Anaerobic digestion of wastewater from the fruit juice industry: experiments and modeling

Souhaib Zerrouki, Rachida Rihani, Fatiha Bentahar and Khaled Belkacemi

ABSTRACT

Anaerobic digestion of wastewater from the fruit juice industry was carried out in a batch digester. To study the effect of the pH values as well as the nutrient medium on the fermentation process, different parameters were monitored under mesophilic temperature, such as cumulative biogas volume, chemical oxygen demand (COD), total sugar, and biomass growth. It was found that for all cases, the COD concentration decreased with time. The lowest value reached was obtained when the nutrient medium was added; it was about 110 g/L after 480 h. In such cases, the COD removal reached about 80%; the highest cumulative biogas volume of about 5,515.8 NmL was reached after 480 h testing; and the lowest value reached was about 2,862.3 NmL in the case of peach-substrate containing sodium sulfite. The addition of nutrient medium improved the cumulative biogas production as well as the COD abatement. Measurement of the biogas composition highlighted three gaseous components, namely, methane (56.52%), carbon dioxide (20.14%), and hydrogen sulfide (23.34%). The modified Gompertz equation and the first-order kinetic model were used to describe the cumulative biogas production and the organic matter removal, respectively. A good agreement was found between simulated and experimental data.

Key words | batch process, biological treatment, industrial effluents, modelling, nutrient medium, pH

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NOMENCLATURE

B (t)	Cumulative biogas production during the digestion time (NmL)
BOD_5	Biological oxygen demand (g/L)
COD	Chemical oxygen demand (g/L)
d	Difference between measured and predicted values
k	Reaction rate constant (h^{-1}).
L_u	Initial amount of biodegradable organic compounds (g COD/L)
m	Number of data pairs
P	Biogas production potential (NmL)
RMSE	Root mean square error
R^2	Correlation coefficient
R_m	Maximum production rate (h^{-1})
T	Temperature (°C)
t	Time (h)
TS	Total solids
TSS	Total suspended solids (g/L)
VFA	Volatile fatty acids
VSS	Volatile suspended solids (g/L)
Y_t	Amount of organic compounds at time t (g COD/L)
y	Measured values.

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GREEK SYMBOLS

λ	Lag phase duration (h)
μ	Maximum specific growth rate (h^{-1})

INTRODUCTION

Effluents produced from the fruit juice industry have different characteristics, depending on the specific types of fruit processing operations. These effluents include wastewater from washing, rinsing and sanitizing operations during fruit crushing and cleaning of tanks (Noronha *et al.* 2002). The management of these wastes is a major problem for fruit processing industries (Kaparaju & Rintala 2006). Indeed, if not treated, they are a source of odour production, toxic gas emissions, and insect attraction. This situation may lead to water contamination and environmental problems. These wastes include high concentrations of organic materials; the major problems encountered in the treatment of the raw effluents from the fruit juices are low pH values, imbalance of nutrients, and low redox potential (Ozbas *et al.* 2006). The discharge of these types of effluents into urban wastewater treatment plants is not allowed and may require further treatment. To improve treatment, aerobic biotreatment, often followed by anaerobic biotreatment, is mandatory.

In recent years, anaerobic biological treatment of fruit effluent is a process to which more attention has been devoted (Bouallagui *et al.* 2003; Ozbas *et al.* 2006; Fang *et al.* 2011). It is an efficient process in comparison to other biological processes, such as bioenergy from algae. Under ideal conditions, biogas production can be carried out under anaerobic degradation of the organic waste.

The advantages of this fermentation are that it offers a clean and sustainable energy production, a low energy requirement for operation, a low investment cost and waste reduction. It is worth noting that anaerobic digestion produces biogas with a high percentage content of methane. This methane can be burned to produce both heat and electricity that are used to warm the digesters or to heat buildings (Sitorus *et al.* 2013).

The improvement of anaerobic digestion technology depends on the understanding of degradation kinetics, mode of operation, i.e., batch, semi-batch or continuous, and optimization of process parameters (Angelidaki *et al.* 1993). Often, in the normal start-up of a batch digester, a certain amount of inoculum should be added to the substrate in order to enable the required microorganisms to start reactions (Liu *et al.* 2009).

During the methanogenesis stage, biogas is produced by methanogenic bacteria converting acetic acid into CO_2 and methane, or by reduction of CO_2 with hydrogen.

Many digester plants have been built and tested for different wastes and industrial effluents. Mixed batch and up flow anaerobic sludge blanket (UASB) digesters are often employed for liquid effluents. This type of reactor is the one most used for the treatment of industrial wastewater (Gomec 2010; Sevilla-Espinosa *et al.* 2010). For high superficial up-flow velocities and higher loading rates, the expanded granular sludge bed (EGSB) is used; the latter is a modified version of the UASB (Puñal *et al.* 2003; O'Reilly & Colleran 2005).

Bouallagui *et al.* (2003) have successfully applied a tubular semi-continuous mixed mesophilic digester to convert fruit and vegetable wastes into a biogas with high stability. Sitorus *et al.* (2013) have carried out the treatment of mixed fruit and vegetable wastes (made of 80% vegetable waste and 20% fruit waste) in a single stage fed-batch anaerobic reactor operated at ambient temperature. One-stage systems are commonly the preferred systems for full-scale anaerobic digestion of organic solid waste. According to these authors, if the pH value cannot be controlled, the appearance of volatile organic components and carboxylic acids will increase the digester's acidity. Digester performances are often related to the gas yield and the retention time of the feed material as well as its amount and type. The use of the whole pulp for anaerobic digestion requires a very long retention time (40–60 days) under mesophilic fermentation, due mainly to the slow degradation of fibrous components (Calzada *et al.* 1981). Furthermore, a two-phase anaerobic digestion system is better for treating coffee pulp juice than a one-phase unit. In such cases, the retention time of half a day for the acidogenic phase and 8 days for the methanogenic phase provide stable fermentation conditions (Calzada *et al.* 1984).

The aim of the present work is to evaluate the performance of an anaerobic batch digester using high organic content industrial peach-tea substrate juice. Different parameters have been monitored such as biogas volume, chemical oxygen demand (COD), total sugars, medium conductivity, and volatile suspended solids. Furthermore, the modified Gompertz equation (Lay *et al.* 1999) and the first-order kinetic model have been used to describe the cumulative biogas production and the organic matter removal, respectively.

MATERIALS AND METHODS

Experimental set-up

The digester used for the experimental investigations is shown in Figure 1. Anaerobic batch tests were conducted in a cylindrical digester of 0.355 m height and a diameter of 0.15 m. The reactor was equipped with a jacket of height of 0.165 m. It was connected to a water-bath in order to keep a constant temperature during the fermentation process. Batches were filled up with 4.5 L peach-tea raw substrate, 4 L of peach-tea substrate supplemented with 0.5 L of the medium containing glucose (2 g/L); KH_2PO_4 (0.45 g/L); $MgSO_4$ (0.1 g/L); $FeCl_3$ (0.02 g/L); $CaCl_2$ (0.05 g/L); yeast extract (0.5 g/L). On top of the reactor, several pipes were placed in order to monitor different

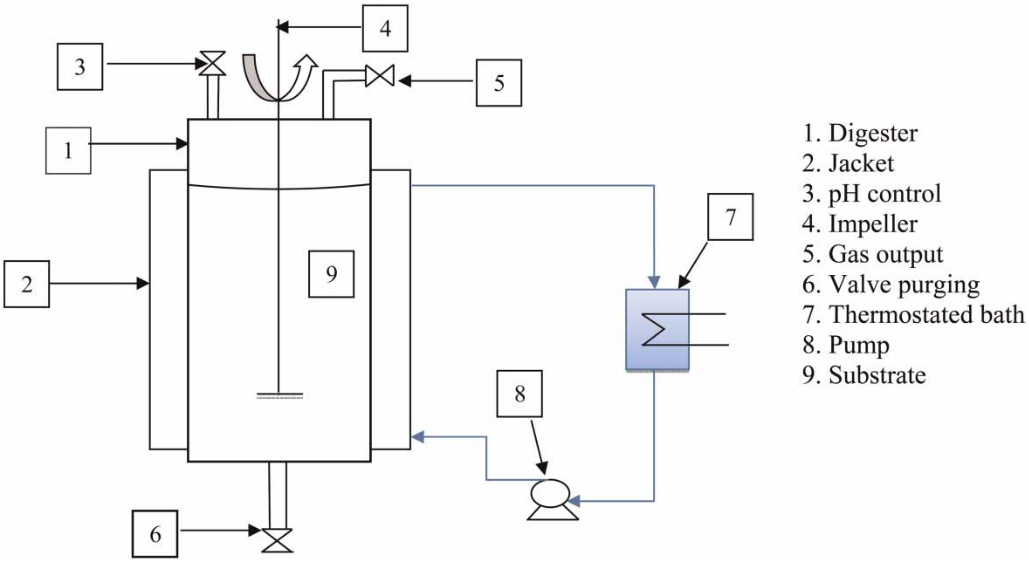

Figure 1 | Experimental set-up.

parameters such as the pH values, the temperature, the conductivity and the output of biogas.

The digester was purged through a valve located at the bottom of the reactor. A stainless steel flange was also included in the digester in order to prevent gas leakage. The mixing during digestion was ensured by an impeller. To avoid gas accumulation in the inner upper zone of the digester, the gas was drawn-off by a gas collecting device. To optimize the operating parameters, especially the pH values for biogas production, in the case of high organic content of peach-tea substrate, the experiments were conducted at initial pH adjusted to the value of 7.35 and at pH value controlled to 7.00 under mesophilic temperature (38 °C). The initial pH value adjustment was carried out by adding 1 M NaOH or 1 M HCl. In this study, the digester was filled initially with 3.36 g/L of suspended solids. Anaerobic digestion of the high organic content of peach-tea substrate to create biogas was conducted by native microbial populations existing within the substrate. Total anaerobic fermentation time was about 336 h in the case of pH effect and 480 h in the presence of nutrient medium and sodium sulfite. The digestion of high peach-tea substrate was carried out in batch operation and the tests were performed in triplicate.

Analytical methods

Standard methods according to APHA (American Public Health Association 1995) were used to monitor biological oxygen demand (BOD), total solids (TS), and total suspended solids (TSS). The organic matter degradation (in the case of controlled and uncontrolled pH values), as well as the effect of the addition of nutrient medium and sodium sulfite, were investigated by measuring COD elimination. The latter was measured according to the procedure reported by Wolf & Nordmann (1977). Total sugars were measured by the phenol-sulfuric acid method (Dubois *et al.* 1956), and protein concentration was determined using the Lowry method (Lowry *et al.* 1951). The pH value, redox potential, conductivity and temperature were measured using an Inolab multi-parameter 720 device (Prolabmas, Murni Swadaya, Jakarta, Indonesia). The biogas composition was measured using a gas chromatograph coupled to a mass spectrometer (GC/MS; Perkin Elmer Clarus 600, Perkin Elmer, Waltham, MA, USA). The percentage by volume (% v/v) of methane and carbon dioxide present in the biogas were determined by comparing the sample biogas with pure standard gases. The GC was fitted with an Rtx®-VMS Column (60 m × 250 μm ID) (Restek Corporation, Bellefonte, PA, USA). Helium was used as the carrier gas at a flow rate of 1 mL/min. The oven temperature was set to 40 °C with a rate increase of 3 °C/min until the temperature of 180 °C was reached; then it was kept at this temperature for 3 min. The injector and detector temperatures were set to 180 °C.

Substrate characterization

The substrate used in this study was a mixture of industrial tea and peach juice. The sample was taken from effluent discharges from a local fruit juice plant. This effluent is considered a pollutant due to its high concentration of organic matter (550 g COD/L). The substrate was stored in a refrigerator at 4 °C until use. The characteristics of the substrate used for batch tests are depicted in Table 1. The tea-peach substrate contains sugars and proteins as major components. They are reported to be suitable for biogas production (Fang et al. 2011).

MODELING ASPECTS IN BIOGAS PRODUCTION BY FERMENTATION

Biogas production

The modified Gompertz, given in Equation (1), was used to fit each cumulative biogas production curve obtained from the batch experiments under mesophilic temperature

$$B(t) = P \cdot \exp\left\{ -\exp\left[\frac{R_m \cdot e}{P} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where $B(t)$ is the cumulative biogas produced during the digestion time t, P is the biogas production potential, R_m is the maximum production rate and λ is the lag phase duration.

This model has been widely used to describe hydrogen, methane, or biogas production in batch experiments assuming that methane production is a function of bacterial growth (Lay et al. 1999; Hegde & Pullammanappallil 2007).

The performance of the model was evaluated using statistical parameters. The correlation coefficient (R^2) and root mean square error (RMSE) were calculated using Equation (2) (Kafle & Kim 2013):

$$\mathrm{RMSE} = \left(\frac{1}{m} \sum_{j=1}^{m} \left(\frac{d_j}{y_j} \right)^2 \right)^{\frac{1}{2}} \quad (2)$$

where m is the number of data pairs, j is the jth values, y is the measured values and d is the deviations between measured and predicted values.

Biodegradation kinetics

According to Chynoweth et al. (1993) and Nikolaeva et al. (2009), the anaerobic digestion of most substrates can be described using first-order reaction kinetics. The biogas production is proportional to the amount of COD consumed during the fermentation process. The substrate removal rate can be described as follows:

$$-\frac{dY_t}{dt} = kY_t \quad (3)$$

The integration of Equation (3) and after taking $Y_t = L_u$ at $t = 0$, leads to:

$$Y_t = L_u.e^{-kt} \quad (4)$$

where Y_t is an amount of organic matter at time t, L_u is an initial amount of biodegradable organic matter, and k is the reaction rate constant.

Therefore, for the first-order reaction, a plot of $ln(Y_t)$ versus time gives a straight line with a slope –k.

Table 1 | Substrate characteristics

Parameters	Values
pH	3.60 ± 0. 01
Conductivity (μS cm^{-1})	682.0 ± 0.1
Oxidation reduction potential (mV)	226.00 ± 0.01
COD (g L^{-1})	550 ± 10
BOD$_5$ (g L^{-1})	175.0 ± 4.3
Total sugar (g L^{-1})	115.8 ± 0.1
Protein(g L^{-1})	0.185 ± 0.001
TS (g L^{-1})	110.92 ± 1.23
TSS (g L^{-1})	3.59 ± 0.03

RESULTS AND DISCUSSION

Experimental process optimization

To optimize the operating parameters, especially the pH value during the fermentation process in the batch reactor, the experiments were carried out under anaerobic conditions using high organic content peach-tea substrate at an initial pH value adjusted to 7.35 and at pH value 7.00 in controlled conditions. The cumulative biogas volume under mesophilic temperature (T = 38 °C) is shown in Figure 2(a) for different pH values. It can be observed that the biogas production started immediately during the

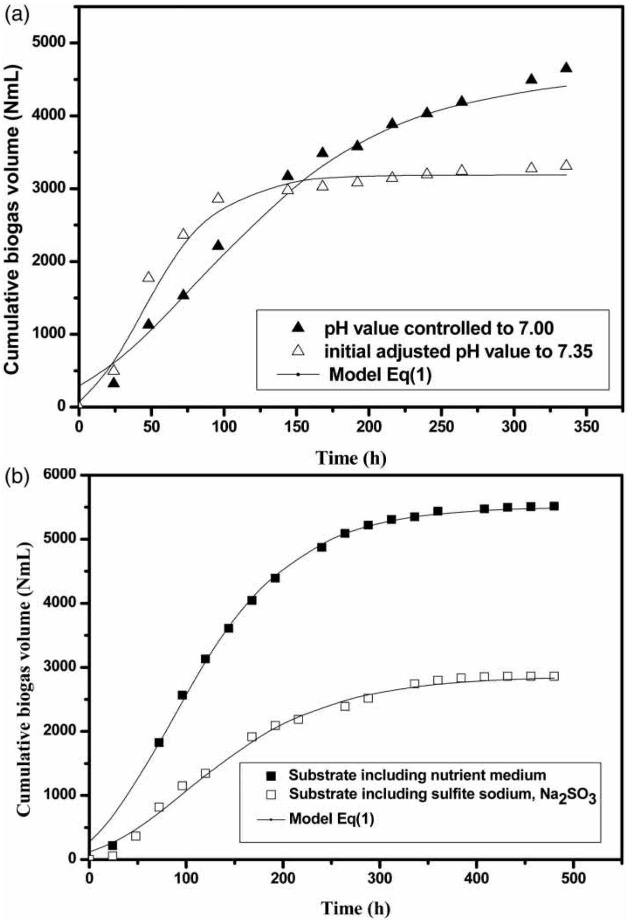

Figure 2 | Simulated cumulative biogas production from the high organic content of peach-tea substrate: (a) at different pH values, (b) effect of nutrient and sodium sulfite.

first hours of fermentation. The advantage of anaerobic digestion for liquid effluent is the short start-up time. Sung & Dague (1995) reported that, in an anaerobic batch reactor, the food to microorganism ratio was at the highest level immediately after the start of the operation. In such cases, the metabolic activity of the microorganisms increased, leading to a faster conversion of peach-tea juice into biogas. The digester operated at a pH value of 7.00 produced significant amounts of biogas (4,650.15 NmL after 336 h) while only about 3,310.35 NmL was produced in the case of the digester operated at initial pH value adjusted to 7.35. This means that maintaining a stable pH value inside the digester improves biogas production due mainly to the consumption of volatile fatty acids by methanogenesis in the anaerobic digester. According to Droste (1996), anaerobic systems require a pH value in the range of 6.50–7.50 to obtain good performances. It has to be mentioned that the methanogenic consortium *Archaea* activity occurred in this optimal pH value.

As for the digester operated at initial pH value adjusted to 7.35, the acid formation rate exceeded the rate of the substrate conversion to biogas, resulting in an unbalanced overall process. Consequently, the pH value decreased from 7.35 to 4.38, leading to weak biogas production. This result is in agreement with that reported by Eckenfelder (2000). Budiyono *et al.* (2013) found that the biogas production rate at a pH value of 7.00 is faster than that obtained at a pH value of 6.00, and Espinoza-Escalante *et al.* (2009) stated that the biogas production rate from vinasse at a pH value of 6.50 was higher than that obtained for acidic pH values.

The effect of nutrient medium and sodium sulfite on biogas production is shown in Figure 2(b). It can be observed that fermentations carried out in the presence of nutrient medium or sodium sulfite have the same cumulative biogas profiles. The biogas production started up from the first hours of the fermentation process. The higher biogas production value was obtained when nutrient medium was added to the peach-tea substrate (i.e., 5,515.8 NmL after 480 h) while only 2,862.3 NmL were produced in the case of peach-substrate containing sodium sulfite Na_2SO_3 and cobalt sulfate ($CoSO_4$). The latter was used as a catalyst. The existing native bacteria in high organic content peach-tea substrate acclimatized easily when nutrient medium was added. This was led to an improvement in the conversion of substrate into biogas. The sodium sulfite used to reduce the medium was supplemented in excess in the digester according to the following reaction:

$$SO_3^{2-} + \frac{1}{2}O_2 \overset{CO^{2+}}{\rightarrow} SO_4^{2-} \tag{5}$$

The addition of sodium sulfite did not enhance the biogas production rate due to both low sugar consumption and slow bacterial growth compared to the experiments conducted with the presence of nutrient medium. This has been previously reported by Petrovska *et al.* (1999).

Three gaseous compounds were detected in the biogas medium: methane was the major gas representing a ratio of 56.52% v/v of the total gaseous compound, followed by carbon dioxide at 20.14% v/v and hydrogen sulfide at 23.34% v/v. It is worth mentioning that these ratios are in good agreement with those reported in the literature (Kim *et al.* 2006; El-Mashad & Zhang 2010; Yu *et al.* 2014). Furthermore, the ratio of methane is higher in the case of fermentations conducted under pH value controlled to

7.00 and under mesophilic temperature, reaching values of approximately 70%; which is in good agreement with the values reported in the literature. Indeed, the average methane content in the biogas produced from food waste is about 73% (Zhang *et al.* 2007). Llaneza Coalla *et al.* (2009) reported that the biogas produced from apple pulp provided a methane concentration between 77 and 80%, with an average concentration of H_2S of about 400 ppm.

Cumulative biogas production modeling

The experimental and simulated profiles of the cumulative biogas volume at different pH values and in the presence of nutrient and sodium sulfite are depicted in Figure 2. The simulated curves were estimated from a parameter fitting process using the experimental data and Equation (1), which represents the modified Gompertz model. A good agreement is observed between this model and the experimental data, giving a good fit with $R^2 > 0.99$, and the RMSE value fell within the range of 0.0017–0.1772 in all cases. The kinetic parameters of the modified Gompertz model are given in Table 2. It was found in the case of sodium sulfite that the *P*-value is at its lowest when compared to values obtained with other experiments while the *P*-value obtained with the nutrient medium is the highest. It is worth mentioning that the *P*-value represents the biogas production that can be potentially produced for a given process. This value was twice as high as that obtained with sodium sulfite.

This difference could be due to both low sugar consumption and slow bacterial growth, meaning that the sodium sulfite presence does not reasonably promote biogas production in comparison to fermentation carried out with suitable nutrients. Moreover, the R_{max} (maximum biogas production rate) and λ (lag-phase time) values confirm this statement. Indeed, the estimated R_{max} is 28 NmL/h for the fermentation conducted with nutrient medium while that of the fermentation conducted with the presence of Na_2SO_3 is only 12.5 NmL/h. Even the lag phase period was shorter in the case of fermentation with nutrient medium. This means that when the digester is operated with a nutrient medium, it ensures good conditions for biomass growth and produces maximum biogas. The value of λ is at its lowest when the digester is working at pH value controlled to 7.00 with a faster growth of the biomass over a short lag time. This relatively enhanced the kinetics of the biogas production. However, the kinetic parameters obtained for the investigated substrates are lower than those obtained with vinasse (Syaichurrozi *et al.* 2013) and water hyacinth waste (Patil *et al.* 2012).

pH control

The variation of pH values during biogas fermentation is given in Figure 3. It can be seen that the pH value was kept at the same level during the anaerobic fermentation in the case of a pH value controlled to 7.00 and when adding nutrient medium and sodium sulfite, i.e., between 7.01 and 7.50. In the case of a pH value adjusted to 7.35, it dropped from 7.35 to 4.38; the reactor medium was acidified due to the accumulation of volatile fatty acids, and resulted in the inhibition of the biomass growth. Consequently, the biogas production dropped. A similar observation was previously reported by Ortega *et al.* (2008). As a consequence, to ensure high biogas production, it is necessary to keep the pH value constant at 7.00.

COD

COD is a good indicator of the degree of completeness of the degradation process (Ward *et al.* 2008). Figure 4(a) shows the comparison between the COD in the case of high organic content peach-tea substrate treated at a pH value initially adjusted to 7.35, and a pH value controlled to 7.00. Results show that the COD concentration decreased with time in both cases. In the case of pH value controlled to 7.00, a significant decrease in the organic compound concentration was observed; this concentration went down to 110.5 g/L after 336 h. At this time, bacteria were readily acclimated to the pH substrate medium, leading to a good

Table 2 | Modified Gompertz model: kinetic constants parameters

	Cumulative biogas volume (NmL)	P (NmL)	R_{max} (NmL h^{-1})	λ (h)	R^2	RMSE
pH value controlled to 7.00	4,650.15 ± 4.35	4,444.25 ± 4.35	21.74	1.107	0.9944	0.0998
Initial adjusted *p*H value to 7.35	3,310.35 ± 4.35	3,275.55 ± 4.35	40.23	8.778	0.9971	0.0017
Nutrient medium	5,515.80 ± 4.35	5,507.10 ± 4.35	28.09	6.061	0.9986	0.0954
Na_2SO_3	2,862.30 ± 4.35	2,849.25 ± 4.35	12.51	11.674	0.9969	0.1772

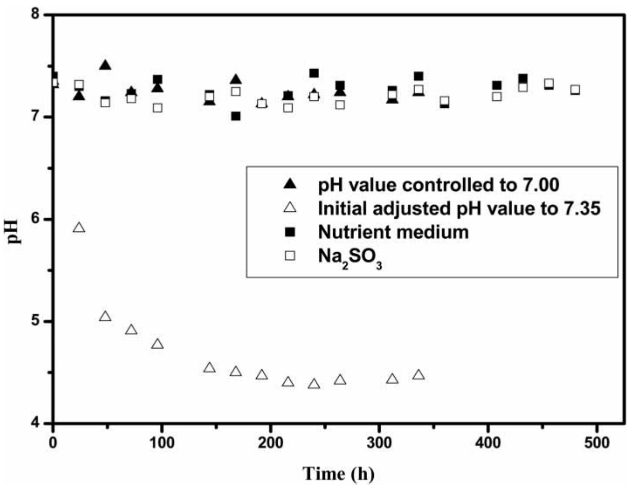

Figure 3 | pH value changes during anaerobic fermentation.

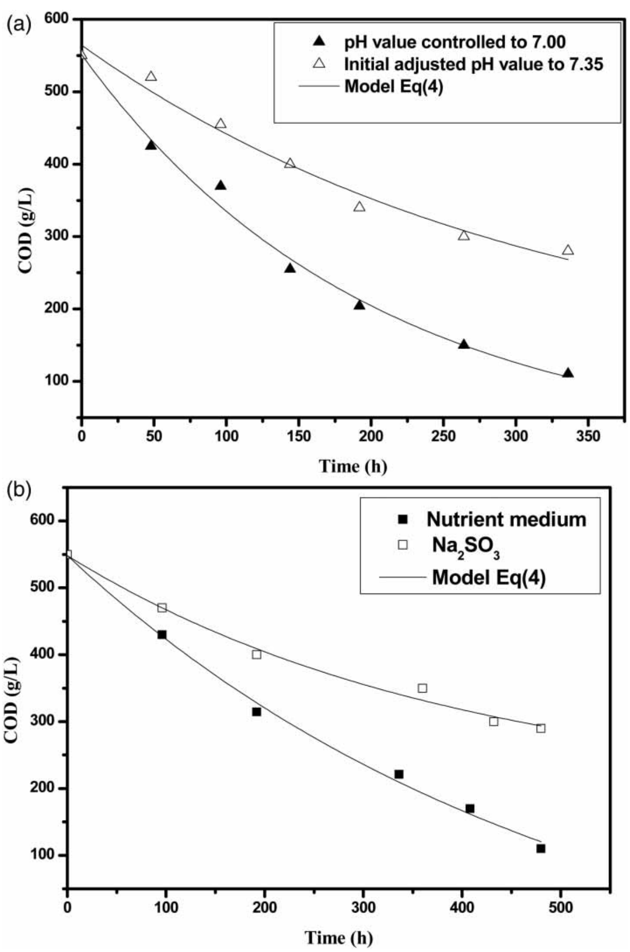

Figure 4 | Kinetic profiles for high organic content peach-substrate: (a) at different pH values, (b) effect of nutrient and sodium sulfite.

biomass growth and a better COD degradation in comparison to the digester operated at a pH value initially adjusted to 7.35.

Conversely, with an initially adjusted pH value, the COD reduction was much less pronounced, it was found that the value of COD concentration was less than 280 g/L after 336 h. Furthermore, the decrease in pH value induces bacterial acidogenesis, leading to the production of several chemical compounds such as acetate, carbon dioxide, and volatile fatty acids (VFA), which are among the important ones. Besides, a low pH value caused the inhibition of the activity of the methanogenic bacteria involved in the biogas production (Speece 1996). In this study, the COD depletion reached about 80%, while it was only about 49% in the case of the digester operated at a pH value initially adjusted to 7.35. These levels in COD depletion reflect a low biodegradability of peach-tea juice at a pH value initially adjusted to a value of 7.35. This might partly be explained by the properties of our substrate being characterized mainly by a high organic matter concentration. The obtained results are in agreement with those of previous studies. In fact, it is worth mentioning that, in the case of beet molasses vinasse, Lutoslawski *et al.* (2011) reported that COD substrate removal at controlled pH is more pronounced than COD removal at an initially adjusted pH value. Parawira *et al.* (2005) found that COD depletion could reach levels ranging from 80 to 97% in the case of solid potato waste. Zhang *et al.* (2005) found that a pH value of 7.00 provides an optimum working condition for anaerobic digestion of kitchen waste. According to these authors, about 82% of COD was solubilised at a pH value of 7.00, while Namsree *et al.* (2012) reported a COD depletion of only 60.41% in the case of pineapple pulp.

Figure 4(b) depicts the effect of nutrient medium and sodium sulfite on COD degradation of high organic content peach-substrate. As shown, there was a significant decrease in COD conversion into biogas in the presence of nutrient medium, until approaching an asymptotic value of about 110 g/L after 480 h. This value was lower than that reached when sodium sulfite was added. In this case, the asymptotic value was 290 g/L after 480 h. It was also the case with controlled and initially adjusted pH values. The addition of nutrient medium under a pH value controlled to 7.00 led to a better COD biodegradation compared to the case of sodium sulfite addition, which resulted in a higher biogas production (Syaichurrozi *et al.* 2013). Therefore, the difference in COD abatement can be attributed, in both cases, to microbial activity efficiently using the nutrient medium and the organic matter. The latter could break-down and be digested easily, while the addition of sodium sulfite can, on the other hand, slow-down the conversion of organic matter into biogas. Yang *et al.* (2013) reported that the pretreatment of rice straw using sodium carbonate and sodium sulfite improved enzymatic hydrolysis.

The kinetics of COD abatement described by Equation (4) is given in Figure 4. The regression technique provides a good agreement between experimental data and the first-order kinetic model, giving a goodness of fit $R^2 > 0.97$. It is worth mentioning that the digestion of high organic content peach-tea substrate operated at pH value controlled to 7.00 exhibited better improved kinetics (Table 3) than that obtained in the case of different pH values and the addition of nutrient medium. The results clearly show a faster degradation of organic compounds.

Total sugars and total biomass growth

Sugars are usually present in a large variety of commercial fruit juices (Fennema 2000), consisting mainly of fructose, glucose and sucrose (Roig & Thomas 2003). Analyses carried out on total sugars revealed that glucose is the major component, accounting for almost 60% of sugars (Kaparaju *et al.* 2010). Its presence may serve as a regular supply of energy to keep cells alive. Thus, it is important to evaluate the degree of sugar uptake by the cells.

Figure 5(a) shows the effect of pH on total sugars and biomass growth profiles as well as the kinetics of total sugar uptake. In the case of a pH value controlled to 7.00, it can be seen that total sugars decrease to 75.33 g/L after 168 h of digestion. This value is lower than that obtained in the case of a pH value initially adjusted to 7.35, i.e., 80.11 g/L. This decrease in total sugars matched well with the increase of biomass growth with a concentration of about 3.4 10^6 cells/mL in the case of pH value controlled to 7.00 at a stationary phase. Nevertheless, this value was lower and attained 2.1 10^6 cells/mL in the case of initially adjusted pH value at the deceleration phase, due to a low pH value. This inhibited the activity of micro-organisms

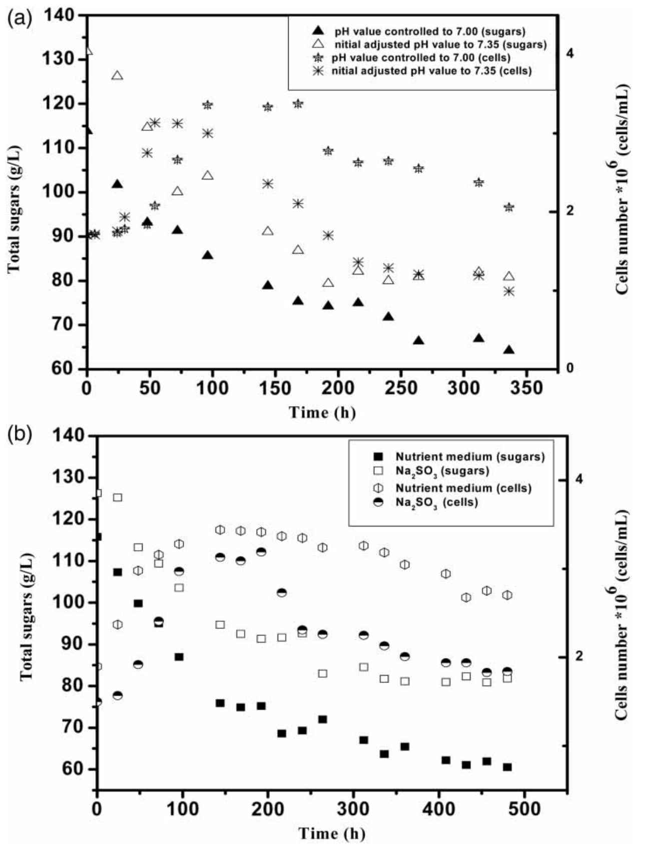

Figure 5 | Kinetic profiles of total sugar and total biomass growth: (a) at different pH values, (b) effect of nutrient medium and sodium sulfite.

involved in biogas production somewhat, especially in the case of methanogenic bacteria (Speece 1996). Besides, the maximum growth rate achieved was about 0.0088 h^{-1} and 0.0084 h^{-1} at pH value controlled to 7.00 and a pH value initially adjusted to 7.35, respectively. This means that sugars were used by the cells as a source of nutrition and energy. After 264 h, the sugar concentration in the case of a pH value controlled to 7.00 during fermentation was almost-constant, with 66 g/L, implying that the breakdown components were the limiting step of the high organic content peach and tea juice fermentation by microorganisms. It can also be noticed that this duration was more than that obtained in the case of a pH value initially adjusted to 7.35, i.e., 192 h. These results agreed well with those reported by Jin *et al.* (2014).

The effect of nutrient medium and sodium sulfite on total sugar consumption is depicted in Figure 5(b). The total sugars seemed to be used at different rates. This sugar depletion was faster in the case of the presence of nutrient medium compared to the addition of sodium sulfite. In fact, the total sugars consumed during the fermentation

Table 3 | Kinetic constants using Equation (4)

	k (h^{-1})	R^2	RMSE
pH value controlled to 7.00	0.00486 ± 0.00018	0.9931	0.0076
Initial adjusted pH value to 7.35	0.00220 ± 0.00016	0.9745	0.0269
Nutrient medium	0.00317 ± 0.00023	0.9794	0.0235
Na_2SO_3	0.00134 ± 0.00008	0.9852	0.0541

were 60.54 g/L after 480 h in the presence of nutrient medium and only 77.1 g/L with the addition of sodium sulfite. This favored biomass growth and a better organic matter conversion compared to the case of fermentation conducted with the addition of sodium sulfite. The addition of nutrient medium improved both the consumption of sugars and the biomass growth, and as a result, a better cumulative biogas volume was obtained.

TSS

Further investigations were carried out on the pH nutrient medium containing sodium sulfite and its effects on TSS. As shown in Figure 6, TSS roughly decreased, reaching the lowest value of 1.40 g/L after 336 h in the case of pH value controlled to 7.00 with the addition of nutrient medium. The TSS value reached 2.36 g/L in the case of pH value initially adjusted to 7.35 (Figure 6(a)). This result is in agreement with that reported in the literature (Álvarez *et al.* 2006). Between 192 and 336 h of digestion, the TSS remained almost constant during the peach-tea anaerobic digestion with a pH value of 7.00 and nutrient medium containing sodium sulfite at the same pH value (Figure 6(b)). This means that undissolved organic components were more persistent and remained in the digester during the fermentation process.

The observed TSS reduction was in the vicinity of 60% of the initial TSS concentration after 336 h, which was slightly higher than that reported by Forster-Carneiro *et al.* (2008). The addition of nutrient medium, under the condition of pH value controlled to 7.00, improved both the solubilization and the reduction of solids during the digestion process.

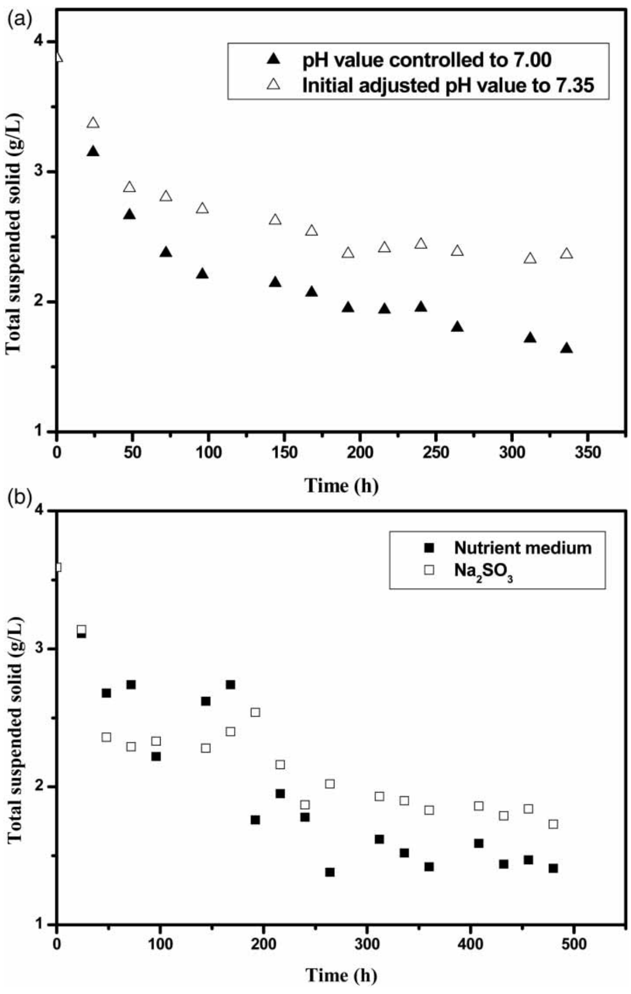

Figure 6 | Total suspended solids: (a) at different pH values, (b) effect of nutrient medium and sodium sulfite.

Biogas calorific value

The calorific value is a measure of the heat produced during combustion. For biogases, this value comprised between 19 and 25 MJ/m^3, depending on the methane percentage in the biogas mix (Forster-Carneiro *et al.* 2008).

The energy equivalent of 1 m^3 of biogas with 60% methane is equal to 4,713 $kcal/m^3$ or 19.7 MJ/m^3 (Deublein & Steinhauser 2011). The methane content of the produced biogas from the investigated substrates was found to be in the vicinity of 60% and its calorific value was estimated to be 19.16 MJ/m^3. Figure 7 compares the calorific value of the different fuel gases. It can be seen that the natural gas provides a slightly higher calorific value compared to that of methane and biogas. The calorific value of biogas represents half the value of the natural gas. Therefore, biogas produced from the studied substrates should be purified before being fed into the natural gas network in order to enhance its calorific value. For that purpose, the obtained biogas could be easily mixed into the natural gas network if the quality of the transported mixed gas is critical for pricing.

CONCLUSION

This study was carried out to evaluate the performance of an anaerobic batch digester using high organic content industrial peach-tea substrate juice. The effects of a pH value controlled to 7.00 and a pH value initially adjusted to 7.35, nutrient medium and sulfite sodium on biogas

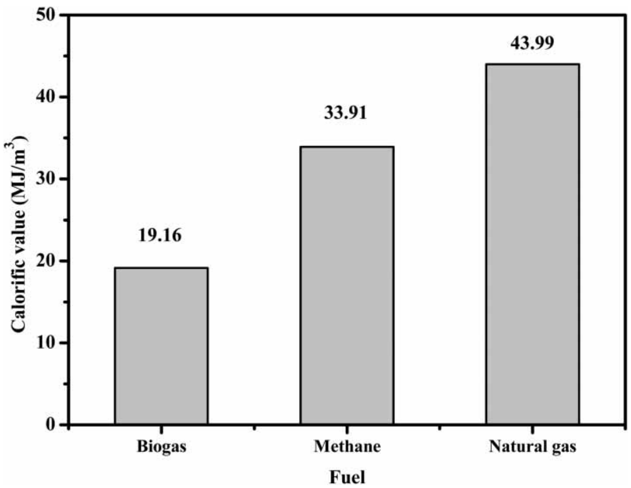

Figure 7 | Calorific values of different fuel gases.

production were investigated. The highest cumulative biogas volume of 5,515.8 NmL was reached after 480 h in the case of the addition of nutrient medium, while it was lower (about 2,862.3 NmL) in the case of peach-substrate containing sodium sulfite. This latter did not enhance biogas production.

The COD removal reached about 47%, 49% and 80%, respectively, in the case of sodium sulfite, a pH value initially adjusted to 7.35, and in the case of both a pH value controlled to 7.00 and nutrient medium. The addition of nutrient medium under the condition of pH value controlled to 7.00 led to a better COD abatement.

The modified Gompertz model well described the experimental values of biogas production and provided kinetic parameters, P, $R_{\max}$, λ. The highest value of P (5,507.1 NmL/h) was obtained in the case of the addition of nutrient medium, indicating that the digester using a nutrient medium ensured good conditions for biomass growth and maximum biogas production.

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