	First-order kinetic constant
Q	Flow rate (L/day)
P	Fraction of biodegradable COD
Y	Growth yield coefficient (g/g)
θ_h	Hydraulic retention time (/time)
S_i	Influent substrate concentration (g/L)
μ_{max}	Maximum growth rate of microorganisms when the substrate is being used at its maximum rate
CH_4	Methane
X	Microbial cell concentration (g/L)
T	Operational temperature (°C)
$\frac{dS}{dt}$	Rate of substrate removal (g/L/day)

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V_r	Reactor volume (L)
$\frac{dX}{dt}$	Rate of change in microbial mass (g/L/day)
μ	Specific growth rate of microorganisms (/day)
B_o	Ultimate methane yield coefficient under normal conditions of temperature and pressure per gram of substrate (COD) added for complete utilization of substrate or at an infinite hydraulic retention time
Y_v	Volumetric methane production rate (L methane/g COD $_{added}$/day)

1 Introduction

Recovery of bioenergy from spent biomass, industrial wastewaters and other types of waste is commonly achieved through the conventional anaerobic digestion (AD) process [16]. AD technology, such as the upflow anaerobic sludge blanket (UASB) reactor technology is used for the treatment of different types of wastewater for biogas production. The efficient functioning of biogas production systems provides different benefits to users and the community resulting in energy and cost savings, environmental protection and conservation of resources [34, 40]. However, bioconversion of organic substances to biogas depends on many operational factors [32]. Sometimes, reactors may fail or encounter serious problems, depending on factors such as influent composition, pH, temperature, organic loading rate (OLR), hydraulic retention time (HRT) and carbon to nitrogen ratio of the source material. These factors affect microorganisms that are responsible for the degradation of organic matter in bioreactors [37].

A UASB reactor depends on granular sludge as the core unit in order to convert the organic component of wastewater to biogas [7, 27]. The sludge granules consist of dense microbial communities that typically include various bacterial communities in the sludge bed [17], and the gas-liquid-solid phase at the top of the UASB reactor helps in sludge retention. Optimal operational conditions of upflow velocity, influent COD, pH and temperature are needed for efficient biological treatment of wastewater to produce biogas in the UASB reactor [43]. Thus, it is important to improve the operational parameters in order to enhance the efficiency of the UASB digestion process particularly for the production of methane (CH_4)-rich biogas. This could be done by several methods such as predicting and optimizing the operational conditions; satisfying the nutritional requirements of microbes by using different biological and chemical additives and manipulating the feed proportions [44]. Some other ways include the recirculation of digested slurry, returning microbes back into the reactor and modifying existing biogas plant design [44]. Hence, an in-depth understanding of process dynamics including (i) feedstock characteristics, (ii) operational and environmental parameters, (iii) reactor design and (iv) microbial ecology are important for the optimization of AD systems.

A simple mathematical model that defines some of the conditions that describe the anaerobic treatment process is a generally accepted approach in defining the specific parameters for efficient system performance. Thus, models based on process kinetics can be used to understand the underlying biological and transport mechanisms within the reactor [3], thus, giving more useful information on the state of the reactor and any impending failure.

Recently, mathematical modelling of bioreactors has greatly helped in controlling and improving the treatment efficiency of such systems, as well as in facilitating the experimental procedure to enhance the degradation of organic material in the waste feedstock used for biogas production (especially methane) [10, 23, 28, 30, 50] and to improve the effluent quality [2]. Models have been used to account for reactor performance along with the associated principles and conditions that affect CH_4 production [35]. In addition, models could be used to predict the compounds that are produced or consumed as well as the rate of production [31, 39]. The results of modelling can be used to estimate treatment efficiencies and system characteristics of full-scale reactors operating under similar conditions.

To study the kinetics of biogas formation from complex organic matter, two approaches can be adopted. The first approach is to find the rate-limiting substrate for the kinetic evaluation, and the second approach is the use of COD or volatile solids concentration as an indicator of substrate concentration [13]. Methane production is said to be directly related to COD removal, and biogas yield is not the same as CH_4 yield because the composition of biogas comprises of CH_4, CO_2, water vapour and a few other gases, such as hydrogen sulphide and hydrogen gas [26].

Several studies have been carried out on the development of suitable models that best explain the conditions that will enhance the conversion of organic substances present in the wastewaters to biogas (methane) production during AD [7, 8, 14, 33]. However, one of the main drawbacks of the available mathematical models for anaerobic reactors is their complexity. Several models, based on different concepts and parameters, have been reported to be difficult to apply to a UASB reactor because they involve many variables [14, 39, 49]. The application of these models is limited by the parameters needed to describe them.

For this reason, the development of an applicable model for a UASB reactor with the aim of reducing the complexity will be helpful for better understanding of the behaviour of bioreactor and to enhancing bioenergy generation. More studies are needed to derive simple and convenient models that can predict and optimize biogas yield, especially methane. This paper presents a model that describes the kinetics of an intermittent flow UASB reactor treating brewery wastewater based on mass balance principles. We considered that untreated COD as the primary substrate with no additional oxidizing agents added into the reactor would be converted to biogas (CH_4 and CO_2) [48]. We also considered the reduction of COD to hydrogen gas and hydrogen sulphide as insignificant in this study [13]. At standard temperature and pressure (STP), the digestion of 1 g COD added is equal to the formation of 0.35 L of CH_4. Thus, knowing the influent COD concentration and quantity, we could deduce the volume of CH_4 produced from a reactor. The remaining COD in the reactor could then be calculated and the energy equivalent released through AD of the wastewater could be determined. This is possible because most of the energy contained in biogas is represented by CH_4. Thus, our model describes the behaviour of the reactor with respect to substrate degradation and the effect of endogenous decay rate on CH_4 production based on modified Chen-Hashimoto equations by Ghaly et al. [20].

2 Materials and Methods

2.1 Ghaly et al. Model

Various mathematical models have been proposed to describe substrate and biomass concentrations as well as biogas production in a batch or continuous process reactor [14, 19, 48]. Among these models for anaerobic digestion, that of Ghaly et al. [20] was found to be suitable for our study. The governing equations for the process are obtained from the mass balance of substrate and concentration of biomass in the reactor compartment (see details in Appendix 1). The model follows Monod kinetics. The principle of the process is based on modified Chen-Hashimoto equations, in which the concentration of biomass in the system depends on the growth and decay rate of microorganisms under steady-state conditions for an intermittent flow of organic matter into the biological treatment unit.

2.2 Modified Methane Generation Model

Ghaly et al. [20] model does not consider temperature or the amount of non-biodegradable COD of the feedstock, which are important factors in wastewater treatment. We now describe the Modified Methane Generation Model (MMGM), which integrates the effect of temperature and non-biodegradable COD, based on the model of Ghaly et al. [20] (Appendix 1 Eq. A.18) using a UASB reactor under anaerobic conditions with the following assumptions:

1. The UASB reactor was treated as a single compartment.
2. It was considered as a completely mixed system with continuous influent flow into the reactor and no return of microbial solids back into the reactor (it is non-recycling).
3. The substrate was a single biodegradable substance.
4. Substrate consumers were uniformly distributed in the reactor (bed and blanket) under perfect mixing.
5. Reactor operation is at steady state.
6. The kinetic model follows first-order kinetics using the Monod model with respect to substrate and biomass concentration.

The developed model outcomes include the quantification of the growth rate of biomass, substrate consumption and the effect of endogenous decay on biogas formation. The ultimate methane yield coefficient B_o is assumed to be constant based on the literature survey. Studies have shown that B_o depends on the organic loading rate (OLR), which is the sludge or hydraulic retention time used during the treatment of brewery wastewater [32, 19]. Oktem and Tufekei [32] investigated a pilot scale UASB reactor for the treatment of brewery wastewater in the mesophilic range. An increase in methane yield of 0.25–0.30 m^3 CH_4/kg $COD_{removed}$ was observed when OLR was increased with a rise in COD removal efficiency from 60 to 95 %.

As observed by Chen and Hashimoto [13] and Yetilmezsoy [45], the value of B_o depends on the type of waste that is being treated and the environmental conditions. Most especially, bioreactor temperature was mentioned to affect the ultimate methane yield coefficient [13, 45]. Therefore, we added operational temperature to our calculations (Eq. A.18). Chen and Hashimoto [13] defined an empirical relationship between the maximum specific microbial growth rate (μ_m) and temperature (T) for temperatures between 20 and 60 °C on the analysis of data sets obtained from the literature as found in Eq. (1) [45].

$$\mu_m = 0.013(T) - 0.129 \quad (1)$$

Studies have shown that maximum specific microbial growth rate in the Chen and Hashimoto equation (Eq. (1)) depends on operational temperature and it increases linearly as the temperature increases [41, 46]. Therefore Eq. (1) can be substituted into Eq. A.18 to obtain Eq. (2).

$$Y_v = \frac{B_o S_i}{\theta_h}\left[1 - \frac{K}{\frac{[\theta_h \ (0.013 \ (T) - 0.129)]}{K_d \theta_h + 1} + (K - 1)}\right]. \quad (2)$$

According to the model (Eq. (2)), the theoretical methane output for any given values of S_i and θ_h is determined by the specific characteristics of the biodegradation of substrate and the first-order kinetic constant coefficient, K and μ_{max} (See notation for definition). In addition, the value of K, according to the Monod equation, may be associated with the ability of microorganisms to degrade the substrate present in the waste to produce methane. A high K value is an indication that the microorganisms present in the reactor have greater difficulty in converting the organic matter to methane [19]. The physicochemical parameters such as temperature have been shown to be the primary factors affecting μ_{max}. The effect of temperature on μ_{max} could be described by the empirical relationship mentioned in Eq. (1); for K, the concentration of the organic matter in the substrate and for B_o the kind of substrate. The biodegradable substrate in the reactor in terms of its COD concentration is considered to be directly proportional to the actual methane generated under normal conditions of temperature and pressure. The fraction of non-biodegradable COD (Eq. (3)) was included in the model with respect to the initial substrate concentration, where P is the fraction of biodegradable COD removed:

$$_{\mathrm{nb}}\mathrm{COD} = (1-P) \qquad 0 \leq P \leq 1 \tag{3}$$

Hence, Eq. (2) can be written as shown below (Eq. 4), which indicates that the biodegradable substrate concentration in the reactor is directly proportional to the actual methane volume. Then, modified methane generation model (MMGM) can be obtained as:

$$Y_{\mathrm{V}} = \frac{(1-P)\ B_o S_i}{\theta_h}\left[1-\frac{K}{\frac{[\theta_h\ (0.013\ (\mathrm{T})-0.129)]}{K_d\theta_h+1}+(K-1)}\right]. \tag{4}$$

The kinetic constant K shows the level of microbial growth in the digestion process. This is an extension of Ghaly et al. [20] model. This model can be used for anaerobic processes at steady-state operation under perfect mixing and also takes into consideration the material balance for a mixed reaction; the substrate being the rate-limiting factor. The design and operation of an anaerobic digestion system is based on fundamental knowledge of kinetics and stoichiometry of biological reactions. Thus, prediction of industrial-scale anaerobic reactor performance based on UASB technology in treating brewery wastewater depends on the estimated values of parameters such as K, μ_{max}, K_d, Y and B_o. Often, the kinetic values estimated from laboratory-scale data are inadequate to describe the actual plant performance [22, 38]. Thus, it is important to determine these parameters from the actual full-scale treatment plant data such as the influent and effluent COD concentration, VSS concentration in the reactor, flow rate and reactor volume. The determination of model coefficients (K, B_o, μ_{max} and K_d) is important for the validation of the model to predict and to optimize not only the volumetric methane production rate of a UASB reactor treating brewery wastewater, but also other different wastewater sources.

2.3 Determination of MMGM Parameters (K, μ_{max}, K_d, Y and B_o)

The determination of a first-order reaction is represented by Chen and Hashimoto [13]. They developed a kinetic model based on substrate utilization of the Contois model as:

$$\frac{\mu_{max}}{\mu} = K\frac{S_i - S_e}{S_e} + 1. \tag{5}$$

This model has been widely adopted and used in many studies in the investigation of anaerobic treatment of high-strength wastewater [11, 45, 48]. Equation (5) becomes Eq. (6) when divided by μ_{max}.

$$\frac{1}{\mu} = \frac{1}{\mu_{max}} + \frac{K}{\mu_{max}}\frac{S_i - S_e}{S_e}. \tag{6}$$

In a completely mixed system,

$$\frac{1}{\mu_{max}} = \theta_h \ \text{ and } \theta_h = \frac{1}{\mu_{max}} + \frac{K}{\mu_{max}}\frac{S_i - S_e}{S_e} \tag{7}$$

$$\text{Let} \quad \frac{S_i - S_e}{S_e} = S. \tag{8}$$

Then, the first-order kinetic constant coefficient K and μ_{max} can be determined by plotting θ_h against S using Eq. (7). The ultimate methane yield (B_o) is the intercept obtained from the straight line graph between the actual methane yield and reciprocal of hydraulic retention time ($1/\theta_h$) determined using a least-square method through nonlinear regression. The endogenous decay constant, K_d, of the model can be determined as a function of HRT and VSS values using equation proposed by Bhunia and Ghangrekar [9], Eqs. (9) or (10). These equations

Table 1 Influent and effluent composition of the full-scale UASB treating brewery wastewater and the biogas composition

(a) Wastewater concentrations		
Parameters	Digester inflow[a]	Digester outflow[a]
Temperature (°C)	29.21	29.46
pH	6.90	6.93
COD	2005.73	457.25
BOD_5	1877.09	370.46
TSS	2449.40	3268.97
Orthophosphate (mg PO_4/L)	21.25	25.34
Total oxidized nitrogen (mg N/L)	0.52	0.48
Sulphate	178.25	826.28
Alkalinity (mg $CaCO_3$/L)	3172.78	2462.42
(b) Biogas composition[b]		
Biogas content		%
Methane, CH_4		65.9
Carbon dioxide, CO_2		30.7
Nitrogen, N_2		3.4

[a] All the concentrations are mean and in mg/L except otherwise stated

[b] Enitan et al. [17]

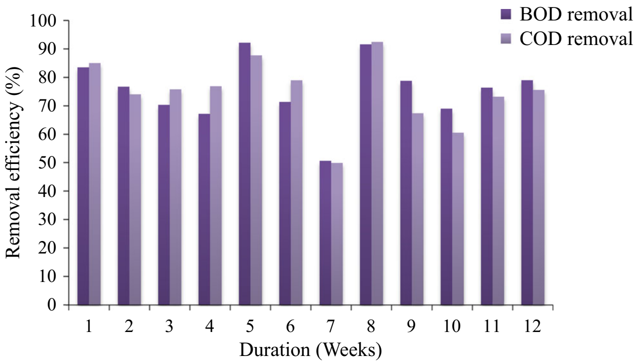


Fig. 1 The time course of COD and BOD_5 removal efficiencies for the full-scale UASB reactor treating brewery wastewater over the period of time in this study

can be used to obtain the values of K_d by plotting a linear regression of $1/\theta_h$ against $(S_i-S_e)/(X_e\theta_h)$. The intercept is equal to K_d and Y is the slope of the straight line that passes through the plotted points.

$$\frac{1}{\theta_h}=\frac{\mathrm{Y.Q}\ \ S_i-S_e}{V_b.X_e.\theta_h}-K_d \tag{9}$$

or

$$\frac{\mathrm{Q}(S_i-S_e)}{V_b.X_e}=\frac{1}{Y}\cdot\frac{1}{\theta_h}+\frac{1}{Y}.K_d. \tag{10}$$

2.4 Software Used and Statistical Analysis

Data obtained from the full-scale reactor were used to derive the parameters in our model. Nonlinear and linear regressions were applied using the GraphPad Prism v. 5.0 program as the statistical software and for drawing of graphs. The nonlinear regression was conducted based on a least-squares method to analyse the predicted methane yield and volumetric methane production rate. Correlation analysis between the observed and the predicted production values was carried out; the probability of fit was calculated and accepted when $P<0.05$. The MMGM equation was coded and simulated using the MATLAB 7.14 software (R2010a, The MathWorks, Inc. Natick, Massachusetts, USA).

2.5 Description of the UASB Reactor System used and Wastewater Sampling

An industrial full-scale UASB reactor treating brewery wastewater was used in this study [17]. For maximum substrate utilization by the microorganisms, different OLRs and the HRT were used in wastewater treatment. The biogas produced in the reactor was separated from the effluent and the biomass in three-phase separators at the top of the reactor. A series of pre-screened brewery wastewater (reactor influent) and the full-scale UASB reactor effluent ready to discharge into the municipal sewer system were collected in 1-L sterile glass bottles and transported to the laboratory at 4 °C. Physico-chemical analyses were conducted within 48 h of collection with the necessary preservation techniques adapted from standard methods [5]. Biogas evolved from the reactor was collected in a gas holder (Tedlar bag, Sigma-Aldrich) for analysis.

2.6 Analytical Procedure

The influent and effluent samples were analysed for COD, biological oxygen demand (BOD), total oxidized nitrogen (TON), pH, temperature, orthophosphate, total suspended solids (TSS) and sulphate using appropriate classical and instrumental methods according to standard methods [5]. The COD was determined according to standard method 5220D [5] using a microwave digester (Milestone, Start D) and measured using a Thermo Gallery photometric analyser (Thermo Scientific, UK). Temperature and pH were measured daily with a combination of thermometer and pH probe (Beckman pH 211 microprocessor). The biogas produced was collected, and its composition was determined using a gas chromatograph equipped with a thermal conductivity detector. Porapak Q column 1.8 m×2.10 mm with the column oven, injector and detector temperatures set at 40, 100 and 100 °C, respectively,

Table 2 Data (average) obtained from our experimental full-scale UASB reactor treating brewery wastewater

θ_h (h)	Q (L/h)	COD loading rate (g/L)	S_i (g/L)	S_e(g/L)	X_e (g/L)	Methane production (L/h)	Methane yield (L/g COD $_{added}$)
8	167	171.43	1.03	0.52	0	224.30	0.18
9	180	167.24	0.93	0.23	2.19	44.35	0.27
9	300	929.53	3.10	1.01	4.40	219.11	0.24
11	180	520.05	2.89	0.43	1.00	154.67	0.30
12	250	248.66	1.00	0.23	6.11	66.88	0.27
12.1	156	170.16	1.10	0.11	4.00	53.70	0.32
13	300	900.62	3.00	0.23	1.73	291.34	0.32

Table 3 Data used for the determination of MMGM parameters

θ_h	$1/\theta_h$	X_e	$X_e\theta_h$	S_i	S_e	S_i-S_e	$X_e\theta_h/(S_i-S_e)$	$(S_i-S_e)/(X_e\theta_h)$	S (g/L)= (S_i-S_e/S_e)
8	0.13	0	0	1.03	0.51	0.51	0	0	1.00
9	0.11	2.19	19.71	0.93	0.23	0.70	28.00	0.04	3.13
9	0.11	4.40	39.60	3.10	1.01	2.09	18.98	0.05	2.06
11	0.09	1.00	11.03	2.89	0.43	2.46	4.49	0.22	5.66
12	0.08	6.11	73.34	1.00	0.23	0.76	95.96	0.01	3.32
12.1	0.08	4.00	48.40	1.10	0.11	0.98	49.21	0.02	9.18
13	0.08	1.73	22.52	3.00	0.23	2.78	8.12	0.12	12.20

and helium serving as the carrier gas at 20 mL/min. Tests were carried out in duplicate.

2.7 Calculation for Methane Production and Yield

$$\text{Methane production} \quad (L/d) = \frac{\text{Biogas production } (L/d) \times CH_4 \text{ content } (\%)}{100} \tag{11}$$

$$\text{Methane yield(L/day)} = \text{Load of COD to digester(g/day)} \times \text{COD}_{\text{removed}} \times 0.362 \ (\text{L CH}_4/\text{g COD}_{\text{removed}}) \tag{12}$$

3 Results and Discussion

3.1 UASB Reactor Operation

Removal efficiencies for both BOD_5 and COD were found to be 80 and 79 %, respectively, and the mean biogas (methane content) produced was 65.9 %. This indicated that the organic matter in the industrial wastewater was converted to usable biogas with good effluent composition (Table 1). Figure 1 shows the time course for the performance of full-scale UASB reactor in treating brewery wastewater during the monitoring process, in terms of COD and BOD_5 removal efficiencies over the time period. However, the carbon, nitrogen and phosphorus ratio (C/N/P=250:0.07:2.66) indicated low concentration of nitrogen in the influent wastewater to the reactor as shown in Table 1. Therefore, urea was added as supplemental nitrogen source in the influent wastewater to meet the required amount for anaerobic treatment [1].

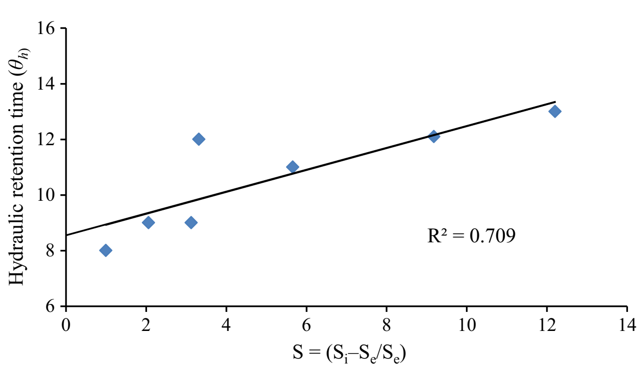


Fig. 2 Estimation of the kinetic parameter, K and the maximum growth rate of microorganism's, μ_{max} from data collected from the full-scale UASB reactor treating brewery wastewater. The plot of θ_h against S [where $S=(S_i-S_e/S_e)$] gives a straight line with 1/intercept as μ_{max} and slope/intercept as K

3.2 Estimated MMGM Parameters

Table 2 shows the experimental data used to determine MMGM parameters as shown in Table 3. The first-order kinetic coefficient K and μ_{max} were determined by plotting θ_h against S using Eq. (7) (Fig. 2). The graph produced a straight line with μ_{max} given by 1/intercept and K as slope/intercept. The values of μ_{max} and K derived in this study were 0.117 day^{-1} and 0.046 g/g, respectively (Table 4). The kinetic parameters could then be used to determine the behaviour of a bioreactor, which would help to characterize the microbial-substrate interaction for better treatment efficiency. The ultimate methane yield (B_o) was determined using a least-square method through nonlinear regression of $1/\theta_h$ and methane

Table 4 Estimated MMGM parameters as obtained using the data collected from the full-scale UASB reactor treating brewery wastewater

Parameter	Estimated value	Units	R^2	P value
μ_{max}	0.117	day^{-1}	0.709	0.017
K	0.046	g/g	0.709	0.017
K_d	0.083	day^{-1}	0.767	0.009
B_o	0.516	L methane/g COD $_{added}$	0.988	0.006
Y	0.357	g/g	0.767	0.009

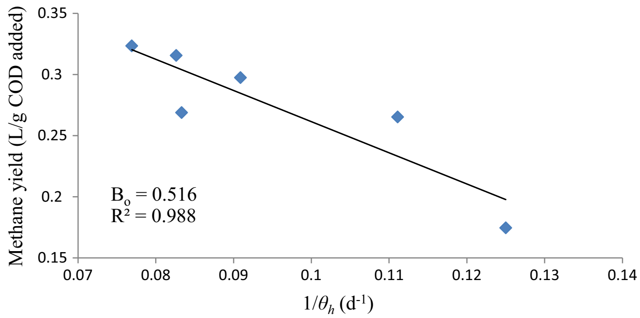


Fig. 3 Ultimate methane yield (B_o) obtained from data collected from the full-scale UASB reactor treating brewery wastewater by plotting methane yield against the reciprocal of hydraulic retention time

yield. Figure 3 shows the graph of methane yield against $1/\theta_h$ with the intercept, B_o, corresponding to 0.516 L CH_4/g COD_{added}. The estimated endogenous decay coefficient, K_d value of 0.083 day^{-1} is represented by the intercept of the graph, while the slope *Y*, correspond to 0.357 g/g as shown in Fig. 4.

The estimated model coefficients for brewery wastewater used in this study are shown in Table 4. The values are within the range of values reported in the literature for mesophilic anaerobic digestion for waste types that include wastewater, banana stem and peel waste, palm oil mill wastewater, dairy manure and the organic fraction of municipal solid waste from a full-scale plant (Table 5). The value of μ_{max} obtained from the UASB reactor treating brewery wastewater was higher than the value (0.111 day^{-1}) reported by Zainol [48] and lower than 0.135 day^{-1} reported by Fdez-Güelfo et al. [19]. However, our value of B_o is very similar to those reported in the literature (Table 5). Hence, the values of coefficients *K*, B_o, μ_{max} and K_d were used to validate the model and to predict treatment efficiency, determine the HRT and predict volumetric methane productivity of an UASB reactor treating brewery wastewater.

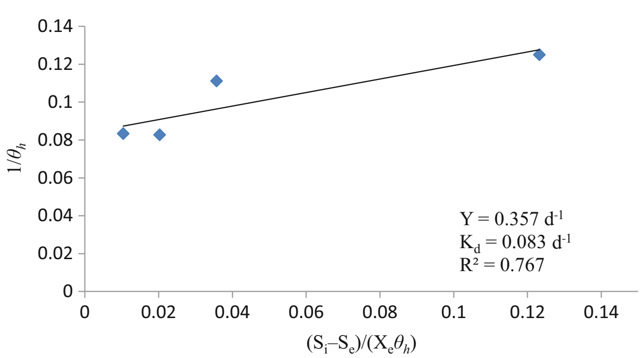


Fig. 4 The endogenous decay coefficient, K_d, and the growth yield coefficient, *Y*, were calculated from the intercept and slope of the straight line of the plotted graph using the data obtained from the full-scale UASB reactor treating brewery wastewater

3.3 Validation of the Modified Methane Generation Model

The values of *K*, μ_{max}, K_d, B_o and θ_h presented in Table 4 were used in the model to simulate methane yield. The simulations were carried out for a fixed substrate concentration at different hydraulic retention times based on Eq. A.16. The simulations indicated the methane yield as a function of hydraulic retention time. The application of the model was shown by regression analysis of the predicted methane yield with determination coefficient of 0.991 at 95 % confidence range with *P* value of 0.0001. Only 0.009 % of the total variations could not be explained by the regression analysis. A high coefficient of determination R^2 of 0.991 shows a strong goodness of fit of the model (Appendix 2). Figure 5 shows the expected behaviour when compared with experimental values obtained from the full-scale reactor investigated. There was a strong correlation coefficient of 0.747 between the predicted and the observed values for methane yield, which showed the applicability of the model to predict methane yield.

In order to further validate our model, the observed volumetric methane production rate and predicted values obtained from our model were compared at different temperatures and OLR. For a randomly selected operating scenario, a volumetric OLR between 2.0 and 11.8 g COD/L/day and the initial substrate concentration (S_i=6 to 12 g COD/L, B_o=0.516, T=26 and 32 °C) using MMGM (Eq. 4) shows that increasing the volumetric OLR to 8.26 g COD/L/day would stimulate good methane yield (corresponding to the maximum volumetric methane production rate of Y_v=1.46 L CH_4/g COD_{added}/day).

To evaluate the fitness of MMGM, the predicted values of the volumetric methane production rates were plotted against the observed values for different OLRs (Fig. 6a), and when the OLR increased from 2.0 to 8.26 g COD/L/day, the predicted Y_v increased from 0.29 to 1.46 L CH_4/g COD_{added}/day. However, Y_v decreased as the OLR rose to 11.8 g COD/L/day. The coefficient of determination value (R^2=0.994) for the methane production rate showed the goodness of fit of our model. The coefficient of determination (R^2=0.994) showed that 99.4 % of the variance in the model could be explained by the model and it was shown to be extremely significant with p<0.0001 (Appendix 3).

A similar trend was noticed in the observed methane production rates, although there was fluctuation in the observed values due to operational and environmental parameters. However, the highest value for the observed Y_v (0.51–0.81 L CH_4/g COD_{added}/day) was recorded at OLR between 4.4 and 9.29 g COD/L/day, and the observed Y_v decreased when the OLR reached 11.8 g COD/L/day. The data indicates that the volumetric methane production rate fluctuate with an increase in OLR up to 2.76 g COD/L/day. Up to this point, the correlation between OLR and Y_v was very strong (R^2=0.990, Appendix 4), showing a linear relationship between these parameters (Fig. 6b). A noticeable decrease in Y_v observed at

Table 5 Kinetic parameters obtained in this study compared to other studies

Substrate	B_o (L CH_4/g COD_{added})	K (g/g COD_{added})	μ_{max} (day^{-1})	K_d (day^{-1})	References
Brewery wastewater	0.516	0.046	0.117	0.083	This study
Banana stem waste	0.326	0.33	0.111	–	[48]
Synthetic organic fraction of municipal solid waste	1.167[a]	–	0.238	–	[19]
Organic fraction of municipal solid waste from a full-scale composting plant	1.15[a]	–	0.135	–	[19]
Distillery spent wash	–	–	2[b]	–	[3]
Vegetable product—pea	0.36	–	–	–	[29]
Vegetable product—leek and fried onion	0.36	–	–	–	[29]
Banana peel	0.277[c]	–	0.089	–	[21]
Palm oil mill wastewater	0.381	–	0.304	–	[18]
Dairy manure at 25 °C	0.230[c]	0.883[c]	0.279	0.038	[20]
Dairy manure at 35 °C	0.230[c]	0.883[c]	0.317	0.036	[20]
Brewery wastewater	–	–	0.022	0.037	[4]

[a] L methane/g DOC

[b] kg m^{-3} day

[c] L methane/g VS added

higher OLR suggested that OLR could influence the kinetic parameters due to presence or accumulation of inhibitors or toxic compounds in the reactor and also reduce volatile solids removal, thus affecting the volumetric methane production rate [6]. However, at higher OLRs, the values between the observed and predicted methane production rates vary considerably and the MMGM overestimated the methane production rates.

A similar trend was reported in the anaerobic digestion of banana stem waste [48] and with a UASB reactor treating poultry manure wastewater [45]. Overloading the bioreactor with a high substrate concentration has been reported to be one of the factors contributing to the reduction in the methane production rate. A reduced methane production rate signifies the presence of a possible inhibiting factor in the process, such as a decrease in pH as a result of an increase in the concentrations of volatile fatty acids [40, 45]. The influence of hydraulic retention time and OLR on the microbial communities and the performance of an anaerobic reactor to treat olive waste at steady state have also been reported [36]. The authors observed the maximum methane production rate of 1.7 L CH_4 STP/L day when the OLR was increased from 1.5 to 9.2 g COD/L/day at 17 days HRT. However, when the OLR was increased to 11.0 g COD/L/day at HRT of 15 days, there was a reduction in the pH value (from 7.5 to 5.3) as well as increase in the effluent total volatile fatty acids by about 400 % [36]. This further confirms that the OLR affects the value of methane production rate.

The effect of operational temperature (26–32 °C) on the volumetric methane production rate (Y_v) was simulated using the developed model in Eq. (4). The predicted volumetric methane rate at 29 °C was higher than that at other

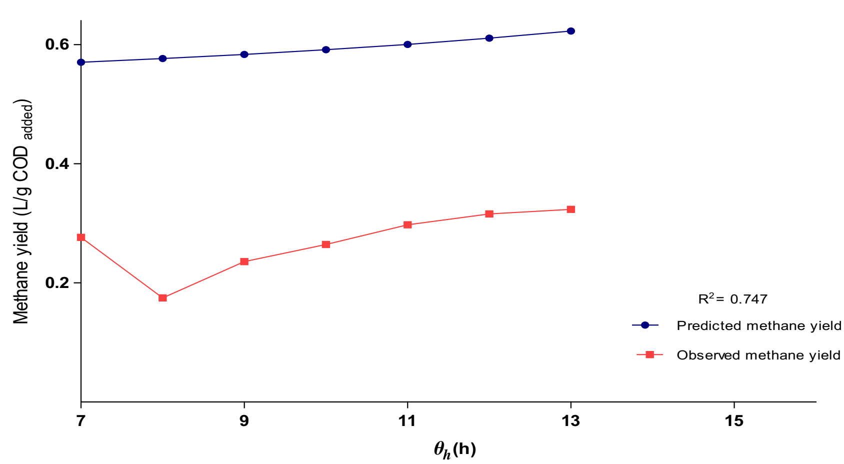


Fig. 5 Observed and predicted methane yields at different hydraulic retention times

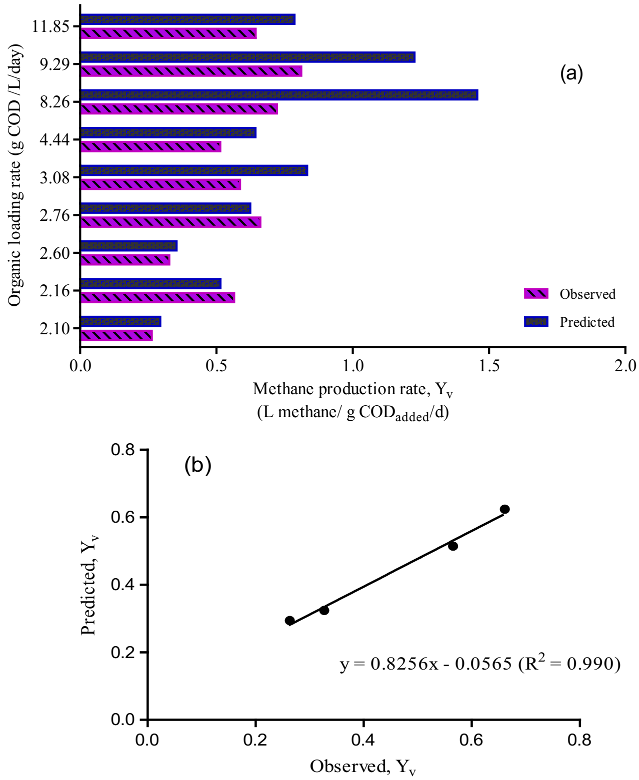


Fig. 6 **a** The trend between observed and predicted volumetric methane production rates at different organic loading rates using the newly developed model and **b** the scatter plot of predicted vs observed volumetric methane production rates at lower organic loading rates

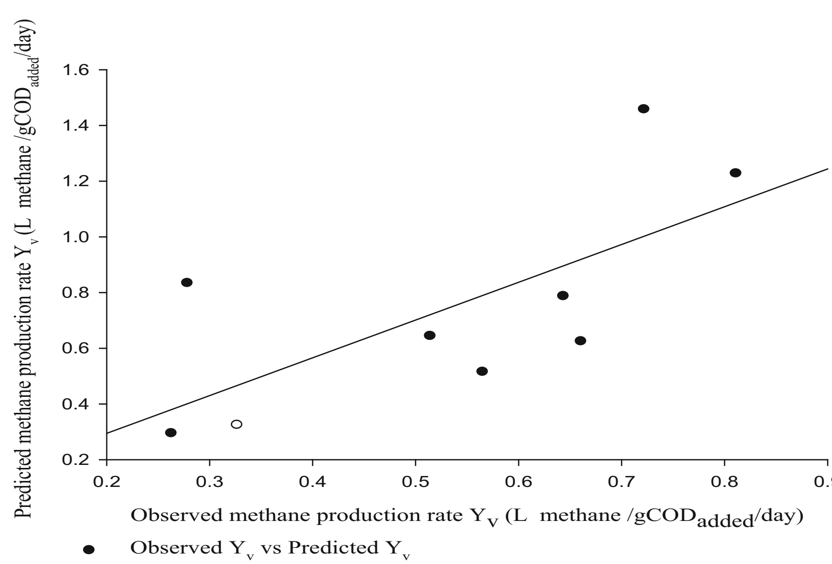
temperatures. Comparison of the predicted and the observed was carried out as shown in Fig. 7. The regression analysis shows the goodness of fit of our model with determination coefficient of 0.717 (Appendix 5). A higher value of the correlation coefficient (R=0.847) shows a strong positive correlation between the predicted and the observed Y_v; this advocate for high significance of the model [25, 47]. Therefore, the modified methane generation model can be used to predict volumetric methane production from a UASB reactor treating brewery wastewater.

The effect of operational temperature on the activity, survival and growth of the microbial consortium in an anaerobic digestion system has been reported by Khalid et al. [24]. Several studies have shown the crucial effect of even a slight change in the operating temperature on biogas production, especially its methane content. Any sudden change might lead to a drastic decrease in biogas production due to change in microbial populations and reduced methane content and volume [12, 42]. Chae et al. [12] reported the maximum methane yield at 35 °C when compared to that at 30 and 25 °C. Therefore, for better treatment efficiency and high volumetric methane rate, operating temperature should be optimized for the reactor design and operation [42, 45].

4 Conclusions

A modified methane generation model (MMGM) for an UASB reactor that treats brewery wastewater was validated with respect to substrate degradation and the effect of endogenous decay rate on the methane production. Quantification of model parameters indicated that the composition of the wastewater strongly affects the kinetics of the digestion process. The developed model (MMGM) predicted the rate of methane production for anaerobic digestion of wastewater at different temperatures and OLRs. We showed that OLR, influent substrate concentration, HRT and operational temperature affect the methane production rate. Even a slight change in the

Fig. 7 The predicted and observed volumetric methane production rates at different temperatures using the newly developed model (MMGM)



operating temperature was demonstrated to result in a sharp decrease or increase in production of biogas, especially methane. The model is easy to use due to its simplicity with only a few variables that facilitate the calibration of the model. It is believed that this model would be used to predict methane production rate of anaerobic digestion process treating brewery wastewater.

Appendix 1

The Microbial Mass Balance

The microbial mass balance of an UASB reactor (Fig. 8) was described as follows by Ghaly et al. [20]:

$$\begin{aligned}\text{Microbial change rate} &= \text{Microbial input rate} + \text{Microbial growth rate} \\ &\quad - \text{Microbial death rate} - \text{Microbial output rate}\end{aligned} \tag{A.1}$$

The microbial growth rates in a batch experiment have traditionally been measured, in which a single species of microorganisms passes through a logarithmic growth phase during the conversion of the organic substrate. The microbial growth rate, dX/dt, is described by

$$\frac{dX}{dt} = \mu X, \tag{A.2}$$

which can be written as

$$\frac{dX}{dt} = \mathrm{QX_i} + \mu X_{\mathrm{r}} V - K_{\mathrm{d}} X_{\mathrm{r}} - \mathrm{QX_e}. \tag{A.3}$$

During steady-state conditions, the biomass concentration in the influent is negligible ($X_i \approx 0$), compared to the biomass concentration in the reactor. In addition, X_r is equal to X_e due to perfect mixing in a completely mixed reactor. The rate of substrate removal from the reactor is therefore neglected. In steady-state conditions, dX/dt=0 and Eq. (A.3) can be rearranged to obtain Eq. (A.4). Thus,

$$\begin{aligned}&Q \quad X_i \approx 0 \\ &0 = X_e(\mu V - K_d V - Q) \\ &\mathrm{Q} = \mathrm{V}\ (\mu - \mathrm{K_d})\end{aligned} \tag{A.4}$$

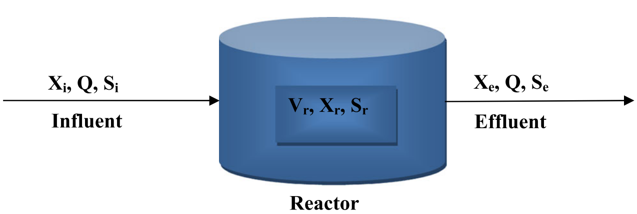


Fig. 8 Schematic diagram of a single compartment of an upflow anaerobic sludge blanket reactor (See abbreviations for definition of symbols)

Eq. (A.4) can be rewritten as

$$\frac{Q}{V} = \mu - K_d. \tag{A.5}$$

The hydraulic retention time, θ_h, is defined as V/Q. The inverse of θ_h can be substituted into Eq (A.4) as

$$\mu - K_{\mathrm{d}} = \frac{1}{\theta_h} \tag{A.6}$$

As shown in Eq. (A.6), the net specific growth rate is $\mu - K_d$.

Substrate Mass Balance and Effluent Substrate Concentration

The rate of substrate balance in the UASB reactor can be expressed using Eq. (A.7)

$$\begin{aligned}[\text{Substrate change rate}] &= [\text{Substrate input rate}] \\ &\quad - [\text{Substrate utilization rate}] \\ &\quad - [\text{Substrate output rate}]\end{aligned} \tag{A.7}$$

Mathematically, Eq. (A.7) can be written as

$$V\frac{dS}{dt} = QS_{\mathrm{i}} - (\mu - K_d)V\frac{X_r}{Y} - QS_{\mathrm{e}}\ . \tag{A.8}$$

At steady state, Eq. (A.8) was divided by V, and Q/V was substituted for θ_h. At equilibrium the substrate balance of a working system was obtained as

$$\frac{S_{\mathrm{i}} - S_{\mathrm{e}}}{\theta_h} = (\mu - K_{\mathrm{d}})\frac{X_{\mathrm{r}}}{Y}. \tag{A.9}$$

Thus, under perfect mixing of the reactor content ($X_r = X_e$), the microbial mass concentration in the effluent can be written as Eq. (A.10). This gives the concentration of microorganism in the effluent as

$$X_{\mathrm{e}} = \frac{Y\ (S_{\mathrm{i}} - S_{\mathrm{e}})}{\theta_h(\mu - K_{\mathrm{d}})}, \tag{A.10}$$

where $(S_i - S_e)/\theta_h$ is the rate of substrate utilization. Contois [15] defined the relationship between limiting substrate concentration and specific growth rate for effluent substrate concentration as

$$\mu = \frac{\mu_{\max} S_r}{bX_r + S_r}. \tag{A.11}$$

Under perfect mixing ($S_e = S_r$ and $X_e = X_r$), the association between the rate-limiting substrate concentration and specific growth rate can be expressed as

$$\mu = \frac{\mu_{\max} S_e}{bX_e + S_e}. \quad (A.12)$$

Equations derived from the combination and rearrangement of Eqs. (A.6), (A.10) and (A.12) are:

$$S_e = \frac{S_i K}{\frac{\mu_{\max}\theta_h}{K_d\theta_h + 1} + (K-1)} \quad (A.13)$$

$$\frac{S_e}{S_i} = \frac{K}{\frac{\mu_{\max}\theta_h}{K_d\theta_h + 1} + (K-1)}, \quad (A.14)$$

where Eq. (A.14) shows that the influent substrate concentration is inversely proportional to the substrate concentration in the final effluent.

Biogas Production

In the reactor, the biodegradable COD is proportional to (B_o-B). B_o is directly proportional to the biodegradable COD loading rate [48]. Therefore, from Eq. (A.14), the methane yield (B) is described by

$$\frac{B_o - B}{B_o} = \frac{K}{\frac{\mu_{\max}\theta_h}{\mu_m\theta_h + 1} + (K-1)}. \quad (A.15)$$

Methane production per gram of substrate (COD) added, B is described by

$$B = B_o\left[1 - \frac{K}{\frac{\mu_m\theta_h}{K_d\theta_h + 1} + (K-1)}\right]. \quad (A.16)$$

Since B is equal to the volume of methane produced per unit of COD added, the volumetric methane production rate, Y_v is equal to B, multiplied by the organic loading rate, S_i/θ_h. The equations describing the theoretical methane output rate per unit of reactor volume therefore are written as Eqs. (A.17) and (A.18):

$$Y_v = \frac{BS_i}{\theta_h} \quad (A.17)$$

$$Y_v = \frac{B_o S_i}{\theta_h}\left[1 - \frac{K}{\frac{\mu_{\max}\theta_h}{K_d\theta_h + 1} + (K-1)}\right] \quad (A.18)$$

Appendix 2

Table 6 Predicted methane yield at different hydraulic retention times

Goodness of fit	
r^2	0.9914
Sy.x	0.00156
Is slope significantly non-zero?	
F	461.9
DFn, DFd	1.000, 4.000
P value	<0.0001
Deviation from zero?	Significant

Appendix 3

Table 7 The trend between observed and predicted volumetric methane production rates at different organic loading rates using the newly developed model (Fig. 6a)

Goodness of fit	
r^2	0.9941
Sy.x	0.001561
Is slope significantly non-zero?	
F	461.9
DFn, DFd	1.000, 4.000
P value	<0.0001
Deviation from zero?	Significant

Appendix 4

Table 8 The scatter plot of predicted vs observed volumetric methane production rates at lower organic loading rates (Fig. 6b)

Goodness of fit	
r^2	0.9902
Is slope significantly non-zero?	
F	201.7
DFn, DFd	1.000, 2.000
P value	<0.0049
Deviation from zero?	Significant

Appendix 5

Table 9 Nonlinear regression for the predicted volumetric methane production rates at different temperatures using the newly developed model (Fig. 7)

R	R sqr.	Adj. R sqr.			
0.8470	0.7174	0.6232			
Analysis of variance:	DF	SS	MS	F	P
Regression	1	0.5875	0.5875	7.6147	0.0702
Residual	7	0.2315	0.0772		
Total	8	0.8190	0.2047		

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