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ORIGINAL PAPER

Kinetic studies on anaerobic co-digestion of ultrasonic disintegrated feed and biomass and its effect substantiated by microcalorimetry

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Abstract Studies were carried out on anaerobic co-digestion of primary and secondary excess sludge obtained from tannery effluent treatment plant. Anaerobic biomass collected from a treatment plant was used as the source of micro-organisms. The optimum feed to micro-organism ratio was evaluated as 0.7 on the basis of volatile solids reduction cum gas production. Both feed and anaerobic biomass were subjected to ultrasonic pre-treatment in order to enhance the digestion process. Experiments carried out on batch mode showed significant increase in the gas production for pre-treated feed and biomass. Optimum pre-treatment durations were evaluated as 5 min for feed and 3 min for anaerobic biomass. Heat flow analyses of the anaerobic biomass using isothermal microcalorimetry throw light on different stages of digestion process. The effect of ultrasonic pre-treatment on anaerobic biomass was also substantiated using this technique. The heat energy released by pre-treated and untreated anaerobic biomass was evaluated as 16.3 and 7.6 kJ/kg, respectively. Kinetic analysis revealed that the overall rate constant of digestion process increased by 1.5 times due to pre-treatment. However, the initial lag time increased by about 20 % for the optimally pre-treated sample compared to untreated sample. Modified Gompertz equation was used to model, and the parameters were evaluated. The significance of this work lies on energy production (bio gas) and at the same time increasing the maintenance metabolism rate thereby minimizing excess sludge biomass generation.

Keywords Activated sludge · Anaerobic digestion · Isothermal microcalorimetry · Ultrasonic pre-treatment

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Introduction

Nearly 2,000 tanneries are located throughout India with a total processing capacity of about 700,000 tonnes of hides/skins per annum (Balakameswari et al. 2010). Waste-activated sludge or excess sludge is an unavoidable by-product generated in common effluent treatment plants (CETPs) as a consequence of treating tannery wastewater. On an average of about 50–60 kg of primary sludge and 15–20 kg of secondary sludge are produced per ton of raw hides/skins (NEERI Report 1997). It has been observed that 60–65 % of the sludge generated from tanneries is predominantly organic and putrescible in nature. It contains mostly micro-organisms and biodegradable organic compounds such as proteins, carbohydrates, fats and mineral parts (Saravanabhavan et al. 2004). Disposal of sludge is a major concern in terms of environmental protection (Balakameswari et al. 2010). Sludge management requires about 30–40 % of the capital cost and approximately 50–55 % of operation and maintenance cost of the tannery wastewater treatment (Weemaes and Verstraete 1998; Appels et al. 2008). Therefore, the sludge needs to be treated in order to reduce its associated volume and also to reduce the associated health problems. Large quantities of sludge can be better processed using appropriate biological techniques to stabilize the wastes and to produce biogas (Braguglia et al. 2012). Anaerobic digestion is one such technique which can be used to reduce the volume of sludge and also for generation of biogas.

Anaerobic co-digestion of waste-activated sludge

Details about biological aspects of the anaerobic co-digestion process have been reported in exclusive literature on the subject (Stronach et al. 1986; Gerardi 2003; Deublein and Steinhauser 2008). Anaerobic co-digestion of waste-activated sludge or any organic material is a complex process which essentially consists of following steps in sequence viz. hydrolysis, acidogenesis, acetogenesis and methanogenesis. This process requires strict anaerobic conditions to proceed (oxidation reduction potential of less than −200 mV) (Appels et al. 2008). Hydrolysis is considered as the rate-limiting step in the digestion process (Safari et al. 2011). During the above step, the insoluble organic material and high molecular weight compounds such as lipids, polysaccharides, proteins and nucleic acids are degraded into soluble organic substances such as amino acids and fatty acids. The products of hydrolysis are further converted into volatile fatty acids, ammonia and carbon dioxide during the acidogenesis step by acidogenic bacteria. Higher organic acids and alcohols produced during acidogenesis are further digested during acetogenesis by acetogens to produce mainly acetic acid, CO_2 and H_2. Methane is produced by methanogenic bacteria in final step called methanogenesis. Temperature plays a major role in the digestion process. Digestion can take place at moderate temperatures (30–38 °C) as well as at relatively higher temperatures (50–57 °C). The former is mesophilic digestion and the latter one is thermophilic digestion, and each of these digestion methods has their own merits and demerits (Amani et al. 2011).

Need for pre-treatment operations

Technological developments in the area of bioreactor design for the treatment of solid organic wastes have increased the interest in anaerobic digestion (Zhang et al. 2012; Khalid et al. 2011; Selvamurugan et al. 2012). However, due to low biodegradability and high solid content, sludge requires long retention time of about 20–30 days to reach even moderate efficiencies of 30–50 % (Pavlostathis and Gossett 1986). Therefore, in order to reduce the residence time and to enhance volume reduction/gas generation, appropriate pre-treatment techniques should be considered prior to the digestion process. Moreover, most of the organics trapped within the microbial cell membrane contains glycan strands cross-linked by peptide chains which are resistant to biodegradation (Weemaes and Verstraete 1998). Pre-treatment unit operations could improve the digestion efficiency by converting slowly degradable particulates into readily degradable compounds through pre-treatment mainly by disintegration.

Pre-treatment techniques such as oxidative, mechanical, thermo-chemical, microwave, biological have been investigated by researchers on waste-activated sludge (Weemaes et al. 2000; Carrère et al. 2010; Nagai et al. 2012; Uma Rani et al. 2013; Uan et al. 2013; Merrylin et al. 2013; Kavitha et al. 2014; Lakshmi et al. 2014). Wang et al. (1999) studied the effects of ultrasonic pre-treatment on the solubilization of waste-activated sludge and on methane generation. Ultrasonic pre-treatment increased the methane production by 64 % as compared with the untreated sludge. Lin et al. (2009) and Uma Rani et al. (2012, 2014) employed alkali–mechanical combined pre-treatment process to improve anaerobic co-digestion. Recently, micro-aeration has been reported (Lim and Wang 2013) as an alternative pre-treatment method to enhance hydrolysis during the anaerobic co-digestion of brown water and food waste.

All these reported works have studied the influence of pre-treatment on feed (sludge). However, the effect of pre-treatment on anaerobic biomass is yet to be studied. Diligent disintegration of anaerobic biomass by techniques such as ultrasonic pre-treatment would enhance the microbial activity due to increase in the maintenance metabolism. Therefore, the purpose of this work was to study the influence of ultrasonic pre-treatment on anaerobic biomass as well as feed sludge followed by anaerobic digestion. The feed sludge refers to the mixture of primary and secondary sludge generated from tannery wastewater treatment plant along with cow dung which is a co-substrate.

Biological processes and heat measurement

Heat production in biological systems and processes has been discussed in detail in the literature (Battley 1987; Gustafsson 1991; Alklint et al. 2004). In all these studies, calorimetry was used as an analytical tool to gain insight into the biological processes. With recent advances in calorimetry such as the development of highly flexible and ultrasensitive calorimetric instruments, the focus is on to use these techniques to obtain kinetic as well as analytical information from biological process. Any biological/biochemical process is associated with a definite amount of heat change. Conversely, precise measurement of magnitude and profile of heat change curves for the system could provide information about the microbial growth and associated process. This underlying principle has been utilized in the present study by employing microcalorimetry technique for the precise measurement of ultrasonic pre-treatment effect on anaerobic biomass. Although the optimal digestion temperature lies around 35 °C for mesophilic treatment, the operating temperature in this study was maintained at standard temperature of 25 °C for both control (untreated) as well as experiment (pre-treated). The main objective was to compare and analyse the heat production rate for both the cases at a constant temperature. Similar comparison study at 25 °C has been carried out by Alklint et al. (2004) for studying the shelf life of fruit juices.

Therefore, the objectives of this work were as follows.

- To study the effect of individual feeds and mixed feed (primary sludge, secondary sludge and cow dung) with biomass for anaerobic digestion
- To select an optimum F/M ratio required for efficient digestion
- To study the disintegrability studies on feed
- To select the optimum pre-treatment durations for feed and biomass based on gas production
- To study the effect of ultrasonic pre-treatment/disintegration on anaerobic biomass by isothermal microcalorimetry
- To model the sludge digestion process and to determine the kinetic parameters

Materials and methods

Materials

Substrate

Primary sludge and secondary sludge from tannery effluent treatment plant were used as the substrates. These sludge samples were collected from tannery common effluent treatment plant, Ranipet, Tamilnadu, India.

Co-substrate

Cow dung collected from a nearby farmhouse was used as a co-substrate in the studies. It helps to reduce the toxic effects present (if any) in the primary sludge. The use of co-substrates during anaerobic co-digestion has been reported to improve the gas yield from anaerobic digesters. This is due to the positive synergisms established in the digestion medium and the supply of missing nutrients by the co-substrates. Sometimes the use of co-substrates may also be required to maintain moisture content of the digester feed (Alvarez et al. 2000).

Source of micro-organisms

Anaerobic biomass collected from an anaerobic treatment plant near Chennai, India, was used as the source of micro-organisms.

Chemicals

Analytical grade reagents such as potassium dichromate, mercuric sulphate, concentrated sulphuric acid and potassium hydrogen phthalate procured from S D Fine Chemicals Limited, Mumbai, were used in the study.

Methods

Sample stabilization and characterization

Primary, secondary sludge samples and cow dung were stabilized and stored at 4–5 °C to arrest any degradation. Anaerobic biomass was sieved using a 2 × 2 mm mesh sieve to remove large lumps and was stored under anaerobic conditions. Little quantities of oil cake and cow dung were mixed with anaerobic biomass to prevent starvation of the micro-organism. Sludge samples were characterized according to the methods described in Standard Methods for Examination of Water and Wastewater (APHA 1998). pH was measured using ELICO LI120 pH meter, and soluble chemical oxygen demand (SCOD) was evaluated by closed reflux, colorimetric method (5220D). UV-2101PC, Shimadzu UV–Vis scanning spectrophotometer was used in the study. Total and volatile solids were determined by 2540 G method. The characteristics of primary, secondary sludge and anaerobic biomass are given in Table 1.

CHN analysis

Earlier studies have reported the optimum feed to micro-organism ratio and the corresponding carbon to nitrogen ratio (C:N) along with it (Navaneethan 2007). In this study, C/N ratio was determined by CHN analysis using the Elemental Analyzer, Euro EA 3000, Euro Vector, Italy. The sample was weighed in tin or silver capsules and introduced into the combustion reactor where the sample was combusted with proper amounts of oxygen and catalysts. Products of combustion reaction (CO_2, H_2O, NO_X and SO_2) were carried by helium flow to the copper reactor where excess oxygen was consumed and NO_X products were converted to N_2. The products were carried through a gas chromatography column that separated the combustion gases and was detected by a thermal conductivity detector.

Table 1 Characterization of feed and anaerobic biomass

S. No	Parameters	Unit	Primary sludge	Secondary sludge	Cow dung	Anaerobic biomass
1	pH	–	8.0–8.8	7.1–7.9	5.9–7.3	5.2–6.9
2	Soluble COD	g/L	1.25–1.4	1.1–1.3	–	–
3	Total solids	g/L	65.3	48.3	74.6	77.6
4	Volatile solids	g/L	24.9	19.7	59.1	52

Ultrasonic pre-treatment

The sludge samples were pre-treated by ultrasonic homogenizer (Sonics vibra cell, USA). The frequency of 20 kHz turned out to be the most efficient and economical (Zielewicz and Sorys 2008). Transducer and Sonotrode form the major components of the instrument. Sonotrode is made up of a booster and a horn. The booster is a mechanical amplifier that helps to increase the amplitude generated by the converter. The horn or the probe is a specially designed tool that can deliver ultrasonic energy to the sludge (Navaneethan 2007). Schematic of the ultrasonic sludge disintegration set-up is shown in Fig. 1a. Pre-treatment of anaerobic biomass was done with multi-probe (4 horns) throughout the study. The important operating parameters considered during the study were sonication time, sludge volume, TS content of the samples and power input. Hydro-mechanical shear forces produced during ultrasonic pre-treatment were expected to disintegrate the sludge flocs and rupture the cell wall (Tiehm et al. 2001). Pre-treatment of anaerobic biomass (micro-organisms) was carried out to increase the activity of micro-organisms.

The specific energy input provides information about the energy required to achieve a certain degree of disintegration which can be calculated using the following equation.

$$\mathrm{SE} = \frac{Pt}{\mathrm{TS} \times V} \tag{1}$$

where *SE* is specific energy in kJ/kg, *P* is the ultrasonic power in kW, *t* is the sonication time in seconds, *V* is the volume of sludge in litres and TS is the total solids in kg/L.

Microcalorimetry studies

In this study, microcalorimetry technique has been employed successfully to quantify the effect of ultrasonic pre-treatment on anaerobic biomass precisely. Microcalorimetric experiments were carried out using TAM III instrument, supplied by TA instruments, USA. This instrument is equipped with a high-precision temperature controller that could control temperature to within 0.0001 °C. Batch experiments were performed under standard mode with 4 mL glass ampoules at 25 °C. Untreated fresh anaerobic biomass taken from the digester was used as the control sample. Ultrasonic pre-treated anaerobic biomass (of the same batch as the control sample) was used as the experiment sample. Experiments involving both untreated and treated samples took more than 40 h each. Heat flow profiles of the control and the pre-treated samples were compared, and the energy released was computed using the following equation.

$$E = \int_{t_0}^{t_f} Q \cdot \mathrm{d}t \tag{2}$$

Anaerobic digester set-up and gas collection

Schematic of the typical anaerobic digester set-up is shown in Fig. 1b. Experiments were carried out in triplicates for both control and experiment using identical digesters each with working volume of 1 L. These digesters were capped with butyl rubber stoppers and sealed with aluminium caps in order to make them air tight. Gas generation from the digesters was measured by Mariotte principle water displacement method reported elsewhere (Itodo et al. 1992). The digesters were manually shaken for every 12 h, and the gas generation was measured at an interval of 24 h.

Modelling of gas production

Experimental gas production data obtained during the anaerobic digestion process were simulated using modified Gompertz model, and the parameters were estimated using data analysis software *CurveExpert Professional 2.0.3*.

Results and discussion

Effect of feed on gas production

Experiments were conducted to study the effect of individual feeds (primary sludge, secondary sludge and cow dung) and mixed feed with anaerobic biomass for gas production. Individual and mixture of feeds (on volatile solid content basis mixed in the ratio 1:1:1) were subjected to digestion in separate anaerobic digesters. F/M ratio of 0.5 was maintained for this study. In the case of individual feeds, cow dung contributed to the maximum gas

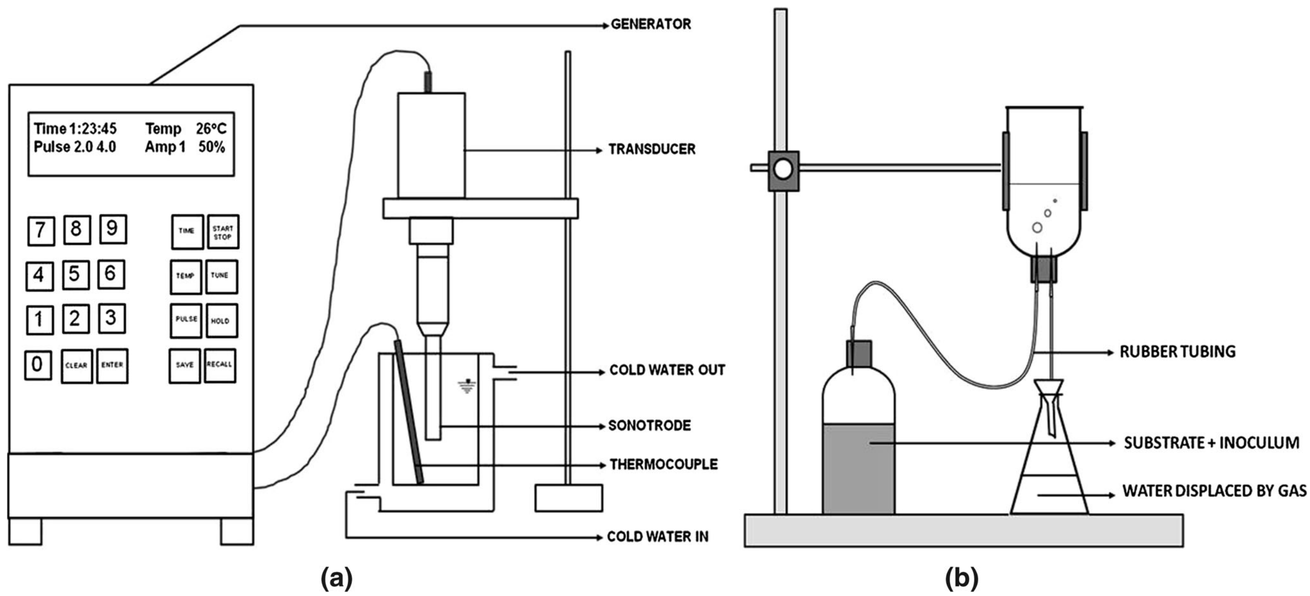

Fig. 1 Schematic of the **a** ultrasonic sludge disintegration set-up, **b** anaerobic co-digester set-up

production closely followed by primary sludge. Secondary sludge contributed to least gas production. The amount of gas produced is based on the relative amount of volatile solids present in the individual feeds. The mixed feed contributed more gas production compared to that of individual feeds. At the end of 45 days of retention time, gas production from mixed feed was about twice to that of secondary sludge. It was higher than individual gas productions of primary sludge and cow dung by 46 and 38 %, respectively. Cumulative gas production as a function of time for different feeds is shown in Fig. 2a. In case of mixed feed, the contributions of cow dung, primary sludge and secondary sludge for gas production are 38, 36 and 26 %, respectively. Based on the gas production profile, average rate of production using mixture of feeds, cow dung, primary sludge and secondary sludge is found to be 18, 14, 13 and 10 mL/day, respectively. The above results suggest that cow dung is a suitable additive for anaerobic digestion of primary and secondary sludge derived from tannery effluent treatment plants.

Selection of optimum F/M ratios

Primary, secondary sludge and cow dung were mixed together based on the mass of volatile solids and was considered as feed for the digestion process. This feed was in turn mixed with micro-organisms in three different proportions (F/M = 0.3, 0.5 and 0.7) to determine the optimum ratio. F/M ratio is an important operating variable that refers to mass of food supply to mass of micro-organisms in the system. A too high F/M ratio can affect the process efficiency. On the other hand, too low ratio can lead to limited growth. Therefore, an optimum F/M ratio is required for efficient digestion. Based on the volume of gas production, the optimum feed to micro-organism ratio was found as 0.7 and this corresponds to a C/N ratio of 18.2:1. This value is within the quoted range of 15:1 and 30:1 (for sludge co-digestion process) of previous work (Navaneethan 2007). Therefore, F/M ratio of 0.7 has been considered throughout the study. The results of CHN analysis are given in Table 2.

Selection of optimum pre-treatment time durations

In this study, both anaerobic biomass and the feed were individually subjected to ultrasonic pre-treatment for different treatment durations prior to anaerobic co-digestion. The optimum pre-treatment duration refers to the ultrasonic pre-treatment time of sludge and biomass that result in maximum volatile solids reduction cum gas production. Maximizing/enhancing gas production through ultrasonic pre-treatment has been the main aim of this work. The corresponding specific energy (energy required to achieve a certain degree of disintegration) is calculated using Eq. 1, and care has been taken to achieve better disintegration at specific energies as low as possible. The different time durations are presented in Table 3. Treatment time durations were found to affect the gas production. Better performances (in terms of volume of gas produced) were observed for the following treatment combinations viz., biomass (3 min) + feed (5 min), biomass (5 min) + feed (5 min), biomass (5 min) + feed (3 min). Other treatment combinations led to relatively low gas production. Hence, for clarity of presentation, data for the above-mentioned

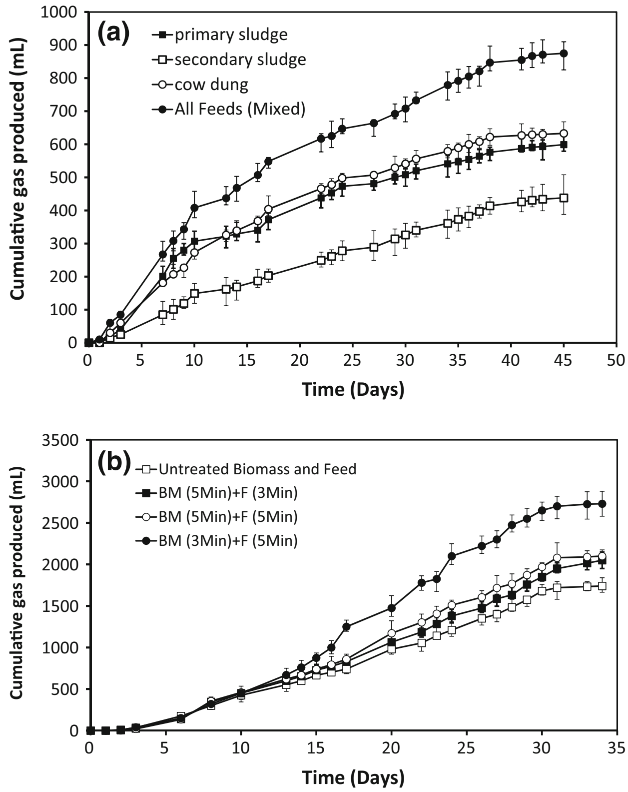

Fig. 2 **a** Influence of individual feed on gas production (F/M = 0.5), **b** pre-treatment combinations showing significant production of gas [F/M = 0.7 (optimized)]

Table 2 Results of CHN analysis

F/M ratio	% Carbon	% Nitrogen	C:N ratio
0.3	30.19	2.52	12:1
0.5	30.3	2.76	11:1
0.7	29.4	1.62	18.2:1

Table 3 Cumulative gas production (34 days) for all treatment combinations

Biomass treatment time (min)	Feed treatment time (min)	Cumulative gas produced (mL)
0	0	1,740
1	1	1,795
1	3	1,820
1	5	1,964
3	1	1,880
3	3	1,914
3	5	2,730
5	1	1,870
5	3	2,050
5	5	2,100

three combinations are presented in Fig. 2b and compared with average gas production for untreated biomass and feed mixture. The average values of cumulative gas produced in 34 days for all treatment combinations are also provided in Table 3.

Out of several pre-treatment time combinations considered for feed and biomass, higher gas production has been realized for cases where feed was pre-treated for a maximum duration of 5 min. This may be due to the effective release of organic materials from the feed debris by perpetual attack of large numbers of collapsing cavitation bubbles at higher treatment times. In addition, this could have led to the dispersion of aggregates and solubilization of particulate matter in the feed as reported in the literature (Foladori et al. 2007). Further increase in feed treatment time beyond 5 min would have improved gas production. However, higher energy requirement at longer treatment times was considered as a limiting factor.

As far as pre-treatment of biomass is concerned, relatively better gas production has been achieved for pre-treatment time of 3 min. This could be the optimum time when the disaggregation of flocs, cell damage and rupture occurred due to disintegration leading to release of micro-organism in the bulk liquid. Lesser gas production observed at treatment times less than 3 min may be due to ineffective disruption. Decline in gas production for treatments beyond 3 min could be attributed to the decrease in the number of live micro-organisms. Treatments exceeding a certain specific energy limit have been reported to bring disintegration and disruption of the micro-organisms leading to decrease in their number (Foladori et al. 2007).

Microcalorimetric analysis of the digestion process using anaerobic biomass

Figure 3 represents the normalized heat flow profile of untreated anaerobic biomass at 25 °C when enclosed in an ampoule over a period of 2 days. Normalized heat flow refers to the amount of heat energy released per unit mass of the biomass. Consistent profiles with a similar trend were obtained on repeating this experiment. These observations possibly throwlight on different stages of the anaerobic co-digestion process. Since the biomass was hermetically sealed in the ampoule and subjected to calorimetric studies, the micro-organisms start to utilize the limited amount of substrate available to them. Owing to technical difficulties, air inside the ampoules could not be flushed using nitrogen. The micro-organism present inside being facultative bacteria initially utilizes the oxygen trapped in the sealed ampoule. As oxygen is consumed continuously, it gets depleted over a period of time. This refers to aerobic process represented in Fig. 3. Due to the

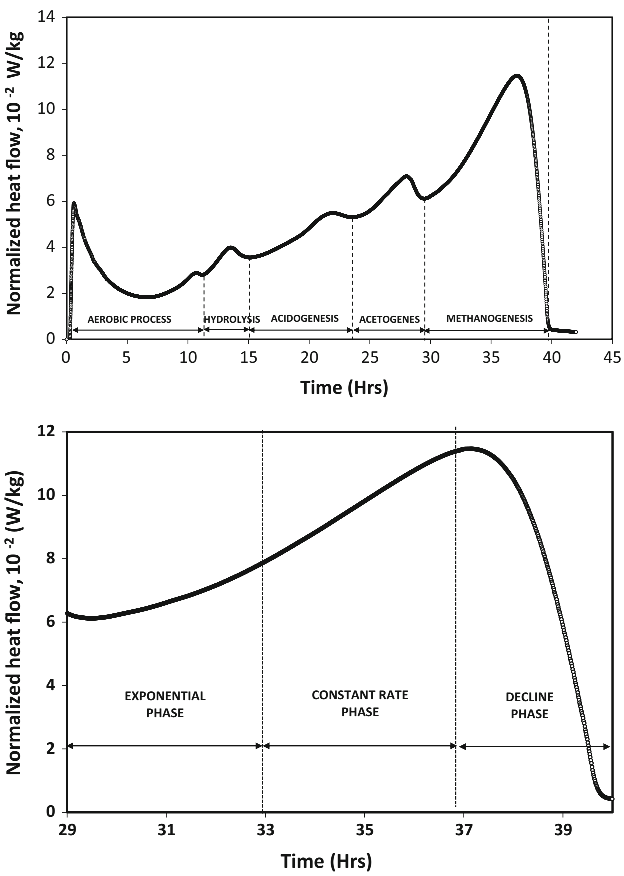

Fig. 3 Heat flow analysis of untreated anaerobic biomass (enclosed in ampoule) at 25 °C, magnified profile of methanogenesis step

absence of oxygen, probable anaerobic process could have been started with hydrolysis. It is during this step that the micro-organisms break the feedstock into simple sugars, amino acids and fatty acids. This is followed by acidogenesis when the components of previous step are broken down into volatile fatty acids, ammonia, carbon dioxide, hydrogen sulphide and other by-products. The molecules created are further digested by the microbes to produce acetic acid, carbon dioxide and hydrogen during the third step called acetogenesis. Microbes convert the intermediate products into methane, carbon dioxide and water, making up the majority of the gas output during the last step called methanogenesis. The heat released during each of these steps is shown in Fig. 3. After methanogenesis, the digestate is left with lesser number of microbes which eventually vanishes completely. Although different stages of anaerobic digestion process would occur simultaneously, the heat flow profile of the digestion process indicates a possible hypothesis that respective stages of the digestion sequence (viz., hydrolysis, acidogenesis, acetogenesis, methanogenesis) are predominant at their respective time intervals, while other stages also prevail during the process.

A close look at the methanogenesis step (Fig. 3) reveals three distinct regions in the process of gas generation reported elsewhere (Stronach et al. 1986). viz. exponential phase, linear phase and declining phase.

Microcalorimetric substantiation of ultrasonic pre-treatment

Figure 4 shows the normalized heat flow profile of 3 min pre-treated anaerobic biomass in comparison with that of untreated anaerobic biomass described in Fig. 3. Similarity in the trend of heat flow profiles clearly validates the occurrence of different anaerobic stages in the pre-treated sample as well. Using Eq. 2, the heat energy released was calculated for both untreated and treated anaerobic biomass. Higher energy release was observed in treated sample (16.3 kJ/kg) compared to that of untreated sample (7.6 kJ/kg). Release of more energy in treated sample could be due to the increase in microbial maintenance energy requirements arising out of pre-treatment process. All these microcalorimetric observations clearly substantiate the increased maintenance energy requirements of micro-organisms due to ultrasonic pre-treatment.

Disintegrability studies on feed

Ultrasonic disintegration of sludge flocs has been reported to disrupt microbial cell walls and release soluble substances (Wang et al. 2005). This in turn can result in the increase of soluble chemical oxygen demand (SCOD) which can be determined by the method suggested by Mueller (2000). Figure 5 illustrates the change in SCOD with respect to ultrasonic specific energy. The SCOD release increased linearly up to 27 % on supplying the specific energy = 15,000 kJ/kg. This specific energy corresponds to the treatment time of 5 min. Additional 18 % increase in SCOD release was observed for specific energy = 45,000 kJ/kg (corresponding to treatment time of 15 min). Further extension of disintegration time (up to 35 min) led only to a marginal increase in SCOD release (i.e. 9 %). Therefore, it can be concluded that pre-treatment for 5 min is sufficient to treat the feed and still achieve a better SCOD release. This would require very less specific energy consumption. This is in accordance with the findings of Chu et al. (2002), who demonstrated that "weak" ultrasound pre-treatment greatly increased both the production rate and ultimate yield of methane.

Kinetic studies

Anaerobic digestion process has been expressed by a first-order kinetic model by several researchers (Thangamani

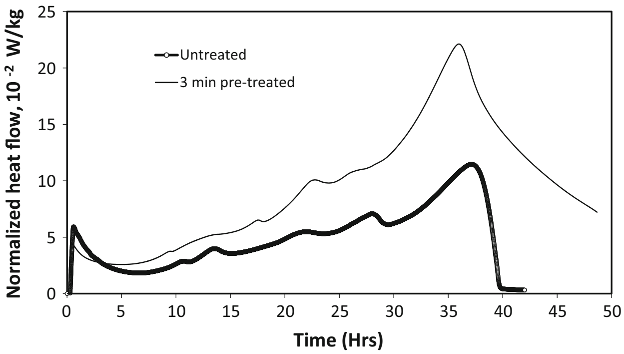

Fig. 4 Heat flow analysis of untreated and pre-treated anaerobic biomass

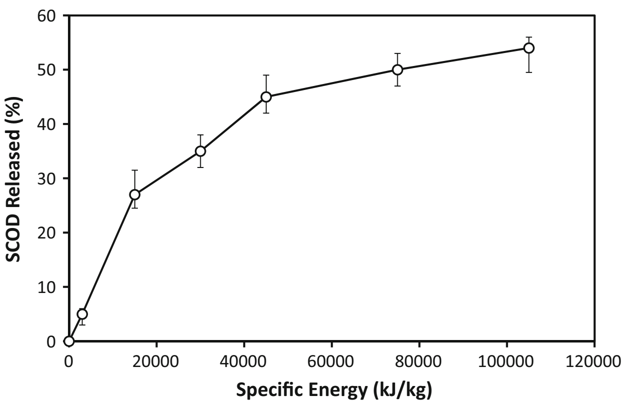

Fig. 5 Effect of ultrasonic disintegration on SCOD

et al. 2010; Mahmoud et al. 2004; Parker 2005). This model is based on the following two facts.

1. The rate of substrate conversion to biogas is directly proportional to the substrate concentration.
2. The volume of gas generated is proportional to the mass of the substrate destroyed.

These facts could be expressed in the form of equations as follows.

$$\frac{dS}{dt} = -kS \tag{3}$$

$$Y = CV(S_0 - S) \tag{4}$$

where k is the overall rate constant (day^{-1}), Y is cumulative gas production (L), C is yield constant (L/g) and V is volume of reactor (L).

Integration of (3) gives

$$S = S_0 \exp(-k(t - t_0)),$$

where t_0 is the lag time (days) and $t > t_0$

Substituting S in (4) gives,

$$Y = CVS_0[1 - \exp(-k(t - t_0))] \tag{5}$$

Rearranging (5) gives,

$$\ln\left(1 - \frac{Y}{CVS_0}\right) = -kt + kt_0 \tag{6}$$

Yield constant, C was calculated from the experimental data. A plot of $\ln\left(1 - \frac{Y}{CVS_0}\right)$ versus time gave the overall rate constant "k" and lag time "t_0" which are presented in Table 4.

Modelling of gas production

Experimental gas production data obtained during the anaerobic digestion process were modelled using modified Gompertz equation (Li et al. 2012; Uma Rani et al. 2012) given below.

$$y = A\exp\left\{-\exp\left[\frac{\mu_m e}{A}(t_0 - t) + 1\right]\right\} \tag{7}$$

where y is the gas accumulation (L g^{-1}), t is the time (days) of the digestion period. A is the gas production potential (L g^{-1}). μ_m is the maximum gas production rate (L g^{-1} d^{-1}), while t_0 is the lag time (days) and e is equal to 2.7183. The model parameters were estimated using a data analysis software and are given in Table 4.

Figure 6a shows the logarithmic plot of gas production. It can be observed from the slope of the plots that the

Table 4 Comparison of kinetic and model parameters for untreated and pre-treated samples after sludge retention time of 34 days

Sample	Parameters	Experiment	Modified Gompertz model	First-order kinetic model
Untreated	Gas production potential [A (L g^{-1})]	0.3833	0.5554	–
	Maximum gas production rate [μ_m (L g^{-1} day^{-1})]	0.0143	0.0149	–
	Lag time [t_0 (days)]	5.4	5.6	3
	Rate constant [k (day^{-1})]	–	–	0.0042
Pre-treated	Gas production potential [A (L g^{-1})]	0.4279	0.5443	–
	Maximum gas production rate [μ_m (L g^{-1} day^{-1})]	0.02	0.019	–
	Lag time [t_0 (days)]	7.1	7.8	3.5
	Rate constant [k (day^{-1})]	–	–	0.0063

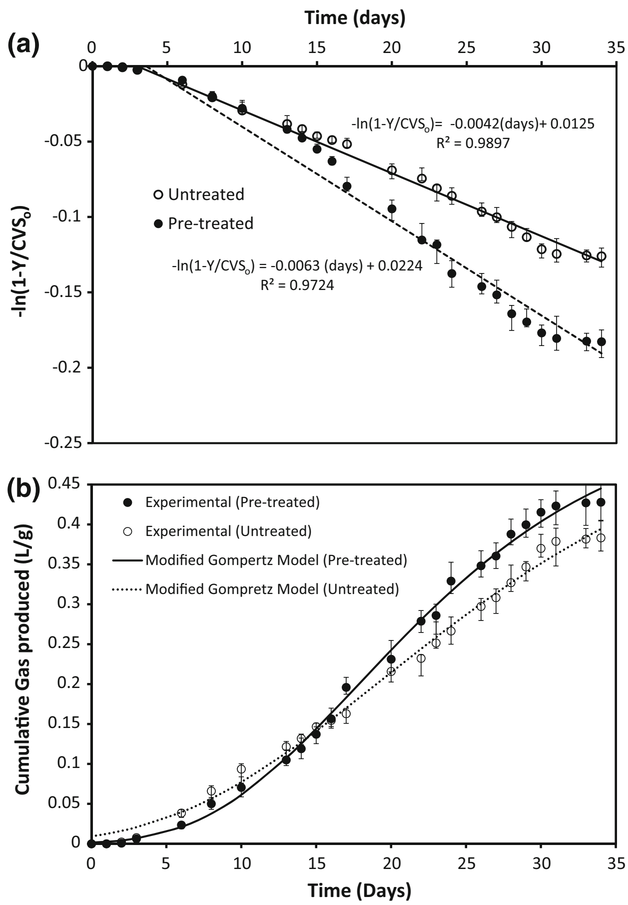

Fig. 6 **a** Logarithmic plot gas production and time, **b** comparison of experimental gas production with modified Gompertz model

digestion of ultrasonic pre-treated sample is 1.5 times faster than that of untreated sample. Pre-treated sample refers to the optimized combination of 3 min treated biomass together with 5 min treated feed. However, the lag time of pre-treated sample is about 20 % higher than that of untreated sample. Soon after pre-treatment, the microorganisms are in a state of stress that they require additional time to recover and actually start the digestion process. This could be the reason for higher lag time of pre-treated sample. Figure 6b shows the comparison of experimental data with the gas production predicted by modified Gompertz model. The model parameters for the best fit are given in Table 4.

Conclusion

The present study investigated the anaerobic co-digestion of ultrasonic disintegrated feed and biomass, and the disintegration effect on biomass was substantiated by isothermal microcalorimetry. Ultrasonic pre-treatment on feed and biomass has been found to maximize gas production with minimum sludge retention time. Longer treatment time on feed may results still improved gas production, but higher mechanical energy input could be a limiting factor. Moderate treatment of biomass (3 min) yielded better gas production, and when it is less or higher than 3 min, there is a retard in gas production. A microcalorimetric heat flow analysis of the anaerobic digestion process indicates the possible hypothesis that the respective stages of the digestion sequence are predominant at their respective time interval. It is observed that more heat energy released by pre-treated biomass sample compared to untreated sample, due to increase in cellular maintenance energy requirements. Kinetic analysis showed that the overall rate constant of ultrasonic pre-treated sample is 1.5 times higher than that of untreated sample. Modified Gompertz model fitted well with the experimental data, and model parameters were evaluated.

Ultrasonic pre-treatment of sludge and biomass could be an economically viable and technically feasible option for enhanced digestion. However, a thorough analysis of the energy requirements and cost economics should be made based on pilot scale studies.

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