Comparative appraisal of pretreatment strategies for improving biogas yield from waste flower mix

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Abstract

Anaerobic digestion is recognized as good alternative for waste management and energy production. However, if waste content is high in lignin, (recalcitrant material), may hamper the smooth operation of anaerobic digester. Pretreatment, on the other hand, may enhance the biogas production by cleaving the lignin cellulose complex. In present study, liquid hot water, alkaline and dilute acid pretreatment was attempted for anaerobic digestion of mixed flower waste. Results showed that mixed flower waste pretreated with liquid hot water showed maximum biogas production (692 L/kg VS) and was 1.86-fold higher compared to untreated flower waste. Also, pretreatment of flower waste before anaerobic digestion with alkaline and dilute acid showed 548 and 524 L/kg VS of biogas yield respectively.

Keywords: Anaerobic digestion, biogas, waste flower mix, pretreatment, liquid hot water

Introduction:

Waste flower-mix (WFM) from dump yard, roadside verges and local municipal sanitary sites generated from city's worship places is usually not used, but cut, crushed, and left in place for putrifaction which usually have adverse impact on socio-economic development of city. Greening and subsequent maintenance of city is conducted by local authorities for public interest, but the process of dumping flower waste may have lost its energy value associated. However, utilizing these wastes to generate renewable fuel (here biogas) may be fruitful for sustainable environment [1, 2]. Bioenergy recovery from flower waste might not only contribute to the local energy provision and unburden public coffers, but also aid to achieve the nation-wide environmental and economic aims.

WFM is a lignocellulosic biomass with a complex structure formed by cellulose, hemicellulose and lignin, which makes it significantly intractable to digestion. In order to enhance the digestibility of lignocellulosic biomass and consequent methane yield; many researchers have applied pretreatment techniques for other biomass like birch, giant reed, using various methods, such as steam explosion, diluted acid, cellulose solvent-based lignocellulosic fractionation (CSLF), liquid hot water (LHW), and alkaline [3,4,5].

Pretreating substrate using LHW may increase the accessibility of cellulose in the grid of lignocellulose by solubilizing hemicellulose using high temperature and pressure [4]. Generation of organic acids, such as acetic acid by applying the LHW process may further accelerate the hydrolysis of hemicellulose into monomer [6]. Moreover, major advantages of using hot water for pretreatment are no consumption of chemical and no use of corrosive resistance material for experimental process as compared to other leading pretreatment technique such as diluted acid, ammonia fibre explosion (AFEX) and sulphur dioxide-impregnated steam explosion [7, 8]. Apart from this, in LHW, inhibition is less as compared to steam explosion pretreatment technique as both uses high temperature and pressure [9].

On the other hand, alkaline pretreatment is well known chemical pretreatment methods [10, 11]. Alkalis may disrupt lignin-carbohydrate linkages, dissolve the lignin associated, or may alter the assembly of lignin in lignocellulosic biomass [12]. Alkaline pretreatment is generally effective in improving digestibility of lignocellulosic biomass as lignin is the most recalcitrant element of lignocellulose, particularly residues derived from agriculture and herbaceous crops [13]. Alkaline pretreatment may be preferable to other complicated pretreatment techniques as it may be conducted at room temperature and *in-situ* making it favourable for on-farm application [14]. However, after pretreating with alkali, pretreated substrate needs to be washed again till neutral pH as they may have some residues of chemical used for pretreatment as a result morewater is wasted.

[14]. Furthermore, pretreatment liquor consist of residual alkali which may be reused to reduce the environmental impacts and cost of chemical [14].

To the best of our knowledge, there has been no study reported so far on comparison of three different pretreatment processes of WFM for enhanced biogas production till now. The aim of this study was to evaluate and compare the three different pretretments condition on WFM's methane yield.

Materials and methods:

2.1 Raw materials

WFM was used as feedstocks in the experiment and was collected from different worship places, temples situated in Jaipur city (India) (Figure 1). WFM mainly contained marigold, red rose, china rose, daffodil and *Chrysanthemum*. Feedstocks was shredded uniformly using an electrical grinder and stored at 4^0C until further use.

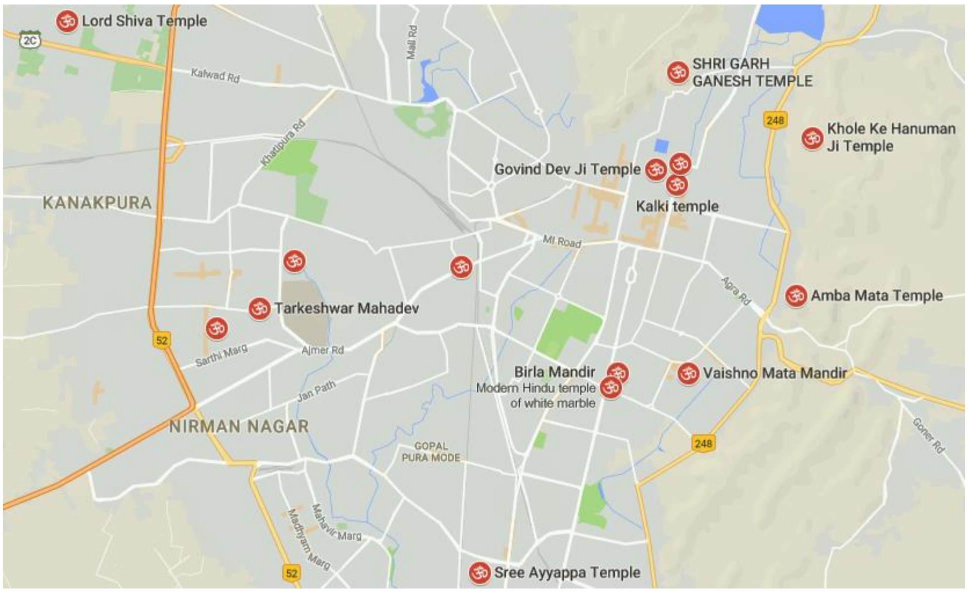


Figure 1: Collection sites of WFM in Jaipur

2.2 Biogas inoculum

Active microbial inoculum utilized for biogas experiments was collected from a local active biogas plant at Rajasthan Gosewa Sangh-Durgapura, Jaipur (26.8°N, 75.7°E) running large-scale continuous stirred type bioreactor of capacity 60 m^3. The plant was operating at mesophilic temperature using cow manure as feedstock with the presence of a large array of the highly active methanogenic community for AD process. Fresh inoculum initially had TS, 7.53%, VS as percent of TS, 64.87%, pH 7.57 and conductivity of 3.25 mS.

The inoculum was pre-incubated anaerobically in the chamber (37°C) similar to the typical operating temperature of biogas plant up to 10 days in order to reduce the endogenous biogas production by undigested biomass. Following the storage, the inoculum was diluted with water and divided into 400 mL aliquots into 610 mL bottles for batch experiments. Diluted inoculum had TS concentration of 1.2%. Batch bottle digesters were prepared and stored accordingly until further use.

2.2 LHW pretreatment

LHW pretreatment was conducted in a water bath (Thermotech PID – 71 S, India). Three sets of boiling tubes (55 ml, Borosil) having 9 test tubes in each set; were prepared for the treatment. All sets of tubes were filled with distilled water (40 ml). First set of tubes placed into water bath at 50 °C. After 30 minutes substrates were added into the tubes (1g : 10 ml) and covered with parafilm. After 5 minutes three tubes were taken out and substrates were separated from liquid. After that substrate was dried at room temperature and stored in a zip lock packet at 4 °C till further use. Same process was repeated for 10 and 15 minutes at 50 °C. Again, water bath was heated at 70 and 90 °C and process was repeated for 5, 10 and 15 minutes.

2.3 Alkaline pretreatment

150g of WFM were added to 1000 mL of $Ca(OH)_2$ solution in a 2000-mL beaker with concentration of 0.5, 1, 1.5% respectively. The flasks were covered with Parafilm on the top and incubated at room temperature (24 ± 1 °C) for 4 and 7 hours. After incubation hours, the pretreated WFM was washed with tap water using a sieve (325 Mesh) until the pH reached around 7. The neutralized material was then drained, washed, and dried for further analysis.

2.4 Acidic pretreatment

100g of WFM were added to 500 ml solution of acetic acid (CH_3COOH) in a 1000 ml beaker with a concentration of 0.5, 1, 1.5, and 2% respectively. The flasks are covered with parafilm and placed in waterbath to maintain temperature of 70 °C for 1.5 hours. After the incubation time, the pretreated WFM are washed with tap water using a sieve (325 Mesh) until the pH becomes neutral (i.e., 7 pH). The neutralized material was then drained, washed and dried for further analysis.

Table 1: Characteristics of untreated waste flower-mix and inoculum for anaerobic digestion

Parameters	**Waste flower mix**	**Inoculum**
DM %	15.0 ± 0.7	7.5 ± 0.05
ODM %	93.27± 1.8	65.29 ± 1.2
Moisture %	85.0 ± 0.3	92.5 ± 0.9
C %	44.3 ± 1.3	35.13 ± 1.8
H %	7.8 ± 0.5	4.35 ± 0.7
N %	1.4 ± 0.2	1.7 ± 0.3
C/N	31.64 ± 0.6	20.67 ± 0.6
pH	6.68 ± 0.5	7.58 ± 0.1

2.5 Analytical methods

Characterizing the feedstock is one of the most important aspects of biogas potential test. The TS, VS, and ash content were determined for raw materials and inoculum as per the standard method (APHA, 1989). Ultimate analysis viz. nitrogen, carbon, and hydrogen present in WFM was performed using Elemental Analyzer (FLASH 2000; Thermo Scientific, USA). Measurement of pH and electrical conductivity was performed for each sample.

2.6 Evaluation of biogas potential of different combinations of raw materials in batch mode

AD of feedstocks alone and their blends along with cellulose (Avicel, Sigma, USA) as standard reference material was performed, in sealed batch bottle digesters. Inoculum alone was used as control (without any substrate or cellulose). Experiments were performed using substrates corresponding to a final concentration of 1.5 g VS L^{-1}. A total of three groups (LHW pretreated, alkaline pretreated and acidic pretreated) were designed in which inoculum, cellulose, untreated and pretreated WFM were evaluated for biogas potential. Prior to incubation, the bottles were flushed with nitrogen to have the anaerobic conditions; closed with rubber stoppers and aluminium screw caps; transferred to the orbital shaker (REMI CIS 24, India) for incubation (37°C, 90 rpm, 40 days) [3].

2.7 Biogas measurements

Biogas production was calculated by measuring pressure in the head space of each batch bottle digester. The pressure generated in bottles was measured using digital pressure meter (Testo 512, Germany). The biogas in the head space was purged to reduce the pressure close to the atmospheric pressure. After releasing the biogas, the pressure in the head space was noted again as an initial condition for the next-day measurement.

Gas calculations were performed as described by Vivekanand et al. [3]. Using the headspace volume of the bottles, the ideal gas law was applied for calculating biogas production during the experiments. All experiments were run in triplicates and the average results are given along with standard deviations. The reported biogas yields are the values only after subtracting the endogenous biogas production from the inoculum alone (control).

$$V_{Biogas} = \frac{(P.V_{head}.C)}{R.T} \quad (1)$$

where:

V_{Biogas} = daily biogas volume (L),

P = absolute pressure difference (mbar),

V_{head} = volume of the head space (L),

C = molar volume (22.41 L mol^{-1}),

R = universal gas constant (83.14 L mbar K^{-1} mol^{-1}),

T = absolute temperature (K).

3. Result and Discussion

3.1 Effect of different pretreatment on methane production from WFM

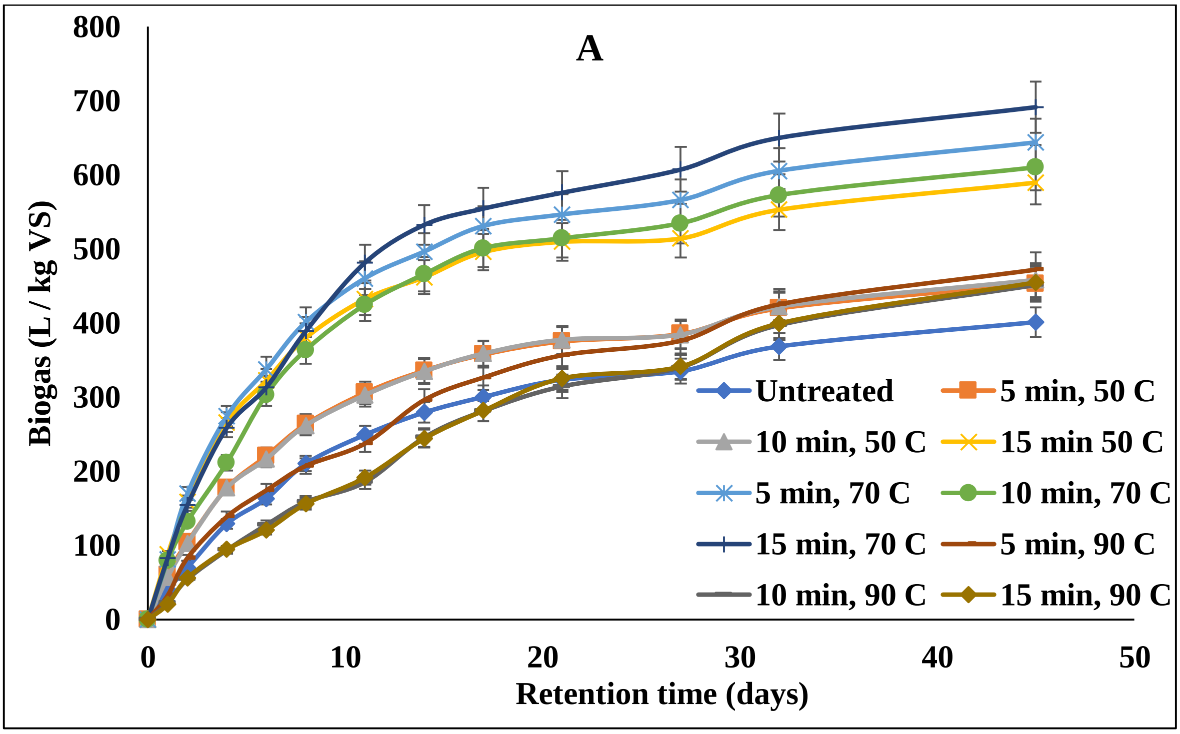
As shown in figure 2, daily methane yield of pretreated flower waste at 50°C for 15 mins and 70°C for 5 mins almost have same maximum yield of biogas production (107 L/kgVS and 105 L/kgVS respectively per day) on 4^{th} day of LHW experiment than those of untreated is 59 L/kgVS maximum biogas yield per day. Flower waste pretreated at high temperature at 90°C (5, 10,15 mins) reaches at its highest yield on 14^{th} day which was 10 days later than treated and untreated flower waste. Methane content of biogas from untreated and pretreated (70°C and 50°C) increased to 50 % on 4 – 5 day during AD, while those pretreated at 90°C reached 50 % on 14^{th} day, since pretreated flower waste was washed prior to AD it is unlikely that the delayed methane production is due to inhibitors generated during LHW pretreatment at high temperature and the pretreated biomass showed decreased digestibility .

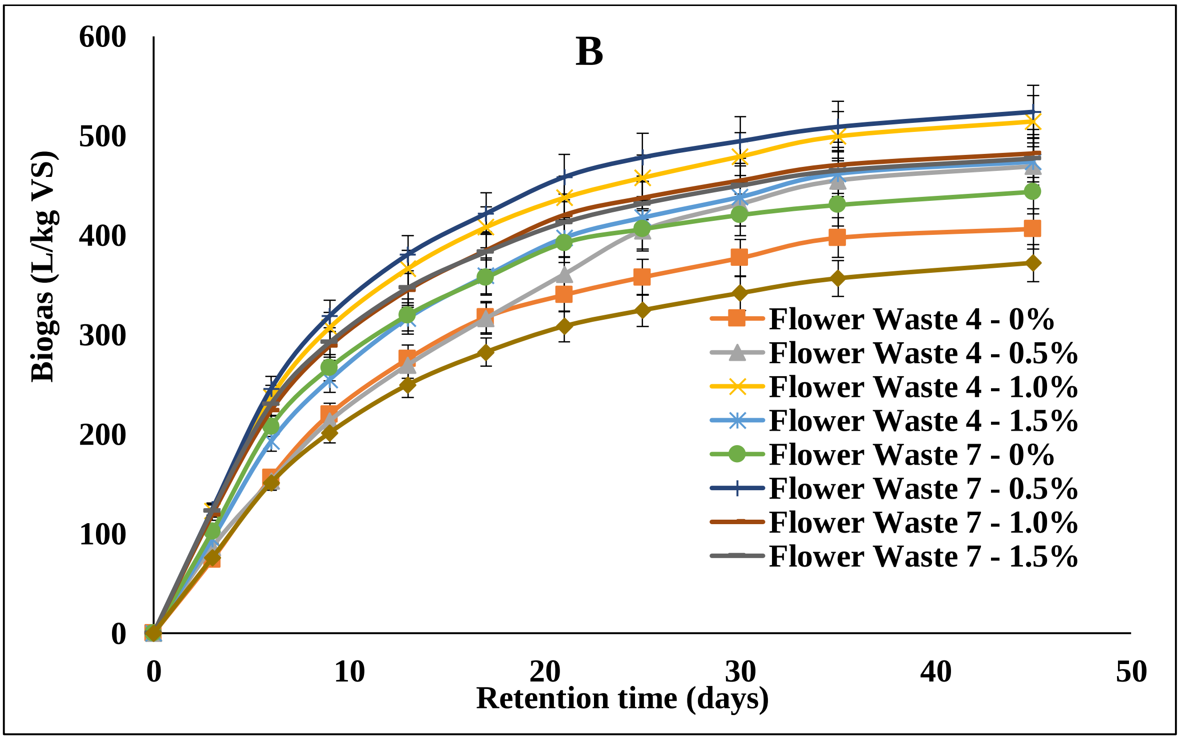
During AD of flower waste pretreated with different concentration of calcium hydroxide , daily methane yield was maximum (i.e. 50%) at 3-6 days and the maximum daily methane yield increases with increased exposure for longer time even at low concentration (0.5%) of calcium hydroxide except that high concentration of 1.5% did not improve the methane production. Flower waste pretreated with 0.5% of calcium hydroxide for 7 hrs achieved the highest daily methane yield of 125 L/kg VS which is almost double amount of untreated flower waste.

During another pretreatment of flower waste under acidic conditions at different concentrations of acetic acid the highest daily methane yield or 50% production was achieved for 4-7 days. Yield of methane increases with concentration of acetic acid as highest yield of 121 L/kg VS is achieved at 1.5% acetic acid. When treated at 2% according to above mentioned statement the methane yield should increase but it was observed that its methane yield was almost comparable to that of untreated flower waste, this is due to acetic acid at high concentration degrades the flower waste completely which decreases the methane yield .

Figure 2 shows the effect on cumulative methane yield from flower waste . The untreated flower waste have 372 L/kg VS which is comparable to that reported on pretreatment on giant reed biomass by [14, 15]. LHW pretreatment at different temperatures (50, 70, 90°C) for different time 5mins, 10 mins and 15 mins obtained a significant increase in biogas yield. Alkaline pretreatment with different concentration of calcium hydroxide (0% -1.5%) for 4 hrs and 7 hrs also has improved cumulative methane yield from AD of flower waste. Acidic pretreatment with different acetic acid concentration with 0 % - 2% shows a significant methane yield higher then alkaline pretreatment and lower then LHW pretreatment. However, among all these pretreatment only LHW pretreatment result in significant increase in cumulative methane yield 692 L/kg VS.

It should be noted that methane yield during AD process depends on inoculums characteristic. The C/N ratio of inoculums crucial for AD of flower waste should be low (10.2) , and the C/N ratio of flower waste calculated by elemental analysis is 31.1 which is almost lies in the range of commonly recommended C/N ratio of 20-30 for AD. Besides inoculum maintained the proper pH during AD process as it provides buffering capacity.


A
Biogas (L / kg VS)
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
Retention time (days)
Untreated
5 min, 50 C
10 min, 50 C
15 min 50 C
5 min, 70 C
10 min, 70 C
15 min, 70 C
5 min, 90 C
10 min, 90 C
15 min, 90 C


B
Biogas (L/kg VS)
600
500
400
300
200
100
0
0
10
20
30
40
50
Retention time (days)
Flower Waste 4 - 0%
Flower Waste 4 - 0.5%
Flower Waste 4 - 1.0%
Flower Waste 4 - 1.5%
Flower Waste 7 - 0%
Flower Waste 7 - 0.5%
Flower Waste 7 - 1.0%
Flower Waste 7 - 1.5%

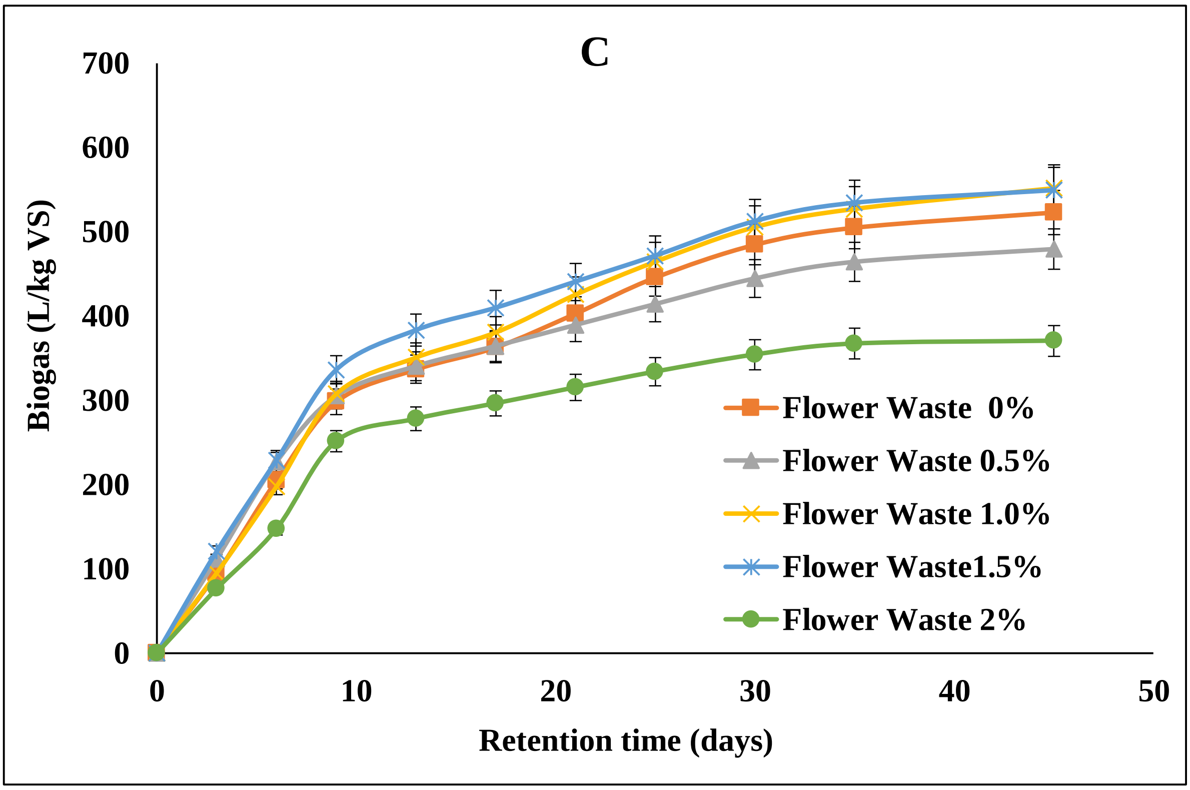


Figure 2: Cumulative biogas yield A – LHW pretreated flower waste; B – Alkaline pretreated flower waste and C – Dilute acid pretreated flower waste

Conclusion

Waste flower mix may be utilized for renewable energy production. Present study showed that waste flower mix may be utilized for biogas production which may further used for energy application. However, to enhance biogas production, pretreatment strategy may be adopted as recalcitrant nature of waste flowers may hinder biogas production. Liquid hot water pretreatment helped to increase biogas production by 86% as compared to untreated one. Also, alkali and acid pretreatment helped to increase biogas production, liquid hot water showed maximum improvement.

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Conflict of Interest

The authors report no conflict of interest. The authors alone are responsible for content if the manuscript.

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