Research Article

Enhancement of biogas production from organic fraction of municipal solid waste using acid pretreatment

Arpita Dasgupta[1] · Munish K. Chandel[1]

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Abstract

Anaerobic digestion of organic fraction of municipal solid waste (OFMSW) is a potential and economic technique for harnessing bioenergy from Indian municipal solid waste. Pretreatment before anaerobic digestion has been known to improve biodegradability of substrate and enhance biogas production. In this study, the effectiveness of acid pretreatment in enhancing the hydrolysis of complex organic matter and ensuing biogas generation from OFMSW was studied using one strong and one weak acid. Acid pretreatment (pH 6–pH 1) of OFMSW was carried out using hydrochloric acid (HCl) and acetic acid (CH_3COOH) for 24 h before batch anaerobic digestion assays with cow dung as inoculum. Increase in biogas yield ranged between 13.2 and 28.9% as compared to untreated OFMSW after pretreatment with HCl, whereas the same varied between 8.2 and 16% in case of CH_3COOH pretreatment. The highest biogas yield (389.4 ml/gVS) with methane content of 68.3% was obtained after pretreatment with HCl at pH 3, whereas for CH_3COOH, the highest yield (350.2 ml/gVS) with 67.4% methane was observed after pretreatment at pH 1. OFMSW characteristics after each pretreatment step and their variation during the course of anaerobic digestion were also studied. An economic evaluation of all pretreatment scenarios was performed; out of which, pretreatment of OFMSW with HCl at pH 4–pH 6 yielded positive results in terms of net revenue gains.

Keywords Acid pretreatment · Anaerobic digestion · Biogas · Methane · Municipal solid waste · India

1 Introduction

Municipal solid waste (MSW) is one of the potential sources of alternative energy that reduces dependency on fossil fuels and aids in abating the effects of global warming. Approximately, 143,500 tonnes of MSW is generated in India each day, the major fraction (50–70%) comprising biodegradable waste. Improper storage, lack of source segregation and unscientific management of Indian MSW pose serious threats to public health and environment. More than 90% of MSW generated in urban India is disposed of in open dumps. This colossal amount of MSW can be utilized as a source of energy which would not only contribute towards energy security but also prevent problems arising due to improper MSW management and reduce the amount of waste requiring final disposal [1, 2].

Anaerobic digestion is a promising and eco-friendly technique for treatment of organic fraction of MSW (OFMSW). In addition, energy is recovered in the form of biogas which can be utilized for generating electricity and/or heat. It is of great significance from the perspective of waste management and generation of bioenergy [3–5]. However, the heterogeneity and complex chemical characteristics of Indian OFMSW often restrict the efficiency of anaerobic digestion. Lignocellulosic biomass, which constitutes a major fraction of OFMSW, is composed of cross-linked rigid polymers such as cellulose, hemicellulose and lignin. These are difficult to biodegrade as their

✉ Munish K. Chandel, munish.chandel@iitb.ac.in | [1]Environmental Science and Engineering Department, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India.

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complex chemical structures resist microbial attack during anaerobic digestion [5, 6]. As a result, hydrolysis of organic matter into soluble compounds becomes a rate limiting step. Also, lipids in the form of long chain fatty acids (LCFA) present in kitchen waste tend to restrict mass transfer during anaerobic digestion and hence display least hydrolysis rate constants. Consequently, biogas yield and digestion time are adversely affected due to low biodegradability and decreased rate of hydrolysis [5, 7, 8].

Improvement in the hydrolysis rate during anaerobic digestion will therefore enhance biodegradability of substrate and lead to increase in biogas yield within a shorter digestion time [5, 7, 9, 10]. Pretreatment of OFMSW prior to anaerobic digestion is a useful technique to facilitate solubilization of complex organic matter, thereby increasing biodegradability and rate of hydrolysis. Pretreatment can be achieved by several methods, namely physical, chemical and biological or a combination of the same [5, 7, 9, 10]. Chemical pretreatment with acid is an inexpensive but effective method that improves anaerobic digestion by aiding hydrolysis of complex organic matter present in the substrate [11, 12]. Acid pretreatment results in condensation and precipitation of lignin, whereas hemicellulose is degraded into respective monomers. Additionally, the acidic condition is favourable for enzymatic activity of hydrolytic bacteria during anaerobic digestion. The latter specifically holds true for two-stage anaerobic digestion [3, 4, 11, 13]. Various acids like acetic, hydrochloric, maleic, nitric, peracetic, phosphoric and sulphuric have been used with the objective of increasing biogas yield from lignocellulosic materials such as bagasse, cassava residues, coconut fibres, maize plants, newsprint, sorghum forage, waste activated sludge and wheat straw [11, 14, 15]. Pretreatment of lignocellulosic biomass with dilute acids has also been employed to enhance bioethanol production [16]. However, there is shortage of research on acid pretreatment of OFMSW and its subsequent impact on biogas generation through anaerobic digestion [4]. It is essential to analyse the characteristic change in OFMSW post-acid pretreatment and identify the optimum acid concentration required to maximize the bioenergy yield during anaerobic digestion. This would ensure efficient resource utilization and help in understanding economic viability during full-scale implementation.

The objective of this study is to understand the effectiveness of acid pretreatment on solubilization of organic matter present in OFMSW. OFMSW was pretreated using one strong and one weak acid and subsequently analysed for the changes in characteristics of OFMSW before and after pretreatment. Thereafter, batch assays were conducted in order to understand the effects of acid pretreatment on anaerobic digestion with respect to biogas yield, methane content and retention time.

2 Materials and methods

2.1 Characterization of OFMSW

Due to its highly heterogeneous nature, it is very challenging to put forward a composition that would serve as a representative sample of Indian OFMSW. However, in order to ascertain comparison between experiments and draw conclusions, the composition of OFMSW was considered in such a way; so that, it would crudely represent the biodegradable fraction in Indian MSW. Approximately, 12 kg of OFMSW was collected in a single acquisition from various sources inside Indian Institute of Technology Bombay (India) for the purpose of this study. The components (% wet weight) of OFMSW were: cooked food waste (50%), vegetable and fruit peels (25%) and garden waste (25%). The detailed physical composition can be found in an earlier research article published by the authors [9]. The collected samples were ground using a mixer–grinder to obtain homogenized mixture of particle size 2–3 mm. This mixture was refrigerated at 2 °C until further experimentation. Cow dung was collected from cattle shed in Powai, Mumbai, which served as inoculum for anaerobic digestion batch experiments. The characteristics of OFMSW and inoculum (average of three determinations with standard deviation) are presented in Table 1.

2.2 Acid pretreatment of OFMSW

Two different acids were selected for pretreatment of OFMSW prior to anaerobic digestion. Concentrated hydrochloric acid (37% HCl) was chosen to study the impact of pretreatment of OFMSW with a strong acid, whereas glacial acetic acid (99.5% CH_3COOH) was used to study the

Table 1 Characteristics of organic fraction of municipal solid waste and inoculum (cow dung)

Parameter	Unit	OFMSW	Inoculum
pH	–	6.84 ± 0.02	7.58 ± 0.02
SCOD	g/kg	94.87 ± 1.86	70.47 ± 2.68
TS	g/kg	461.40 ± 6.48	191.40 ± 3.74
VS	g/kg	388.41 ± 6.41	163.30 ± 1.90
VFA	mg/l	460.82 ± 1.36	151.17 ± 1.21
Soluble carbohydrate	g/kg	195.02 ± 1.16	nd
Soluble protein	g/kg	77.51 ± 1.24	nd
Lipids	g/kg	113.38 ± 0.82	nd
Cellulose	g/kg	85.28 ± 0.79	nd
Hemicellulose	g/kg	54.81 ± 0.62	nd
Lignin	g/kg	48.93 ± 0.57	nd

nd not determined

effect of pretreatment with a weak acid. In both cases, pretreatment with dilute acids was avoided in order to minimize the effect on final total solid content during anaerobic digestion. pH range of experiment was kept between pH 6 and pH 1, for pretreatment with each acid. Acidification experiments were carried out titrimetrically by addition of acids in a stepwise manner (drop by drop) until the desired pH was achieved. Uniform mixing of acid into OFMSW slurry was ensured by means of both magnetic stirrer and manual mixing. Pretreated OFMSW slurry was then kept aside for 24 h in order to guarantee completion of solubilization or hydrolysis of substrate. After 24 h, the samples were neutralized by titrating with 10 M sodium hydroxide solution (same as acidification step) and the pH was brought up to 7.0 ± 0.2, before subjecting them to batch anaerobic digestion. Volume of acid and alkali required during pretreatment and neutralization is presented in Table 2. pH values attained after acidification and neutralization steps are not exact due to the usage of concentrated acids and alkalis during pretreatment.

2.3 Anaerobic digestion of untreated and pretreated OFMSW

Batch anaerobic digestion of acid-pretreated OFMSW with cow dung as inoculum was carried out using a pulse flow respirometer system (RSA, PF-8000). The substrate–inoculum ratio was kept as 1:1 (volatile solid basis), and total solid content was maintained at 20%. The respirometer assembly was equipped with glass digester bottles of 500 ml, into which 250 ml was kept as working volume. Anaerobic conditions were ensured by purging nitrogen into the glass bottles for about 2 min. The temperature of batch assays was maintained at 37 °C using a hot water bath. Uniform mixing throughout the assay was achieved using a magnetic stirrer. Batch anaerobic digestion of untreated OFMSW served as control. Also, anaerobic digestion of cow dung was carried out separately in order to account for biogas generation from inoculum. The daily biogas generation was monitored and recorded via a sensitive transducer located in the control module of the respirometer system. All experiments and analysis were performed in triplicates, and their average results have been presented here.

2.4 Analytical methods

Soluble indexes were measured after obtaining the filtrate of the sample by diluting it with deionized water and passing through a filter paper with 0.45 µm pore size. pH, TS, VS and SCOD were measured according to standard methods [17]. VFAs as acetic acid equivalents were estimated as per the method proposed by Siedlecka et al. [18]. The procedure for determination of lignocellulosic content given by Ayeni et al. [19] was used to measure cellulose, hemicellulose and lignin content in OFMSW. Soluble carbohydrate was measured using phenol–sulphuric acid method, whereas Bradford dye-binding method was used to determine soluble protein concentration. Lipid content, in the hydrolysate, was determined by fatty acid methyl ester (FAME) analysis. The detailed procedure for extraction and determination of these parameters was adopted from Nielsen [20]. Biogas was characterized using gas chromatography (PerkinElmer Clarus 500) using a thermal conductivity detector (TCD). Packed column (Porapak Q, 50–80 mesh; Sigma) was used with helium (40 ml/min) as the carrier gas. The temperature profile was kept as: column 80 °C, injector 200 °C and detector at 200 °C. Standard gas mixture containing CH_4, CO_2, N_2, O_2 and H_2 was used for calibrating the instrument prior to sample analysis. Values of gas composition are reported with respect to standard temperature and pressure.

2.5 Economic evaluation

An economic evaluation of acid pretreatment is necessary in addition to its effectiveness on anaerobic digestion in order to assess the viability of the process. In this study, only the cost incurred for pretreatment (acidification and neutralization) and the resultant revenue generated in the

Table 2 Amount of acid and alkali required for acidification and neutralization

pH	Volume of acid added (ml/l)		Actual pretreatment pH		Volume of alkali added (ml/l)		Final pH	
	HCl	CH_3COOH	HCl	CH_3COOH	HCl	CH_3COOH	HCl	CH_3COOH
6	1.25	2.25	6.12	6.09	0.50	0.50	7.12	7.09
5	1.50	3.00	5.01	5.05	1.20	1.00	7.06	7.06
4	3.50	7.00	4.09	4.01	4.50	4.00	7.03	7.03
3	5.65	13.50	3.12	3.03	10.50	9.50	7.02	7.02
2	8.75	20.50	2.07	2.21	12.50	12.00	6.98	6.98
1	17.5	38.50	1.28	1.78	22.50	19.50	7.03	7.02

Volume of acid/alkali is presented as ml/l of OFMSW slurry (20% total solid) with initial pH of 6.84 ± 0.02

form of biogas have been taken into consideration. Other costs associated with transportation, storage, pumping, temperature, mixing, etc., have not been considered. Additionally, the cost has been calculated solely with respect to average methane content of biogas generated during anaerobic digestion. Thereafter, equivalence with liquefied petroleum gas (LPG) was drawn on the basis of calorific value. Any cost associated with upgradation, purification or bottling of biogas has not been considered. It has been assumed that scaled-up continuous process would also yield the same results as batch anaerobic digestion assays conducted in this study, and therefore, if and any reduction in the digester size due to potential reduction in hydraulic retention time (HRT) has been disregarded. The expenses incurred and revenue generated have been expressed in terms of rupee per kilogram of OFMSW (₹/kg) and US dollar per kilogram of OFMSW ($/kg). The costs of chemicals (commercial grade) were obtained from M/s Chemtek Scientific Company, Mumbai. The quoted price for HCl and CH_3COOH was ₹50/l ($0.66/l) and ₹170/l ($2.25/l), respectively, whereas NaOH was quoted at ₹156/kg ($2.06/l). The cost of acid pretreatment of OFMSW was calculated based on the volume of acid and alkali required for each pretreatment scenario (Table 2). The amount of average methane generated after anaerobic digestion was equated with the amount of LPG based on calorific value. The net calorific value of methane and LPG was taken as 49.9 and 45.6 MJ/kg, respectively [21, 22]. Finally, the revenue generated was calculated using the price of subsidized LPG in Mumbai [23]. The net gain is presented as the difference between revenue generated and cost incurred for acid pretreatment.

3 Results

3.1 Effects of acid pretreatment on characteristics of OFMSW

The change in characteristics of OFMSW as a result of acid pretreatment is shown in Table 3. SCOD, VFA and VS are essential parameters which indicate the amount of solubilized organic matter and in turn determine biodegradability of any substrate. Hence, they greatly influence efficiency of anaerobic digestion. A significant increase in SCOD of OFMSW was observed after acid pretreatment. This was due to hydrolysis of complex organic matter into simpler and soluble products. Higher values of SCOD were obtained after pretreatment with strong acid (HCl) than weak acid (CH_3COOH). An increase of 14.6–84.5% in SCOD was obtained after pretreatment with HCl, whereas the same ranged between 11 and 75.3% after pretreatment with CH_3COOH. Additionally, in both cases, pretreatment

Table 3 Characteristics of acid-pretreated organic fraction of municipal solid waste

Parameter	Unit	HCl pretreatment						CH_3COOH pretreatment					
pH	–	6	5	4	3	2	1	6	5	4	3	2	1
SCOD	g/kg	108.73 ± 0.88	133.46 ± 1.12	148.73 ± 0.66	165.88 ± 1.19	169.27 ± 0.79	175.04 ± 1.01	105.31 ± 0.81	121.36 ± 0.93	135.74 ± 1.03	151.87 ± 0.67	157.25 ± 1.72	166.37 ± 0.82
VS	g/kg	373.23 ± 0.75	365.37 ± 0.19	349.14 ± 0.53	337.72 ± 0.38	318.86 ± 0.79	309.55 ± 0.62	380.29 ± 0.79	369.83 ± 0.91	357.22 ± 0.65	344.44 ± 0.49	339.37 ± 0.37	324.64 ± 0.73
VFA	mg/l	872.71 ± 1.09	1079.22 ± 1.18	2812.58 ± 0.59	3588.10 ± 1.21	4497.36 ± 0.96	5066.18 ± 0.85	865.88 ± 1.27	978.42 ± 0.72	1284.76 ± 0.49	2973.19 ± 0.68	3317.62 ± 1.06	3891.75 ± 1.18
Soluble carbohydrate	g/kg	203.81 ± 0.24	238.51 ± 0.47	276.92 ± 0.61	308.12 ± 0.77	333.36 ± 0.83	351.92 ± 0.91	197.35 ± 0.53	210.28 ± 0.28	252.37 ± 0.76	283.56 ± 1.03	299.08 ± 1.07	317.46 ± 0.99
Soluble protein	g/kg	80.93 ± 0.36	86.13 ± 0.69	89.10 ± 0.19	97.62 ± 0.92	103.87 ± 0.33	104.25 ± 0.38	79.02 ± 0.73	82.43 ± 1.09	87.84 ± 0.48	92.38 ± 0.13	95.19 ± 0.68	99.99 ± 0.79
Lipids	g/kg	123.32 ± 0.44	134.66 ± 0.91	146.84 ± 0.19	160.03 ± 0.66	169.87 ± 0.83	174.35 ± 0.67	119.19 ± 0.54	127.29 ± 0.52	138.43 ± 1.07	148.92 ± 0.90	156.69 ± 1.02	163.27 ± 0.32
Cellulose	g/kg	80.73 ± 0.72	75.21 ± 0.29	68.73 ± 0.81	61.09 ± 0.73	57.14 ± 0.97	56.38 ± 0.71	83.92 ± 0.82	78.48 ± 0.17	70.18 ± 0.47	66.61 ± 1.16	64.39 ± 0.99	58.54 ± 0.28
Hemicellulose	g/kg	50.26 ± 0.27	44.74 ± 0.73	38.26 ± 0.77	30.62 ± 0.49	26.67 ± 1.03	25.91 ± 0.89	53.45 ± 0.93	48.01 ± 0.28	39.71 ± 0.63	36.14 ± 0.77	33.92 ± 0.58	28.07 ± 1.04
Lignin	g/kg	48.62 ± 1.02	47.78 ± 0.41	47.27 ± 0.57	46.98 ± 1.01	46.03 ± 1.18	45.27 ± 0.29	48.81 ± 0.71	48.37 ± 0.49	47.97 ± 0.57	47.13 ± 0.65	46.87 ± 0.69	46.72 ± 1.17

at lower pH resulted in higher amount of SCOD production, meaning the highest concentration of SCOD was obtained after pretreatment at pH 1. An upsurge in VFA concentration was also observed post-acid pretreatment of OFMSW. VFA content ranged between 872.7 and 5066.2 mg/l after pretreatment with HCl, whereas it was found to be between 865.8 and 3891.7 mg/l after pretreatment with CH_3COOH, as compared to 460.8 mg/l of untreated OFMSW. Results of VFA content also indicate that pretreatment at lower pH yielded better solubilization of complex matter and subsequent release of organic acids. VS content was found to decrease with increase in pretreatment severity, i.e. pretreatment at lower pH resulted in higher solubilization of VS present in OFMSW. Reduction in VS was marginal at pH 6 after treatment with both HCl and CH_3COOH, ranging between 2 and 3.8%. However, amid pH range of 5–1, VS reduction varied between 5.9–20.3 and 4.8–16.4%, for pretreatment with HCl and CH_3COOH, respectively. It should be noted that in case of CH_3COOH pretreatment, rise in SCOD and VFA is also attributed to the addition CH_3COOH. Hence, in order to account for the increase in SCOD and VFA as a result of acid pretreatment, the values of the same were corrected for CH_3COOH addition. Increased solubilization of organic matter as a result of acid pretreatment has also been demonstrated by other researchers. For example, peracetic acid pretreatment of waste activated sludge (100 g/kg DS) yielded SCOD and VFA concentration of 8650 mg/l and 8413 mg/l, respectively, as compared to 2580 mg/l and 328 mg/l of untreated sludge [3].

Acid pretreatment was found to improve solubilization of carbohydrates, proteins and lipids present in OFMSW. Pretreatment at lower pH yielded better results indicating greater degree of solubilization of complex organic matter into respective monomers [11–15]. The highest content of carbohydrate, protein and lipids was obtained in the hydrolysate after pretreatment of OFMSW at pH 1 in case of both HCl and CH_3COOH. Soluble carbohydrate ranged between 203.8–351.9 and 197.3–317.46 g/kg after treatment with HCl and CH_3COOH, respectively. This increase was as high as 80.4% and 62.7% compared to that of untreated OFMSW after pretreatment with HCl and CH_3COOH. Increase in soluble protein ranged between 4.4–34.4 and 1.9–29% as a result of treatment with HCl and CH_3COOH. The lipid content in the hydrolysate varied between 123.3–174.3 and 119.81–163.27 g/kg after treatment with HCl and CH_3COOH, respectively, in comparison with 113.38 g/kg of untreated OFMSW.

The impact of acid pretreatment on change in lignocellulosic structure of OFMSW is shown in Table 3. A significant decrease in cellulose and hemicellulose was observed after acid pretreatment; specifically, at lower pH. Pretreatment with HCl at pH 6 led to reduction in cellulose content by 5.3%, whereas 33.8% reduction was obtained after pretreatment at pH 1. In case of CH_3COOH pretreatment, 1.5% reduction in cellulose was observed after pretreatment at pH 6, while pretreatment at pH 1 yielded 31.3% reduction in cellulose. Hemicellulose, on the other hand, witnessed greater degradation as compared to cellulose. Reduction in hemicellulose after pretreatment with HCl ranged between 8.3 and 52.7%, whereas the same after pretreatment with CH_3COOH varied between 2.4 and 48.7%. It may be noted that the highest degradation of cellulose and hemicellulose was obtained after pretreatment at pH 1, indicating that harsher pretreatment conditions were effective in altering the rigid structure of cellulosic biomass. Pretreatment with acid causes disruption in covalent and hydrogen bonds of cellulosic biomass which in turns leads to degradation of hemicellulose and reduction in cellulose crystallinity [24]. However, lignin fraction largely remained unaltered even after pretreatment with acids at pH 1. Lignin content varied between 45.2 and 48.6 g/kg after pretreatment with HCl and 46–48.8 g/kg after pretreatment with CH_3COOH, as compared to 48.9 g/kg in untreated OFMSW. Hence, it was concluded that acid pretreatment, while beneficial in degrading hemicellulose and reducing cellulose of OFMSW, did not prove effective in removal of lignin. This is in agreement with other studies where acid pretreatment was employed to improved biodegradability of lignocellulosic biomasses [5, 11–16, 24].

3.2 Anaerobic digestion of untreated and pretreated OFMSW

Figure 1 shows the cumulative biogas generation yield (ml/gVS) with respect to time obtained during anaerobic digestion of OFMSW pretreated with HCl and CH_3COOH as compared to untreated OFMSW. As shown, acid pretreatment considerably aided in increasing cumulative biogas generation during anaerobic digestion. An increase in cumulative biogas yield by 13.2–28.9% and 8.2–16% was obtained after pretreatment with HCl and CH_3COOH, respectively. In case of pretreatment with HCl, the highest cumulative biogas yield (389.4 ml/gVS) as compared to 301.9 ml/gVS of untreated OFMSW was obtained after treatment at pH 3, whereas in case of CH_3COOH pretreatment, the highest biogas yield of 350.2 ml/gVS was achieved after pretreatment at pH 1. This is in accordance with the results presented in Table 3 that shows an increase of 74.8–75.3% in SCOD and a reduction of 13–16.4% in VS, reinstating the fact that acid pretreatment was indeed helpful in hydrolysing organic matter that consequently enhanced biogas generation during anaerobic digestion of OFMSW. The technical digestion time (T80), which is defined as the time required to generate 80% of the maximum biogas production, serves as

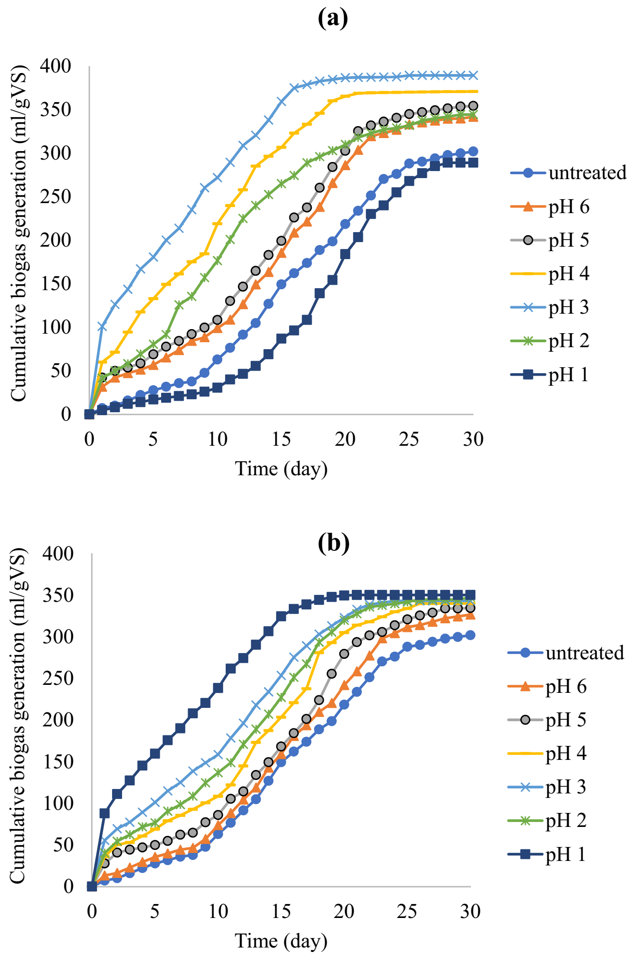

Fig. 1 Cumulative biogas generated during anaerobic digestion of OFMSW pretreated with HCl (**a**) and CH_3COOH (**b**) as compared to untreated OFMSW

a guideline for hydraulic retention time during design of anaerobic digesters [12, 25]. Another advantage of acid pretreatment of OFMSW was the reduction in hydraulic retention time (HRT) that complemented the increase in biogas yield during anaerobic digestion. This is beneficial as minimum attainable HRT is crucial in determining volume of digester and expense operation [8]. Reduction in digestion time is important as it indicates enhanced substrate bio-digestibility and consequently a more efficient anaerobic digestion system.

Modified Gompertz equation was used to simulate biogas generation during anaerobic digestion:

$$M = P * \exp\left\{-\exp\left[\frac{eR_{max}}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where M: cumulative biogas yield (ml); P: biogas production potential (ml); R_{max}: maximum biogas production rate (ml/day); λ: lag phase (day); t: time (day); and e: 2.718282. The parameters of biogas generation for both untreated and acid-pretreated OFMSW were calculated and are shown in Table 4. As seen, lag phase and T80 of untreated OFMSW were 6.77 and 22.33 days, respectively. In contrast, the lag phase and T80 of OFMSW pretreated with HCl at pH 3 (which resulted in the highest cumulative biogas generation) were 0.08 and 11.02 days, respectively, suggesting significant reduction in hydraulic retention time. In case of CH_3COOH, pretreatment of OFMSW at pH 1 resulted in least amount of lag phase and T80 during anaerobic digestion, i.e. 0.20 and 11.79 days. Other essential parameters governing hydraulic retention time in continuous process are the biogas production rate and effective biogas production period. The latter can be achieved by subtracting the lag phase from T80 [12]. For OFMSW pretreated with HCl at pH 3, the maximum

Table 4 Parameters of biogas generation obtained using the modified Gompertz equation

Acid	Pretreatment pH	Lag phase (λ) (day)	R_{max} (ml/day)	P (ml)	T80 (day)	Effective biogas production period (T80-λ) (day)	R^2
HCl	6	3.11	345.33	7083.46	20.70	17.59	0.998
	5	0.85	424.62	7538.18	16.33	15.48	0.997
	4	0.20	495.13	8197.46	14.04	13.84	0.996
	3	0.08	679.12	8267.29	11.02	10.94	0.996
	2	2.26	365.63	7286.69	19.91	17.65	0.997
	1	10.05	255.73	5827.13	24.87	14.82	0.996
CH_3COOH	6	6.50	341.78	7069.22	21.50	15.00	0.995
	5	5.54	387.90	7122.53	19.95	14.41	0.998
	4	3.17	411.54	7243.08	19.04	15.87	0.997
	3	2.66	419.70	7260.15	18.08	15.42	0.998
	2	1.26	467.28	7351.23	16.66	15.40	0.996
	1	0.20	594.33	7583.60	11.79	11.59	0.997
Untreated		6.77	342.27	7096.51	22.33	15.56	0.994

biogas production rate and effective biogas production period were 679.12 ml/day and 10.94 days, respectively, whereas, for OFMSW pretreated with CH_3COOH at pH 1, the maximum biogas production rate was 594.33 ml/day and the effective biogas production period was 11.59 days. In comparison, anaerobic digestion of untreated OFMSW resulted in maximum biogas production rate of 342.27 ml/day and effective biogas production period of 15.56 days. The results obtained in this study are coherent with prior researches that demonstrated the effectiveness of acid pretreatment in augmenting biodegradability of substrate, thereby increasing biogas generation [3, 11, 13, 15, 24]. When pretreated with CH_3COOH at different pH, the sequence of biogas production from OFMSW during anaerobic digestion was pH 1 > pH 2 > pH 3 > pH 4 > pH 5 > pH 6 > untreated. This indicates that high dosage was beneficial in augmenting biogas generation during pretreatment with a weak acid. However, biogas yield did not improve as chemical concentration was increased in case of pretreatment with a strong acid. The sequence of biogas production, when OFMSW was pretreated with HCl, was found to be pH 3 > pH 4 > pH 5 > pH 2 > pH 6 > untreated > pH 1. Biogas generation after pretreatment with HCl at pH 2 witnessed a reduction by 11.5% as compared to the highest cumulative biogas generation of 389.4 ml/gVS, achieved after pretreatment at pH 3. In fact, it is comparable to biogas generation obtained after pretreatment at pH 6. Additionally, biogas yield after pretreatment of OFMSW with HCl at pH 1 decreased by 4.2% as compared to untreated OFMSW. This implies that, while higher doses (pH 2 and pH 1) of strong acid such as HCl did facilitate solubilization of organic matter (Table 3), it necessarily did not lead to increase in overall yield of biogas. This may be due to elevated VFA concentrations which inhibit methanogenic activity during anaerobic digestion. Consequently, VFAs remain unutilized and accumulated in the digester that results in reduction of pH and ultimately leads to inefficient anaerobic digestion [3]. The decrease in biogas yield may also have been due to the presence of excess hydrogen ions as a result of acid pretreatment. Excessive hydrogen ions are toxic to methanogens and are known to disrupt their metabolism during anaerobic digestion [24, 26]. Pretreatment with strong acid at severe conditions (below pH 2) has been known to steer the formation of furan-type compounds such as hydroxymethylfurfural (HMF) and furfural that upset microbial activity and inhibit fermentation during anaerobic digestion [10, 16]. In a comparative study for improving methane yield of corn straw by pretreatment with seven different chemicals, Song et al. [24] witnessed that methane yield did not improve as the chemical concentration increased. The highest methane yield was achieved at different concentrations for different chemical pretreatments. For pretreatment with strong acids such as HCl (1–4% w/w) and H_2SO_4 (1–4% w/w), the highest methane yield was achieved at 2% concentration, whereas for CH_3COOH (1–4% w/w), the highest methane yield was attained after pretreatment of corn straw with 4% concentration. This was attributed to the presence of excessive hydrogen ions that may have potentially caused toxicity to the methanogens by inhibiting their activity and interfering with their metabolism. In a study by Passos et al. [35] on impact of thermochemical pretreatment (0.5–10% HCl for 12 h at 37 °C) on anaerobic digestion of dairy cow manure, the authors found that the highest improvement in methane yield was achieved for 2% dose of HCl. According to them, this was due to the production of recalcitrant compounds and/or degradation of the liquid fraction during the harsher pretreatment step at greater HCl dosages.

The average volumetric concentrations of methane and carbon dioxide in the biogas derived from anaerobic digestion of acid-pretreated OFMSW as compared to untreated OFMSW are shown in Fig. 2. The mean methane and carbon dioxide concentrations in the biogas obtained

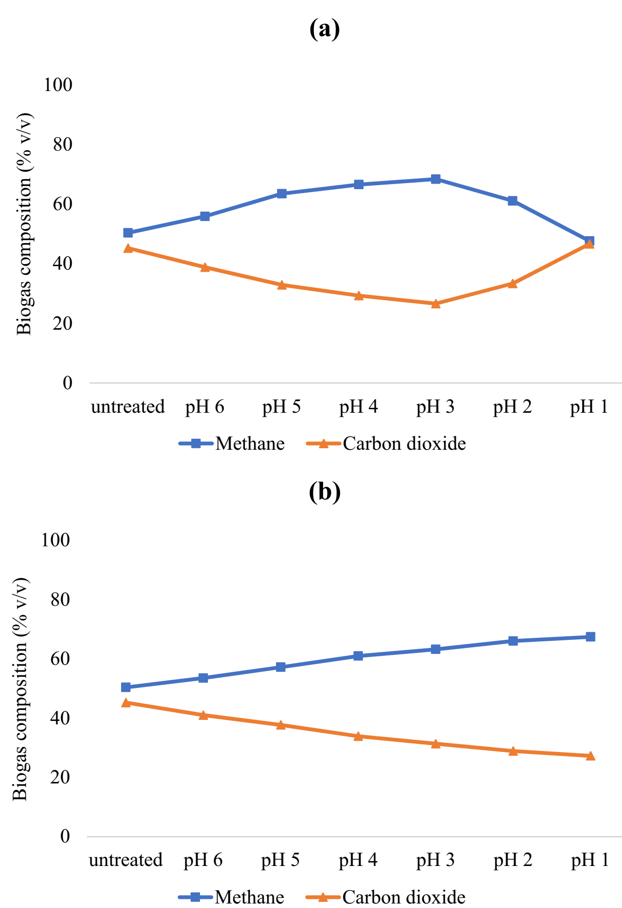

Fig. 2 Average volumetric concentration of methane and carbon dioxide obtained during anaerobic digestion of OFMSW pretreated with HCl (**a**) and CH_3COOH (**b**) as compared to untreated OFMSW

from untreated OFMSW were 50.3% and 45.2%, respectively. Pretreatment of OFMSW with CH_3COOH resulted in average methane content ranging between 53.4 and 67.3%. The highest mean methane content was achieved after pretreatment with CH_3COOH at pH 1, which is 33.8% more than that of untreated OFMSW. In case of pretreatment with HCl, the average methane content varied between 55.8 and 68.3% for treatment between pH 6 and pH 3, with pH 3 yielding the highest volumetric methane concentration (35.7% more than that of untreated OFMSW) during anaerobic digestion. However, methane concentration in biogas dropped after pretreatment of OFMSW with HCl at pH 2 and pH 1. A decrease of 10.6% in methane concentration was seen after pretreatment at pH 2 as compared to pretreatment at pH 3. Additionally, pretreatment of OFMSW at pH 1 yielded mean methane concentration of 47.5% during anaerobic digestion which is 5.4% less than that of untreated OFMSW. This is in compliance with the results of cumulative biogas yield obtained after pretreatment of OFMSW with a strong acid such as HCl (Fig. 1). These results further reinstate that pretreatment of OFMSW with a strong acid at extreme conditions (pH 2 and pH 1) had negative impact on anaerobic digestion and, therefore, must be avoided.

3.3 Effect of acid pretreatment on process parameters during anaerobic digestion

The most influential process parameters that govern the performance of anaerobic digestion are pH and VFA. VFAs are crucial intermediates that are formed as a result of acidogenesis during anaerobic digestion. Subsequently, VFAs are utilized during methanogenesis to generate biogas (methane and carbon dioxide). pH, furthermore, is reliant on and influenced by the production and consumption of VFA and the buffering capacity of the anaerobic digestion system. pH serves as a crucial indicator of anaerobic digester health and robustness. Therefore, quantifying both VFA and pH is essential for monitoring the efficiency and functioning of anaerobic digesters [11, 13, 15]. The impact of acid pretreatment on pH and VFA during anaerobic digestion of OFMSW pretreated with HCl and CH_3COOH is shown in Fig. 3a–d. As evident, the curves of pH and VFA complement each other. pH, for all pretreatment scenarios, decreased in the initial phase of anaerobic digestion as a result of VFA production. Subsequently, with the consumption of VFA by methanogens, pH increased and stabilized as anaerobic digestion proceeded. However, vital differences were observed between pH and VFA curves of untreated and acid-pretreated OFMSW. Increase in VFA and resulting decrease in pH were gradual in case of untreated OFMSW which persisted till the twelfth day of anaerobic digestion. In contrast, acid-pretreated OFMSW witnessed rapid changes in pH and VFA. For pretreatment scenarios that proved to be most effective in terms of cumulative biogas generation, minimum values of pH and corresponding highest VFA content were observed within six days of anaerobic digestion. This implies that hydrolysis of acid-pretreated OFMSW was attained at a much faster rate, thereby leading to reduction in overall digestion time as compared to untreated OFMSW. Another noteworthy occurrence is the increase in total VFA content during anaerobic digestion of acid-pretreated OFMSW. An increase in VFA concentration by 5.3–27.5% was observed which signifies enhanced biodegradability of OFMSW as a result of acid pretreatment. Simultaneously, the efficacy of VFA consumption was also found to have improved. A reduction of 62.6% in VFA content, as compared to its highest concentration during anaerobic digestion, was observed in case of untreated OFMSW. The same was as high as 84.4% and 82.8% after pretreatment with HCl and CH_3COOH, respectively. This is advantageous as both VFA generation and VFA consumption govern the amount of bioenergy generated in the form of biogas during anaerobic digestion [27]. Thus, pretreatment with acid proved to be helpful in boosting efficiency by increasing biogas production within less digestion time. Nonetheless, severe pretreatment conditions (pretreatment with strong acid like HCl at pH 1) must be avoided as they adversely impact biogas generation as is evident in Fig. 1a. Even though it resulted in the highest SCOD concentration signifying most efficient hydrolysis (Table 3), however, it also subsequently led to very high VFA generation during anaerobic digestion that negatively influenced methanogenesis (Fig. 3c). Similar phenomenon has also been validated by other researchers [3, 5, 7–9].

The effect of acid pretreatment on removal efficiencies of SCOD and VS during anaerobic digestion of OFMSW is shown in Fig. 3e, f. The SCOD and VS removal efficiency has been calculated with respect to initial and final content of SCOD and VS in the batch anaerobic digesters. Anaerobic digestion of untreated OFMSW exhibited SCOD and VS removal efficiency of 44.3% and 37.6%, respectively. The highest SCOD and VS removal efficiencies were obtained after pretreatment with HCl at pH 3, whereas in case of CH_3COOH, the highest SCOD and VS removal efficiencies were observed after pretreatment at pH 1. This is in agreement with cumulative biogas generated during anaerobic digestion (Fig. 1). Acid pretreatment augments conversion of VS into soluble compounds, thereby boosting hydrolysis and enhancing biodegradability of OFMSW. Higher biogas generation requires higher degree of substrate digestion as is apparent by greater reduction in SCOD and VS. It may be noted that the least removal efficiency in SCOD and VS was observed post-anaerobic digestion of OFMSW pretreated with HCl at pH 1. This is in accordance with its

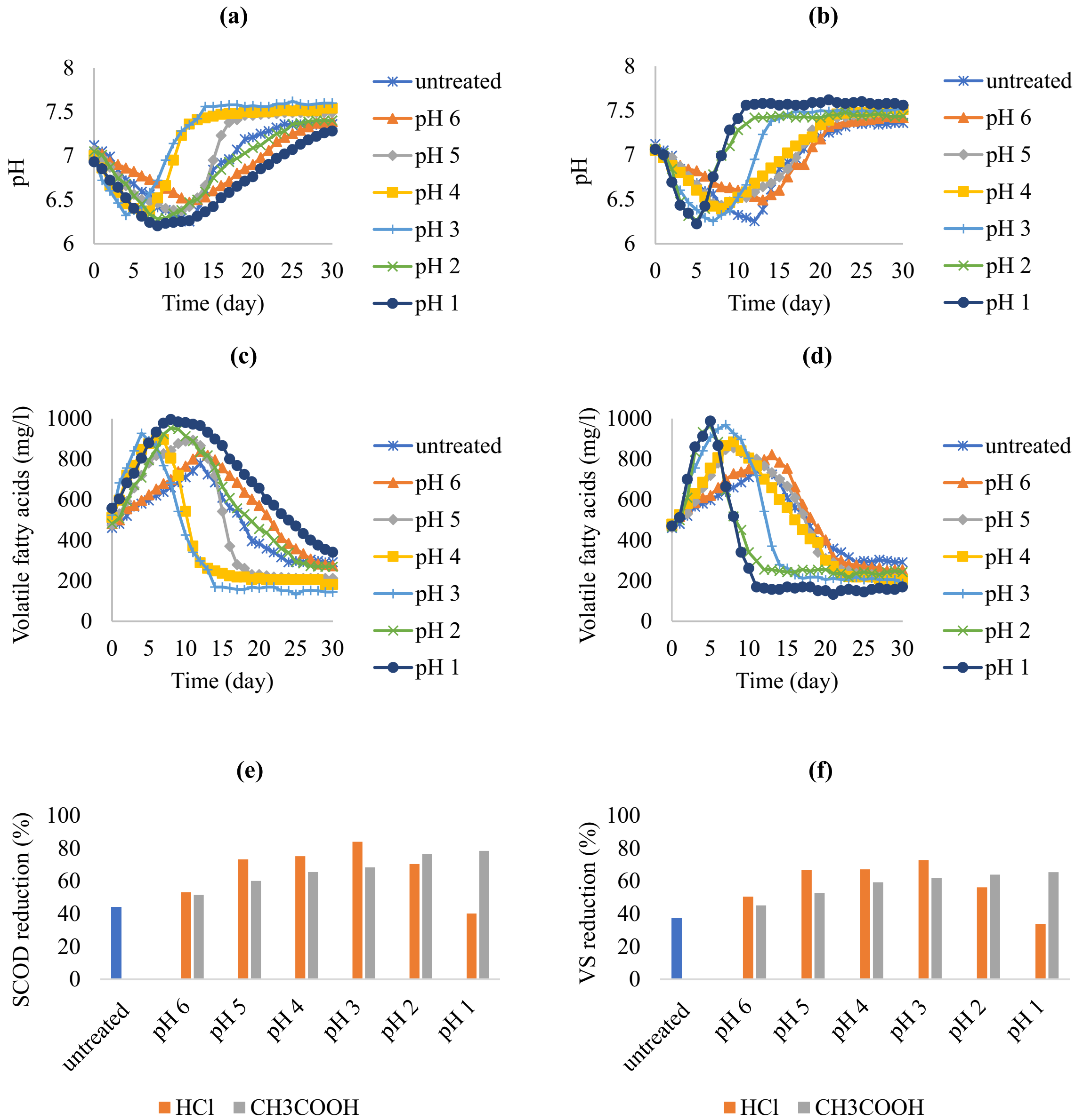

Fig. 3 Effect of acid pretreatment on pH (**a**, **b**) and VFA (**c**, **d**) during anaerobic digestion of OFMSW pretreated with HCl and CH_3COOH, respectively. Reduction in SCOD and VS (**e**, **f**) of pretreated OFMSW during anaerobic digestion as compared to untreated OFMSW

corresponding cumulative biogas generation (Fig. 1a) and further reiterates the fact that severe pretreatment conditions are detrimental.

3.4 Correlation analysis

A positive linear correlation was seen between SCOD content and its resultant cumulative biogas generated during anaerobic digestion (Fig. 4). The coefficient of determination (R^2) was calculated for acid pretreatment of OFMSW with HCl ($R^2 = 0.92$) and CH_3COOH ($R^2 = 0.84$). Similar observation has been reported by various researchers who have corroborated that increase in biogas generation is governed by increase in SCOD content [3, 5, 7, 9, 28]. Nevertheless, an important point to note is the relationship between SCOD and biogas generation when OFMSW was pretreated with HCl at pH 2 and pH 1 (Fig. 4a). Although the aforementioned pretreatment conditions yielded higher SCOD concentrations as compared to others, they necessarily did not result in the proportional increase in cumulative biogas generation during anaerobic digestion. This is ascribed to very high concentration of VFA generated during acidogenesis that adversely impacted methanogenesis, thereby subduing biogas generation

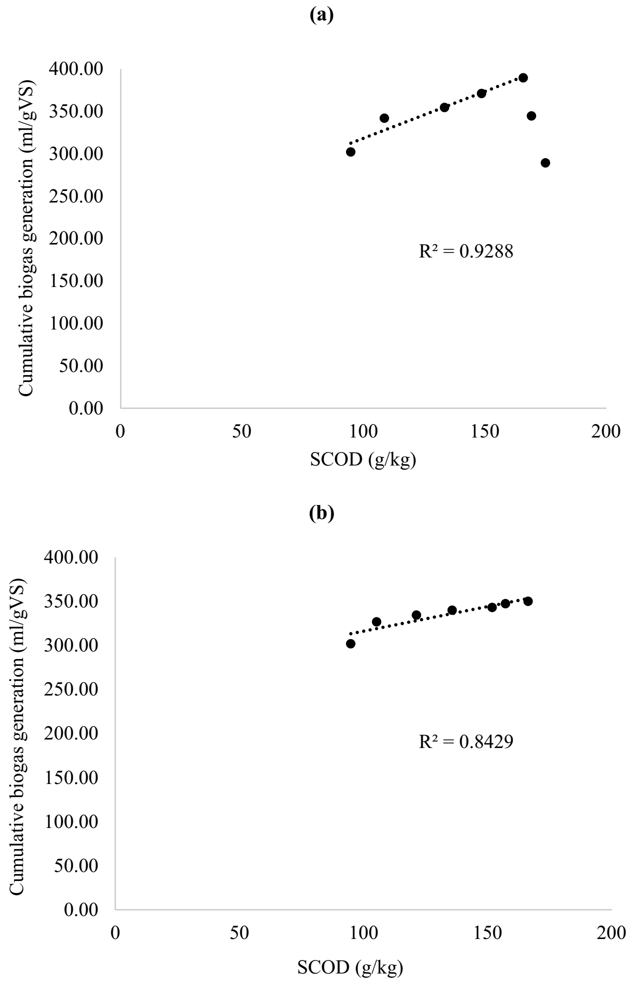

Fig. 4 Correlation between increase in SCOD and cumulative biogas generated from OFMSW pretreated with HCl (**a**) and CH_3COOH (**b**). R^2 denotes coefficient of determination

(Sect. 3.3). Hence, these two points were omitted while plotting the best fit curve that highlighted the correlation between increase in SCOD and corresponding increase in cumulative biogas generation (Fig. 4a).

3.5 Economic evaluation

The expenses incurred during acid pretreatment of OFMSW along with corresponding revenue generation are presented in Table 5. It is clear that pretreatment of OFMSW with HCl is more cost-effective than pretreatment with CH_3COOH. Net revenue gains were negative for all instances of pretreatment with CH_3COOH and for HCl at pH 1–pH 3. This is because the biogas yields obtained during anaerobic digestion of OFMSW pretreated under aforementioned conditions were insufficient to compensate for the expenses incurred during said pretreatment. However, positive results in terms of net revenue gains were obtained for anaerobic digestion of OFMSW pretreated with HCl at pH 4–pH 6. In fact, the highest revenue gain was observed after pretreatment with HCl at pH 5. This corresponds to 17.3% increase in cumulative biogas generation and 58% increase in net revenue, as compared to untreated OFMSW. Pretreatment of OFMSW with HCl at pH 4, on the other hand, did yield positive revenue gains; however, the value is 33.3% less than that of untreated OFMSW. Incidentally, the pretreatment condition (OFMSW pretreated with HCl at pH 3) which yielded the best results in terms of cumulative biogas generation was found to be unprofitable. Hence, anaerobic digestion of OFMSW pretreated with HCl at pH 5 was found to be most favourable in terms of economic assessment. Song et al. [24] compared the economic performance of anaerobic digestion of agriculture corn straw pretreated with seven different chemicals each. They found that H_2O_2 and H_2SO_4 pretreatment showed the lowest costs. Between them, they found H_2O_2 to be more favourable as it led to higher methane yield than H_2SO_4. Within alkali pretreatments, the authors did not observe any considerable economic difference between $Ca(OH)_2$ and NaOH pretreatments; however, they reported $Ca(OH)_2$ to be marginally advantageous over NaOH as the former generated a higher methane yield. Monlau et al. [15] presented an assessment of conversion of methane to heat and to CHP (combined heat and power) for sunflower oil cakes pretreated thermally with dilute acid (170 °C, 1% H_2SO_4). The assessment revealed that for complete conversion of methane into heat, the increase in heat production by thermal-dilute acid pretreatment was greater than the energy required for pretreatment irrespective of solid loading. On the other hand, for CHP, increase in heat production by thermal-dilute acid pretreatment was higher than the energy requirement for pretreatment, only when solid loading was greater than 100 kg/m^3. Increase of 14.3% in methane yield was achieved during semi-continuous anaerobic digestion of waste activated sludge pretreated with HCl at pH 2. However, an initial cost assessment of this pretreatment condition revealed it to be uneconomical [13]. According to a research article by Passos et al. [29], thermal-alkali pretreatment of dairy cow manure resulted in negative total cost as the temperature required for pretreatment could not be attained using the thermal energy generated by the biogas in the CHP unit. On the other hand, even though the total income of thermal-acid pretreatment was reported positive, however, it was lower than that of conventional anaerobic digestion process. In a previous study by the authors [7], pretreatment of OFMSW with NaOH at pH 9 was found to be most economical, with 29.5% and 60.8% increase in net revenue and cumulative biogas generation as compared to untreated OFMSW.

Table 5 Economic evaluation of acid pretreatment of organic fraction of municipal solid waste

Pretreatment pH	Unit	OFMSW	HCl pretreatment						CH_3COOH pretreatment					
	–		6	5	4	3	2	1	6	5	4	3	2	1
Acid cost	₹/kg OFMSW	0.00	0.14	0.17	0.40	0.65	1.01	2.02	0.88	1.18	2.75	5.29	8.04	15.10
Alkali cost	₹/kg OFMSW	0.00	0.07	0.17	0.65	1.51	1.80	3.24	0.07	0.14	0.58	1.37	1.73	2.81
Total cost	₹/kg OFMSW	0.00	0.22	0.35	1.05	2.16	2.81	5.26	0.95	1.32	3.32	6.66	9.77	17.91
Methane generated	kg/kg OFMSW	0.015	0.025	0.038	0.042	0.049	0.030	0.012	0.020	0.026	0.031	0.034	0.037	0.039
Revenue	₹/kg ($/kg) OFMSW	0.55 (0.0073)	0.93 (0.012)	1.45 (0.019)	1.60 (0.021)	1.88 (0.025)	1.14 (0.015)	0.45 (0.0059)	0.76 (0.010)	0.98 (0.013)	1.19 (0.016)	1.30 (0.017)	1.42 (0.019)	1.50 (0.020)
Net gain	₹/kg ($/kg) OFMSW	0.55 (0.0073)	0.71 (0.0094)	1.11 (0.015)	0.55 (0.0073)	−0.29 (−0.0038)	−1.67 (−0.022)	−4.81 (−0.064)	−0.19 (−0.0025)	−0.34 (−0.0045)	−2.13 (−0.028)	−5.36 (−0.071)	−8.35 (−0.11)	−16.41 (−0.22)

Subsidized price of 14.2 kg cylinder of LPG in Mumbai was taken as ₹494.10 (as applicable from 1 July 2018)

₹1 = $0.013 (as of 29 March 2020)

It must be noted that economic evaluation of acid pretreatment process based on batch anaerobic digestion assays is solely aimed at providing a general idea regarding the effectiveness and viability of acid pretreatment in enhancing the efficiency of anaerobic digestion of OFMSW. Hence, they cannot be directly applied to continuous processes. Moreover, costs were compared with that of LPG, in which all real costs are included. Careful extrapolations and thorough techno-economic analyses are, therefore, needed for scaled-up continuous anaerobic digestion systems. Additionally, the cost of chemicals such as acid and alkali is subjected to fluctuations based on market conditions. Therefore, sensitivity analyses become inevitable before implementation of such processes.

4 Discussion

The most vital parameters that govern and determine the efficiency of any pretreatment technology are the physical composition and chemical characteristics of the substrate to be pretreated [14, 29]. The optimal or most favourable pretreatment for any substrate must meet certain norms. It must increase surface area, porosity, solubilization and biodegradability of the substrate and simultaneously minimize production of inhibitory molecules. It must be energy efficient as well as cost-effective. Therefore, optimum pretreatment methods and their conditions vary from substrate to substrate as well as with substrate composition and characteristics [14, 30–32]. For a specific substrate, the optimum pretreatment method and condition cannot be simply adopted or extrapolated on the basis of the literature or existing research works. Hence, necessary experimentations become inevitable [5, 7, 9].

In India, information and research on the impacts of various pretreatment methods and conditions on change in characteristics of OFMSW and ensuing biogas generation are very scarce [4, 6]. And that is precisely the intent behind this study. In research articles published previously, the authors had studied the impact of hydrothermal pretreatment and alkali pretreatment in enhancing biogas generation from OFMSW [7, 9]. The authors had reported an increase in cumulative methane generation by 3–32% as a result of hydrothermal pretreatment of OFMSW at 80–160 °C for pretreatment duration of 0–120 min. The highest increase in cumulative methane yield was observed after pretreatment of OFMSW at 140 °C for 30 min [9]. Results of alkali pretreatment of OFMSW with NaOH in the range of pH 8–13 revealed an improvement of 19.6–34.8% in cumulative biogas yield, with pretreatment at pH 10 being the optimal condition [7].

The purpose of this research work was to study the change in characteristics of Indian OFMSW due to acid pretreatment and its resultant impact on biogas generation, methane yield and digestion time. This study reports an increase in biogas yield ranged between 13.2 and 28.9% as compared to untreated OFMSW after pretreatment with HCl, whereas the same varied between 8.2 and 16% in case of CH_3COOH pretreatment. The highest biogas yield of 389.4 ml/gVS with methane content of 68.3% was obtained after pretreatment with HCl at pH 3, whereas for CH_3COOH, the highest yield of 350.2 ml/gVS with 67.4% methane was observed after pretreatment at pH 1.

The results obtained in our study are comparable with that of other researchers. Song et al. [24] pretreated corn straw with HCl, H_2SO_4 and CH_3COOH at concentrations of 1%, 2%, 3% and 4% (w/w) each and reported the highest methane yield by H_2SO_4 and HCl at 2% concentration and CH_3COOOH at 4% concentration. Pretreatment of tobacco stalks by Zhang et al. [33] with HCl and oxalic acid ($H_2C_2O_4$) at 1%, 3%, 5% and 7% (w/w) concentration each revealed an increase in cumulative methane generation by 19.2% and 21% after pretreatment with 5% HCl and 7% $H_2C_2O_4$, respectively. Pretreatment of thickened waste activated sludge with free nitrous acid (4.9–6.1 mgN/l) for 24 h enhanced methane production in a pilot-scale reactor by 37% as compared to untreated WAS [34]. Improvement of 20.6% in methane potential was observed by Passos et al. [35] during anaerobic digestion of dairy cow manure pretreated with 2% HCl at 37 °C. In a thermochemical pretreatment of wheat plants prior to anaerobic digestion wherein 1% (v/v) of dilute H_2SO_4 was used at 121 °C for 10–120 min, a 15% augmentation for methane production was observed by the researchers [36].

Enhancement of anaerobic digestion process due to pretreatment is reckoned by higher degradation of VS, expedited biogas and methane generation rates and ultimate yields, with lower volume of residual digestate for final disposal. Furthermore, employment of pretreatment technologies not only paves way for higher organic loading capacity but also reduces hydraulic retention time during continuous anaerobic digestion processes. Consequently, volume, cost and footprint of the reactor decrease [5, 30–32]. The results obtained from the experimentation of this research work will aid in understanding the technical and economic viability during full-scale implementation. This holds true, especially, for city-based centralized anaerobic digestion systems that would tremendously benefit with increased biogas generation within a shorter digestion span. Therefore, intricate studies on localized, comprehensible low-cost pretreatment methods such as this research work are prerequisites for the long-term implementation of anaerobic digestion of OFMSW, thereby aiding in realizing the full potential of waste to energy in an integrated MSW management system in India.

5 Conclusions

Acid pretreatment was found to facilitate solubilization of organic matter in OFMSW, thereby enhancing biogas generation and reducing hydraulic retention time. Increase in cumulative biogas yield ranged between 13.2–28.9 and 8.2–16% after pretreatment with HCl and CH_3COOH, respectively. Pretreatment of OFMSW with HCl at pH 3 and CH_3COOH at pH 1 was found to be optimum. Cumulative biogas generation equivalent to that of anaerobic digestion of untreated OFMSW for 30 days was obtained within 12 days after OFMSW was pretreated with HCl at pH 3 and 14 days after pretreatment with CH_3COOH at pH 1. Preliminary economic assessment showed that pretreatment with HCl is more cost-effective than pretreatment with CH_3COOH.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this article.

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