Experiment-based thermodynamic feasibility with co-digestion of nutrient-rich biowaste materials for biogas production

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Abstract

Wild strains of algal biomass, a major contributor for eutrophication in freshwater bodies, can be used as a potential substrate in association with other nutrient-rich biowaste materials like animal excreta and industrial wastewater, for biogas production. This novel concept was experimentally evaluated and analyzed by the modified Gompertz equation for maximum biogas production (μ_m), lag phase (λ), and biogas yield (P). The value of correlation coefficient (R^2) was 0.99 at varying temperature ranges (30, 40, and 50 °C). Thermodynamic functions like enthalpy (ΔH), entropy (ΔS), and Gibb's free energy (ΔG) were evaluated for the chemical oxygen demand removal efficiency. Thermodynamic functions such as ΔG (–), ΔH (+), and ΔS (+) showed the spontaneous and endothermic nature of substrate degradation and biogas production was found to be increased with increasing temperature. So, this novel co-digestion approach using nutrient-rich biowaste materials provides a new insight into biogas production with the aim of waste-to-energy generation.

Keywords Nutrient-rich biowaste materials · Co-digestion · Biogas · Kinetic · Thermodynamic functions

Introduction

Eutrophication can diminish or eradicate the fish population in the concerned pond or lake as a consequence, which can lead to the loss of many enriching services provided by the lake or pond. Due to algal blooms, blue water footprints (BWFP) and green water footprints (GWFP) were reduced into gray water footprints (GrWFP). Algal blooms are not the only cause of river or lake pollution, but industrial sectors also play a crucial role in increasing the gray water (Frank et al. 2017). Food sector is one of the major consumers of

water as well as one of the leading producers of effluents per unit of production; in addition to this, it also produces large volume of sludge during biological treatments (Menon et al. 2017). The global water footprint (GWP) for the agricultural sector is 2422 billion cubic meters (BCM) of water, i.e., about 1/4 of the total GWP. Among the various sectors, dairy industry contributes 19% in GWP of agriculture sector (Mekonnen and Hoekstra 2010). India ranks first among the major milk-producing nations and according to an estimate, Indian dairy industries generate about 275 million tons of wastewater annually (Kushwaha et al. 2011). Pollution caused by industrial and dairy effluents is a serious concern throughout the world. Therefore, a green, low-cost, and eco-friendly step is required to minimize the nutrient-rich waste with an alternative use, i.e., to produce biofuel for the society.

As a renewable biomass feedstock, microalgae forfeited of water bodies can be a boon for the sustainable environment such as its capability of mitigating waste CO₂ (Kobayashi et al. 2013) and its potential to grow in organic-rich wastewater. Algae possess a much higher content of water in contrast to other terrestrial energy crops and this makes it more suitable for wet anaerobic digestion processes (Prussi et al. 2014). Water content is known to

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be one of the most important parameters that can affect the whole process of anaerobic digestion. In general, total solid (TS) content up to 2–10% of the medium is usually used for wet digestion and rest of the fresh water is used to make slurry (Ahmad et al. 2017). Various types of organic-rich biomass are enlisted by Karray et al. (2017) for the production of biogas. It is a very slow process and a huge amount of fresh water consumption is needed to produce the final product. Due to the use of fresh water, the process of reaction also becomes slow. Therefore, to speed up the reaction rates with enhancement of biogas yield and process efficiency, a new option like the use of dairy industry wastewater with high organic content and wild algal biomass was taken as an objective in this experimental study to manage the NRW. Thus, co-digestion of wild algal blooms (WAB) with poultry litter waste (PLW), cow dung (CD) and dairy industry wastewater (DIWW) provides a new dimension in the field of sustainable environment. In recent years, the process of anaerobic digestion has been promoted with the use of various types of digestible products, for these two benefits, i.e., generation of energy (biogas) and compost/digestate as soil enhancer. The main aim of this research is to investigate the potential of co-digestion for energy yield with NRW as a substrate, i.e., WAB, PLW, CD and DIWW to minimize the pressure of organic loads on fresh water bodies. The effect of temperature on process efficiency is also investigated with kinetic and thermodynamic functions (Kumar et al. 2017).

Materials and methods

Substrates for process

Raw materials, i.e., wild algal blooms (WAB), cow dung (CD) and poultry litter waste (PLW) were collected as a substrate and used in an equal amount (66.6 g) with dairy industry wastewater (660.60 g) used as water content for the biogas production process.

Dairy industry wastewater (DIWW)

DIWW was collected from Uttar Pradesh Producer Cooperative Milk Union Limited, Lucknow (U.P.), India, which has capacity to produce about > 1 MLD of wastewater. The industry has a conventional wastewater treatment plant, hence the final discharge of industry contains a substantial amount of nutrients. The samples were collected in plastic jars and carried out to the Department of Environmental Science in Bioenergy and wastewater laboratory at Babasaheb Bhimrao Ambedkar University campus for its initial characterization (Table 1).

Wild algal blooms (WAB)

Wild algal blooms were collected from the pond present in the vicinity of Babasaheb Bhimrao Ambedkar University (BBAU) campus, Lucknow (U.P.), India. The collected algal bloom (biomass) underwent the process of dewatering to convert it into a dry biomass using sunlight only [ambient temperature ($35 \pm 5^\circ\text{C}$)]. Dry biomass was then crushed manually to convert it into a powdered form.

Cow dung (CD)

The fresh cow dung was collected from a local dairy farm nearby the university campus. The collected fresh cow dung was in semi-solid condition. The physico-chemical parameters were also performed to evaluate the initial and final changes (Table 1).

Poultry litter waste (PLW)

The poultry litter waste was collected from poultry farm house situated in the outskirts of the Lucknow city (U.P.), India. The collected poultry waste was initially in its solid condition with a mixture of feathers in it and the waste material other than litter was separated manually. After drying and crushing, the litter was taken into the process of measuring using a 5 mm mesh sieve. The characteristics of the

Table 1 Compositional characterization of substrates

S. no	CD	PLW	DAB	DIWW
pH	7.7 ± 1.1	8.9 ± 0.5	5.9 ± 0.5	5.3 ± 0.5
TS (%)	46.6 ± 1.25	36.7 ± 2.2	16.9 ± 1.2	33.4 ± 15
VS (%)	82.6 ± 3.65	68.8 ± 2.3	57.8 ± 1.4	–
TKN (%)	2.6 ± 0.3	4.9 ± 0.5	1.8 ± 0.1	–
TOC (%)	54.6 ± 1.6	46.8 ± 2.1	43.9 ± 2.3	–
COD (mg L^{-1})	$36,000 \pm 231$	$41,000 \pm 158$	$18,000 \pm 235$	2320 ± 24
C/N ratio	19.8 ± 1.2	9.7 ± 06	23.5 ± 0.41	

substrates are given in Table 1. The inoculum was acclimated sludge from a wastewater treatment plant.

All the selected substrates, i.e., WAB, CD, PLW, and DIWW were mixed in a reactor. Where, WAB, CD, PLW together with DIWW were taken in a 1:10 ratio. All the substrates were mixed well in the reactor to balance the nutrients. Furthermore, the experimental setup was kept at three different temperature ranges, i.e., 30, 40 and 50 °C. The pH value of the sample was declined to below 7 on the 3rd day of the experiment. To maintain the pH of system, sodium hydroxide was added additionally, so that the pH of the system will range between 7.0 and 7.3. The experiments were conducted in batch mode with 2000 mL anaerobic digester to investigate its effect on the final product. Anaerobic conditions inside the digester were maintained while purging the N₂ gas. All the experimental setups were done in triplicate.

Experimental design

Analytical procedures

These composite samples were subsequently analyzed for total solids (TS) concentration, total kjeldahl nitrogen (TKN), pH, and volatile solids (VS). TS were determined by drying it in an oven at 100 °C for 48 h. VS content was determined by the mass of sample remaining after heating the dried milled sample at 550 °C for 4 h (American Public Health Association 2005). The TS and VS of the substrate were determined before and after the anaerobic digestion by following the 2540B protocol, while total nitrogen and chemical oxygen demand was determined by following the protocol 4500C and 5220B respectively (APHA 2005). Total carbon in selected substrate was determined by method prescribed by Walkley and Black 1934. The pH value was detected by a digital pH meter (HORIBA) and temperature was measured by a digital thermometer and ignition of flame for the presence of biogas was analyzed visually.

Kinetic functions

Modified Gompertz equation

In the present study, the modified Gompertz equation (MGE) was employed to calculate the formation of biogas (Kumar et al. 2017):

$$Y(t) = P \exp \left\{ - \exp \left[\frac{\mu_m}{P} (\lambda - 1) + 1 \right] \right\}. \quad (1)$$

The equation given above has been used for the prophecy of maximum biogas production potential, with lag phase time. Where, P is the maximum biogas production potential (mg L⁻¹ COD), μ_m is maximum specific biogas production (mg L⁻¹ COD) and λ is lag time (days), t is time of

biogas production (days), $Y(t)$ is cumulative biogas production (mg L⁻¹ COD). The MGE was carefully used to fit the experimental data of this study to determine some important kinetic parameters necessary for the digester design and optimal operation of large-scale anaerobic plants. The solutions to Eq. (1) and other parameter such as P , μ_m and λ were estimated using nonlinear curve fitting tool, obtained using optimization tools with Origin 9.0 software.

Substrate removal kinetics

The first-order substrate removal model was applicable to the removal of D . The change rate of substrate concentration in the complete mixed system could be expressed as follows (Jin and Zheng 2009):

$$dC_e/dt = K_1(C_e - C). \quad (2)$$

Since, the change rate (dC/dt) is negligible under first-order condition, the Eq. (2) can be derived as:

$$\log(C_e - C) = \log(C_e) - K_1 t / 2.303, \quad (3)$$

where, C_e and C are COD removal (mg L⁻¹) at equilibrium and initial constant, respectively. K_1 is the first-order substrate removal rate constant (day⁻¹) at time (t). So, the unknown K_1 can be derived from the slope of the line by plotting graph between $(C_e - C)$ versus C_e in the above Eq. (3) (Hoseyni et al. 2013).

Thermodynamic functions: Eyring and Arrhenius equation

Eyring equation

The effect of temperature on biogas production can be well-expressed by the thermodynamic function. Eyring equation is used in chemical kinetics to describe the variance of the rate of reaction with temperature. An Eyring plot allows the activation parameter enthalpy (ΔH), entropy (ΔS), to be determined from the temperature dependence on the rate constant. For the determination of the kinetics and the Arrhenius parameter, experiments have been calculated with variations in temperature (Augustine et al. 2011).

The linear form of Eyring equation is expressed as given below (Eq. 4):

$$\ln(K/T) = -\Delta H/RT + \ln K_b/h + \Delta S/R. \quad (4)$$

Thermodynamic functions, ΔH and ΔG can be calculated by following the equations given below

$$\Delta H = E_a - RT, \quad (5)$$

$$\Delta G = \Delta H - T\Delta S, \quad (6)$$

where K is kinetic constant of reaction, R is universal gas constant (8.314 K⁻¹ mol⁻¹), T is temperature, K_b is

Boltzmann constant (1.381×10^{-23}) K^{-1} , h -plank constant (6.626×10^{-34} s). Kinetic constant is obtained by fitting a suitable kinetic model to the time profile of substrate utilization. Value of K and E_a obtained from Arrhenius analysis can be substituted in the above set of equation to yield the thermodynamics parameter viz- ΔH (enthalpy change), ΔS (entropy change), and ΔG (Gibb's free energy) associated with the substrate consumption (Firozeh et al. 2016). Activation energy of biogas production with substrate was estimated using Arrhenius plot of $\ln K$ v/s $1/T$ based on Arrhenius equation $K = A^{-E_a/RT}$ (Augustine et al. 2011). Eyring plot of $\ln K$ v/s $1/T$ revealed that thermodynamic analysis of biogas production in batch aerobic digestion experiment was conducted at a temperature 30, 40 and 50 °C.

The abovesaid equation was applied to know the mathematical relationship between biogas productions using NRW as a co-substrate at various temperatures. Thermodynamic parameters obtained from Van't Hoff graph, which is also known as Eyring type equation is the most widely accepted model that has been taken into consideration to know the rate of reaction after degradation of co-substrates with prescribed condition.

Activation energy of process

Temperature plays an essential role in digestion process, as revealed from the previous experimental data. Different values of first-order rate constant were seen for the variable temperature range. The effect of temperature on the inactivation rate coefficient was estimated by the Arrhenius equation (Eq. 7). The Arrhenius equation expresses the function of temperature in first rate constant. According to the Arrhenius equation, the relationship between rate constant and temperature can be expressed as:

$$\ln k = -\frac{E_a}{RT} + \ln A. \quad (7)$$

The R , T , E_a/R , and A are the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), temperature (K), slope of the regression line, and y-intercept, respectively (Augustine et al. 2011).

Results and discussion

A very few number of studies have been done on biogas production using various co-substrates. Agricultural, municipal, and industrial sectors also produce a wide range of waste substrates which are differ in composition and are suitable for direct use in biogas production. Therefore, the use of NRW with the concept of co-digestion provides a new approach with kinetic and thermodynamic options.

Effect of temperature on biogas production

Biogas production from each digester was measured through the water displacement method in all the sets of digesters with time to the change in production being very small. However, depending on temperature, it took around 2–3 days for acclimatization of the digestion process. After stabilization, the mean cumulative gas yield was found to be 4649, 7028, and 8469 mL with different temperature conditions for 30 days as illustrated in Fig. 1. The experimental data reveals that the obtained gas is comparatively low with respect to 30, 40, and 50 °C temperature. It is due to the low microbial activity at 30 °C condition. Xiaojiao et al. (2012) found that biogas production from manure digestion, including dairy manure, confirmed that there was a wide divergence that has been found among biogas production quantities, ranging from 380 to 3000 mL/L, such wide divergences in biogas production could be interpreted as a result of acclimatization of microorganisms. It was further observed that the biogas generation potential of this co-substrate was affected by different selected temperature ranges. Figure 2a plots the mean yield of biogas for three different temperature ranges. Except for first 2–3 days, which was the process stabilization period; the flame was dark blue and vigorous, indicating a good concentration of methane in the biogas at 40 and 50 °C temperature (Okonkwo et al. 2016). In the initial days of experiment (0–3), the presence of gas in the digester was also analyzed using flame ignition and it has been noticed that after 8–10 days, during the stabilization period, the flame shows a dark blue appearance with vigorous burning, that indicates a good concentration of methane in the biogas with 40–50 °C temperatures.

Fig. 1 Biogas production at different temperature ranges

Fig. 2 **a** Cumulative biogas production, and **b** Gompertz model graph for biogas production

Table 2 Kinetic data with the modified Gompertz equation for biogas production with the selected temperature ranges (°C)

Temperature (°C)	P (mL)	λ (days)	μ_m (day ⁻¹)	R^2
30	4428	3.6	0.2	0.96
40	7135	4.9	0.3	0.99
50	8695	5.7	0.3	0.98

Modified Gompertz kinetic study of anaerobic degradation process

The parameters obtained in the optimization process are summarized in Table 2. There was an overall agreement between the model and the experimental data, to determine the optimum equation that can fit with these kinds of NRW and evaluate the parameters that had influence on the anaerobic digestion process. The final biogas production was achieved from the co-digestion of waste and then compared with the maximum biogas production obtained by applying the models to the different points of the experiment at different temperature ranges in Fig. 2a.

Experimental biogas yield $Y_{(t)}$ depends on the removal of COD at different temperatures. The modified Gompertz equation was used to fit the cumulative biogas production (mL) and time (days). Figure 2b clearly shows the experimental results and the modified Gompertz equation's prediction. The equation kinetic constants P , λ , and μ_m were determined using nonlinear curve fitting using the software Origin-9. Based on the modified Gompertz equation, the

maximum biogas yield potential (μ_m) at different temperatures was found to be ≈ 4732 , 7302 and 9153 mL. Finally, the lag phase (i.e., the time between experimental setup and actual biogas production) is increasing with increase in temperature as shown in Table 2. Although, it is noticed that growth of μ_m and λ was increased in the proportion to the biological sludge in the co-digestion mixture at different temperature ranges. In this manner, the model results indicate co-digestion of NRW substrate that is more easily biodegradable by increasing the temperature ranges. In all the digesters with selected temperatures, the coefficient of determination (goodness of fit), R^2 of the modified Gompertz model was found in a range of 0.96 to 99%.

Thermodynamic function of biogas with different temperature

The digester maintained a constant recital at 30, 40 and 50 °C temperature. The efficiency of COD removal as a function of temperature for the batch reaction was analyzed against the initial substrate concentration of $S_0 = 15,600$ mg-COD/L. The maximum COD removal efficiency ($83.73 \pm 1.53\%$) was obtained from the digester operated at 50 °C, but it has also been noticed that removal rates gradually decreased at temperature lower than 40 °C. Figure 3a shows the level of biogas productions at different temperatures in the batch reaction is almost same as 0.68 mg L⁻¹ COD, but the rate of reaction depends on the temperature. The amount of biogas produced from the digester at 30,

Fig. 3 **a** Pseudo first-order rate kinetics, and **b** thermodynamics function plot at various temperatures (K) with Eyring (Ey) plot and Arrhenius (Ea) plot with COD removal

Table 3 Removal of COD (mg/L) removal during biogas production at various temperatures (°C)

Days	30 °C	40 °C	50 °C
0	15,600 ± 0.0	15,600 ± 0.0	15,600 ± 0.0
5	14,876.66 ± 11.71	14,589.74 ± 60.25	11,558.53 ± 55.6
10	13,510.67 ± 68.63	11,769.4 ± 15.38	6544.97 ± 124.36
15	10,872.867 ± 18.66	7323.82 ± 21.64	2915.93 ± 58.41
20	9632.3 ± 27.7	5587.5 ± 3.65	2688.53 ± 10.279
25	9136.9 ± 62.69	5566.51 ± 21.22	2641.97 ± 109.7
30	8579.3 ± 64.62	5562.69 ± 15.73	2619.54 ± 62.2

40 and 50 °C increased with increasing COD removal rate (Table 3).

Zhu (2014) found that a stabilization period is needed, when digestion is carried out at a temperature lower than 40 °C or higher than 50 °C. This result suggests that the activity of the bacteria used in this study depends on the different operational temperatures, i.e., 30, 40, 50 °C to produce a significant amount of biogas. Experimental data for biogas production using dried algal bloom with other co-substrates (i.e., dairy industry wastewater, cow dung, and poultry litter waste) at different temperatures was found best suited with pseudo second-order kinetic model. The graph plot in $(C-C_e) \text{ v/s } t$ was found significant at all the temperatures and shows a high extent of correlation, i.e., a positive correlation ($R^2 = 0.99$). The kinetic constant k was obtained using Eq. (6). The obtained k values were 0.251, 0.255, and 0.271 at 30, 40, and 50 °C, respectively. COD removal efficiency

increased with temperature up to 50 °C in Fig. 3a. Chen et al. (2012) reported that there is a kinetic advantage in the digestion of livestock manure at thermophilic temperature than that at mesophilic temperature. However, the advantages of carrying out the digestion at a temperature higher than 55 °C are insignificant (Zhao et al. 2012). The feasibility of biogas production at different temperatures was observed through the evaluation of thermodynamics variables. ΔH , ΔS , ΔG and k , obtained from a plot of $\ln(K)$ versus $1/T$ (Fig. 3b) on the basis of Eyring's equation given in Table 4.

In the present study, the value of ΔH was found positive for the COD removal, which shows the endothermic nature of COD removal process. It means that heat needs to be supplied to carry out this process. The calculated value for the activation energy (E_a) in the present co-digestion process was found to be almost equal to the enthalpy, i.e., 29.82 kJ mol⁻¹, which was found to be lower than the value of activation energy required for biogas production using single substrates like cow dung (37.82 kJ mol⁻¹), poultry droppings (37.23 kJ mol⁻¹) as reported by Ngozi-Olehi et al. (2010). An increase in temperature was found to enhance the COD removal efficiency and extent of biogas production (Egharevba et al. 2014). The positive value of ΔS was observed in the present co-digestion process, which shows disorder or randomness of the system. The positive value of ΔS is due to the heat transfer in activation of molecule which can be related to the increasing efficiency of COD removal and biogas production with increasing temperature. The negative value of ΔG depicts that COD removal is highly favorable for biogas production, i.e., the reaction is

Table 4 Thermodynamic parameter of removal from the co-digestate for biogas production

Thermodynamics parameter		Values (kJ mol ⁻¹)
Enthalpy (ΔH)		29.82
Entropy (ΔS)		– 1.98
Activation energy (E_a)		29.82
Thermodynamics parameter	Temperature (K)	(ΔG) (kJ mol ⁻¹)
Gibbs free energy (ΔG)	303	– 57.14
	313	– 59.12
	323	– 61.12

spontaneous (Sun et al. 2013). Thus, the observed value of different thermodynamic functions confirmed the thermodynamic feasibility of the co-digestion process, however, similar type of studies are not found in literature, but similar pattern of results with adsorption process are noticed in a few researches (Firozeh et al. 2016; Kothari et al. 2017).

Conclusion

The present study revealed that anaerobic co-digestion process using NRW (algal blooms, cow dung, and poultry litter waste and dairy industry wastewater) has a potential for biogas production at 30, 40, and 50 °C. Hence, to achieve the best biogas at 50 °C, the kinetic of batch experiment for biogas production was estimated by best fitting the data to the well-known model mentioned. The result showed that the most significant regression coefficient ($R^2 = 0.98$) value was obtained using the modified Gompertz model equation for biogas production and significant reduction in COD with increasing temperature of the reactor. The experimental data is proven significant by the first-order kinetic model and thermodynamic functions. Hence, the results are very much helpful to reduce the capital cost involved in the production of biogas. Therefore, the present experimental result promotes the reutilization of waste (solid/liquid) to sustain the biomass-based biofuel and green economy.

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Compliance with ethical standards

Conflict of interest The authors of this manuscript declare that there is no conflict of interest with anyone.

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