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Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production

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A B S T R A C T

The rise in oil price triggered the exploration and enhancement of various renewable energy sources. Producing biogas from organic waste is not only providing a clean sustainable indigenous fuel to the number of on-farm digesters in Europe, but also reducing the ecological and environmental deterioration. The lignocellulosic substrates are not completely biodegraded in anaerobic digesters operating at commercial scale due to their complex physical and chemical structure, which result in meager energy recovery in terms of methane yield. The focus of this study is to investigate the effect of pre-treatments: thermal, thermo-chemical and chemical pre-treatments on the biogas and methane potential of dewatered pig manure. A laboratory scale batch digester is used for these pre-treatments at different temperature range (25 °C-150 °C). Results showed that thermo-chemical pretreatment has high effect on biogas and methane potential in the temperature range (25–100 °C). Maximum enhancement is observed at 70 °C with increase of 78% biogas and 60% methane production. Thermal pretreatment also showed enhancement in the temperature range (50–10 °C), with maximum enhancement at 100 °C having 28% biogas and 25% methane increase.

1. Introduction

Anaerobic digestion of biodegradable waste products with the aim of energy production has become a widely used technology as it provides both an option for utilizing the waste and reducing greenhouse gas emissions by substituting fossil fuels [1,2,3], but there is need to make this technology economically viable [4,5]. Therefore various pre-treatments are applied prior to the digestion activity for enhancing the energy recovery from anaerobic digestion plants in terms of methane yield [6,7].

A large part of manure is consisting of biofibers which are made from lignocellulosic matter [8]. The hydrolysis of such matter is a slow and difficult process due to complex chemical and physical structure [9,10]. Only 30–50% of the ultimate biogas potential is exploited when pig manure is used as a substrate [11]. Pre-treatments are used to facilitate the methane production by overcoming the limitation of hydrolysis, which include the solubilization and biodegradation of hemicellulosic and lignin parts of the substrates [12,13]. Thermal, chemical and thermo-chemical pre-treatments are mostly used for lignocellulosic substrates [14–18]. Considering the different approaches for improving methane production, this work aims to investigate the effect of thermal, thermo-chemical and chemical pre-treatments.

2. Material and methods

2.1. Origin of materials

The substrate (dewatered pig manure) was obtained from Grøngas (Asdal) biogas plant (Hjøring, Danmark). The substrate was stored at 5 °C after collection. Anaerobically digested sewage sludge from Aalborg East wastewater treatment plant was used as inoculum. It was stored for 10 days in a closed container to reduce its biogas potential. The $Ca(OH)_2$ was used for chemical pretreatment.

2.2. Experimental set up

Effects of thermal pretreatment were observed for seven different temperatures (25 °C, 50 °C, 70 °C, 100 °C, 110 °C, 130 °C,

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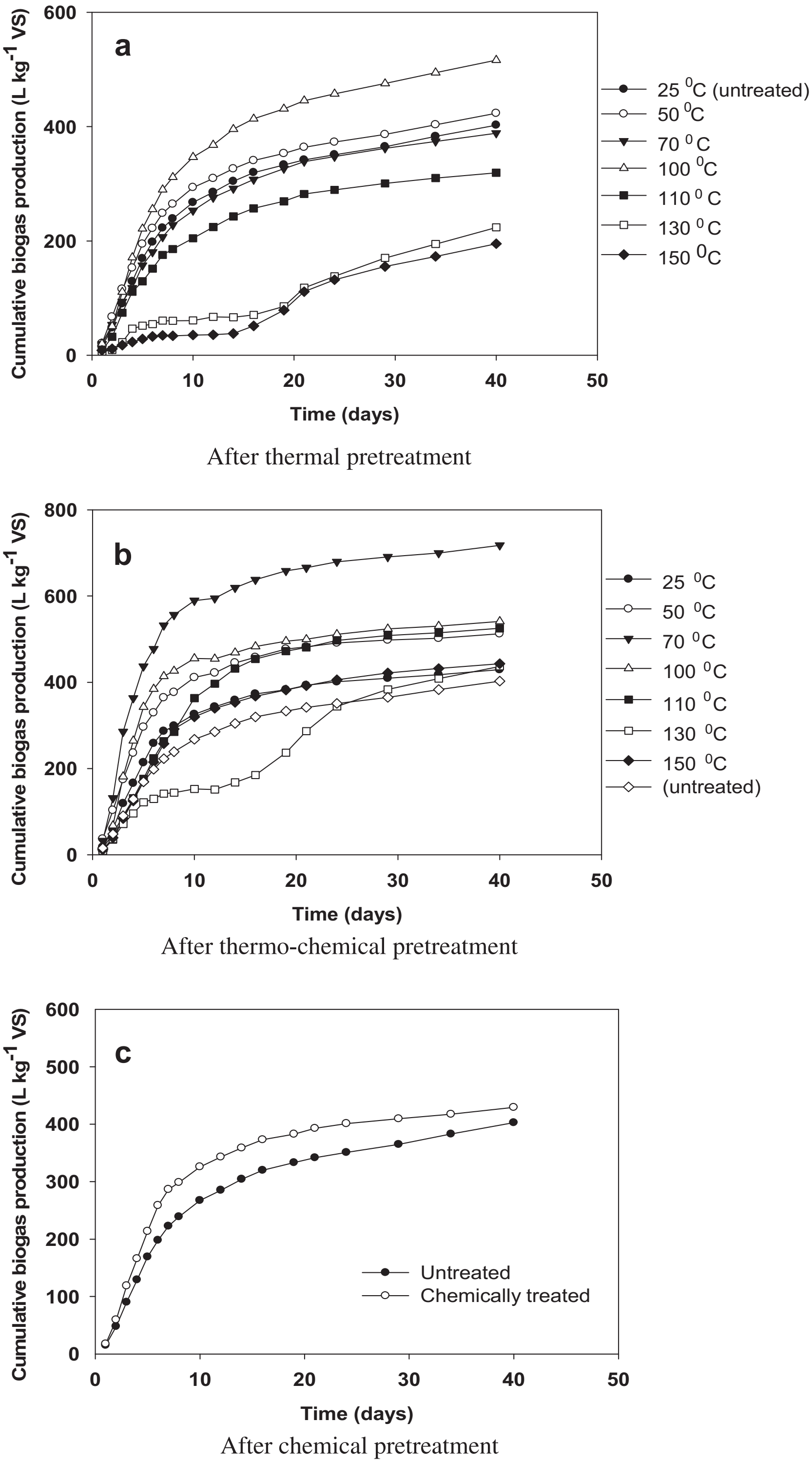

Fig. 1. Biogas production of the substrate. (a) After thermal pretreatment. (b) After thermo-chemical pretreatment. (c) After chemical pretreatment.

and 150 °C) both with and without chemical pretreatment. For the combined thermo-chemical pretreatment, $Ca(OH)_2$ was used at all temperature ranges. Untreated samples were prepared to compare the results of treated samples. Furthermore, 100 °C was selected as reference temperature in order to facilitate the comparison with other temperatures in both thermal and thermo-chemical pretreatments. The temperatures above and below 100 °C are selected to see the effect of rise and decrease in temperatures respectively.

Table 1
Initial rate of biogas production and standard deviations on day 40th.

Temperature °C	25 untreated	50	70	100	110	130	150
Rate of biogas production (l kg^{-1} VS)	33.81	38.91	31.44	44.23	25.84	10.32	5.70
Standard deviation on 40th day	4.61	8.47	13.5	21.5	11.83	55.68	9.14

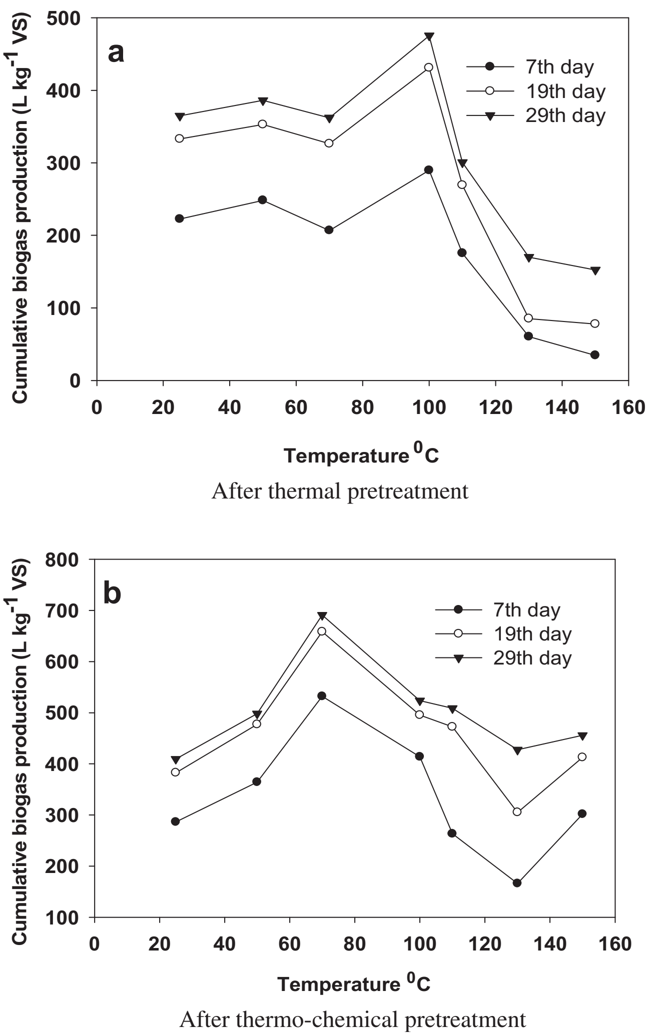

Fig. 2. Cumulative biogas production at 7th, 19th and 29th day. (a) After thermal pretreatment. (b) After thermo-chemical pretreatment.

One sample was treated with 5% lime without thermal treatment to see the effect of chemical alone. Duplicate samples for each type of pretreatment were prepared including two bottles of blank inoculum. Thermal and thermo-chemical pretreatment was carried out in a closed vessel, which was fabricated at laboratory scale.

The mass of untreated sample is selected to have 25 g weight available for biogas production and some additional mass to determine the volatile solid (VS) content after pretreatment. The oven temperature was selected 5 °C higher than the temperature required for pretreatment. Once the desired temperature was reached, it was maintained for 1 h. The oven temperature was controlled to be within ±1 °C. The laboratory ambient temperature was estimated 25 °C and therefore for 25 °C, oven was not in use. The pretreated manure was stored at 5 °C before using for biogas production process. For thermo-chemical pretreatment, $Ca(OH)_2$ was added in the amount of 5% of the dry weight of manure. This chemical and manure were mixed thoroughly and left to react for 1 h. Its pH was maintained at 14. Then this material was also heated in the same way as for thermal pretreatment. After heating, a known amount of HCl was added to neutralize the pH of the substrate. For the samples receiving only chemical pretreatment, the dewatered pig manure was left to react for 2 h after mixing with 5% $Ca(OH)_2$. After 2 h, pH was neutralized by adding a known quantity of HCl. All the samples were stored at 5 °C until further use for biogas production.

Table 2
Initial rate of biogas production standard deviations on 40th day for thermo-chemical pretreatment.

Temperature °C	25	50	70	100	110	130	150	Untreated
Rate of biogas production (l kg^{-1} VS)	42.69	59.23	87.40	68.51	35.17	27.98	41.62	33.81
Standard deviation on 40th day	14.37	15.37	39.94	5.45	13.09	43.78	35.67	4.61

Table 3
Initial rate of biogas production and standard deviations on day 40th for chemical pretreatment.

Temperature °C	Chemically treated	Untreated
Rate of biogas production (l kg^{-1} VS)	39.53	30.03
Standard deviation on 40th day	14.37	4.61

Table 4
Cumulative biogas production after 7, 19 and 29 days as a function of chemical pretreatment.

	At 7th day	At 19th day	At 29th day
Chemically treated	286.50	382.67	409.47
Untreated	222.58	332.96	364.89

2.3. Analysis and calculations

Dry matter (DM) was determined by keeping a known mass (Ws) of sample in the oven at 105 °C for 24 h and measuring the new mass (Wdm) after heating at this temperature. The DM content was calculated from the expression Wdm × 100/Ws. The

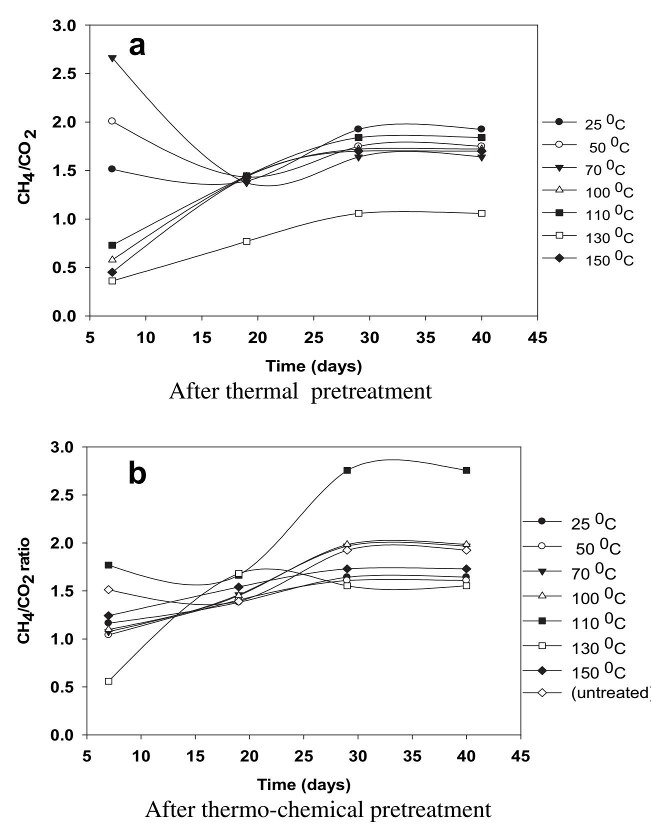

Fig. 3. CH_4 to CO_2 ratio of the substrate. (a) After thermal pretreatment. (b) After thermo-chemical pretreatment.

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dried samples were then ignited at 550 °C for 12 h and the sample weight (Wash) was measured. The percentage of volatile solids (VS) was determined by the expression ((Wdm−Wash) × 100)/Wdm. In half liter serum bottles, the test material and inoculum were added in the ratio of 1:10. To estimate the effect of inoculum, it was put in a serum bottle in the same proportions. The volume of biogas produced was measured with a syringe. Measurements were taken for 40 days. In first 2 weeks, the measurements were taken almost every day, later the frequency was reduced to every second day. The volume was measured in milliliters. The quality of biogas was tested once a week by collecting biogas samples and testing on a Gas chromatograph (Chrompack CP9001) for methane and carbon dioxide content. After 40 days, the volatiles solids of the samples (VSs) and inoculum (VSi) were determined after digestion. Volatile solids content of the material used for biogas production were determined by the expression VSm−(VSs−VSi).

3. Results and discussion

3.1. Biogas production

3.1.1. Thermal pretreatment

Dewatered pig manure showed higher biogas production in the temperature range of 25−100 °C with highest yield at 100 °C. The biogas production from thermally treated at 130 °C and 150 °C showed least production of biogas, although these samples had the measurable potential for biogas at the end of experiment (Fig. 1a). This indicates the formation of complex organic compounds at high temperature, which are difficult to degrade [7,9]. There is a trend of improvement in biogas production with the increase of temperature till 100 °C and then decrease with the further increase of temperature except in the case of 70 °C (Table 1). It can be seen that pretreatment at 100 °C produced higher amount of cumulative biogas. The biogas produced is 30%, 29% and 30% higher after 7, 19 and 29 days respectively than the untreated sample. Their corresponding cumulative biogas productions are (289 ± 22), (431 ± 19) and (475 ± 16) l/kg VS (Fig. 2a).

3.1.2. Thermo-chemical pretreatment

This treatment showed the high biogas production in the temperature range of 25−100 °C and all samples gave more yield than untreated sample but this improvement was maximum in case of 70 °C (Fig. 1b). Thermo-chemical pretreatment did not show any significant effect at lowest and highest temperatures. The initial rate of biogas production is higher for thermo-chemically treated sample at 25 °C, 50 °C, 70 °C and 100 °C, while it is lower at higher temperature (Table 2). The standard deviation values for all the thermo-chemically treated samples on the 40th day are shown in

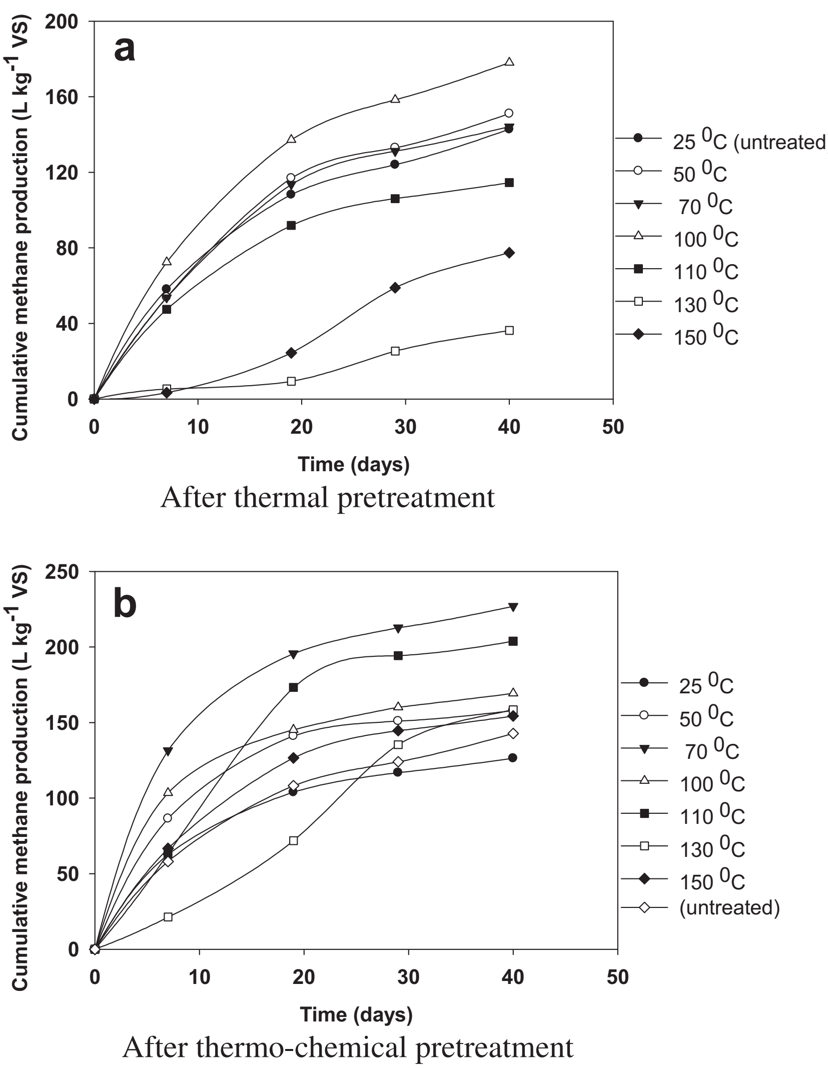

Fig. 4. Methane production of the substrate. (a) After thermal pretreatment. (b) After thermo-chemical pretreatment.

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the Table 2. Out of various thermo-chemical pre-treatments, 70 °C has shown the highest amount of biogas at all intervals of days. The percentage increase in cumulative biogas production in comparison to untreated material after 7, 19 and 29 days is 139%, 97% and 86% and corresponding biogas productions are (532 ± 37,17), (658 ± 37,38) and (690 ± 37,38) l/kg VS respectively (Fig. 2b), (Table3).

3.1.3. Chemical pretreatment

The biogas production from chemically treated sample is higher than untreated (Fig. 1c), as the chemical pretreatment softens the fibers and thus increased the biogas production [9]. From the Table 4 it could be seen that chemically treated samples showed higher biogas production at all intervals of days. The percentage increase in cumulative biogas production in comparison to untreated material after 7, 19 and 29 days is 28%, 14% and 12% respectively.

3.2. Composition of biogas

Variation of CH_4 to CO_2 ratio with the time for substrate after thermal and thermo-chemical pre-treatments is shown in the Figs. 6 and 7 respectively. Biogas composition after chemical pretreatment is shown in the same figure with thermo-chemical. This composition analysis was done for three times and the composition of 29th day was assumed for the 40th day. Fig. 3a shows that the CH_4 to CO_2 ratios for thermally treated samples have different initial values ranging from 0.4 to 2.7 at different temperatures. All samples stabilize themselves between 1.6 and 1.9 except one with thermally treated at 130 °C. This lower value for 130 °C shows that there is poor production of biogas due to various inhibition factors. The methane content in thermally treated sample is about 50%. Fig. 3b shows that the CH_4 to CO_2 ratios for thermo-chemically treated samples have different initial values ranging from 0.6 to 1.8 at different temperature ranges and they stabilized themselves in between 1.5 and 2.0 after 25 days. The methane content of thermo-chemically treated sample is found little more than thermally treated.

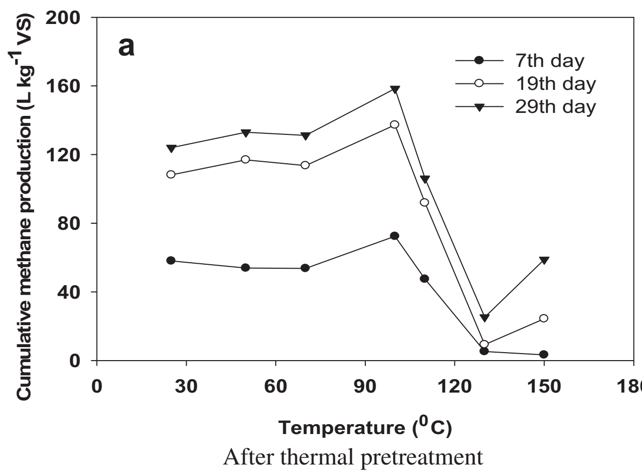
3.3. Methane production

3.3.1. Thermal pretreatment

The maximum increase in methane production after thermal pretreatment in comparison to untreated material is 28% at 100 °C after 29 days and the same increase is assumed at the end of experiment (Fig. 4a). It was observed that pretreatment at higher temperatures like 110 °C, 130 °C and 150 °C has resulted in reducing the amount of methane production as compare to untreated material. At higher temperatures of pretreatment the material appeared as dry and dark brown in color indicating that it has become hard. This reduced methane production can be attributed to the hardness of material, which result in less biodegradation of the material [9,12]. From the Fig. 5a it was observed that the highest cumulative methane production after 6, 19 and 29 days is at 100 °C pretreatment, which is 25%, 27% and 28% higher than the untreated substrate respectively (Fig. 5a).

3.3.2. Thermo-chemical pretreatment

Thermo-chemical pretreatment showed a significant impact on the amount of methane production as seen in the Fig. 4b. The highest amount of methane was obtained at 70 °C which is nearly 72% more than untreated sample. All the samples showed more methane production than untreated samples, except one. It shows that when thermal and chemical pre-treatments are combined, it gives significant production in comparison to thermal or chemical pre-treatments alone. The sample at 70 °C gave more methane yield which is 127%, 81% and 72% higher compared to untreated substrate at day 7, 19 and 29 respectively after thermo-chemically pretreatment (Fig. 5b).



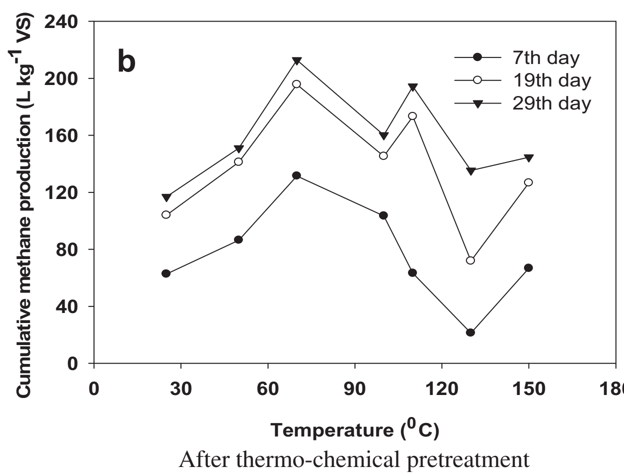


Fig. 5. Cumulative methane production at 7th, 19th and 29th day. (a) After thermal pretreatment. (b) After thermo-chemical pretreatment.

3.3.3. Chemical pretreatment

Chemical pretreatment at room temperature yielded less methane production in comparison to untreated sample. But it was observed that biogas production was high from chemically treated

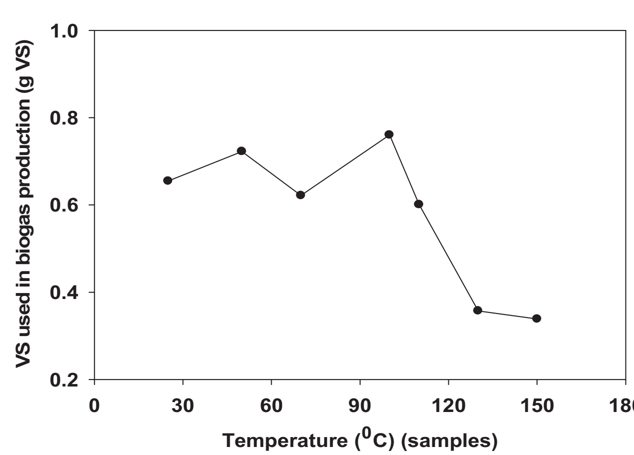


Fig. 6. Volatile solids consumption after thermal pretreatment.

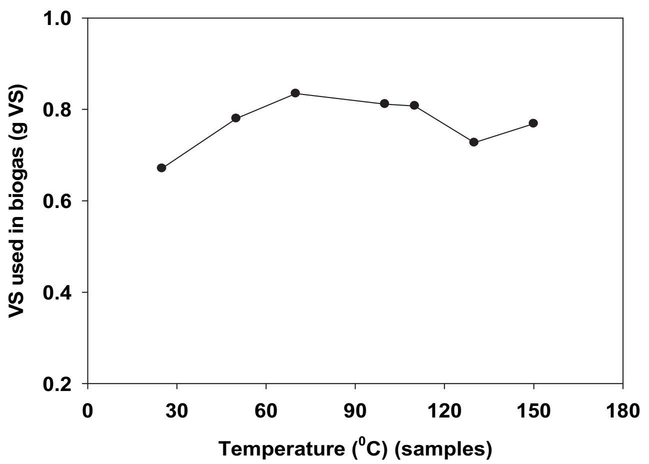


Fig. 7. Volatile solids consumption after thermo-chemical pretreatment.

sample than untreated (Fig. 1c). There were more amounts of other gases like CO_2 and N_2 than CH_4 and more CO_2 is produced due to higher amount of oxidized carbon.

3.4. Volatile solids consumption

It was observed from Fig. 6 that the volatile solid consumption corresponds directly to the production of biogas as shown in Fig. 1a, where higher amount of substrate is consumed at 100 °C followed by 50 °C and 70 °C. Similar observations were made for thermo-chemically and chemically treated samples (Fig. 7). In this case, maximum volatile solids consumption was for 70 °C followed by 100 °C and 110 °C (Fig. 1b).

4. Conclusion

The maximum biogas potential for thermally pretreated manure was observed at 100 °C. Above this temperature, biogas potential decreased rapidly with the increase of temperature. Thermal pretreatment at temperature above 100 °C had no positive effects on the degradability of substrate. The maximum biogas production in thermo-chemically pretreated samples was observed at 70 °C and then decreased with the increase of temperature. This indicates that the higher temperatures do not necessarily yield higher biogas production and this is attributed to the decrease in the biodegradability of substrate due to possible formation of complex organic and toxic compounds. While the increased initial biogas production is credited to the increased accessibility and degradability of substrate with the increase of reasonable temperature.

The CH_4 to CO_2 ratio remained almost constant with values of 1.5–2.0 for both thermally and thermo-chemically pretreated samples. It shows the amount of reduced and oxidized carbon is same in both materials. For the chemically pretreated material, only little improvement in biogas production was observed in comparison to the untreated material. This indicates that chemical increases the accessibility of more oxidized carbon in manure. Volatile solids conversion for thermal and thermo-chemical pretreatments at 100 °C and 70 °C temperatures are 76% and 83.5% respectively after 40 days. While for chemical pretreatment, volatile solid conversion is 67%.

The biogas and methane productions during degradation period for dewatered pig manure were significantly enhanced with thermo-chemical pretreatment in the range of 25–100 °C. At 110–150 °C, biogas and methane productions drop significantly, although they were still above the yield of untreated material. The enhancement of biogas and methane production due to thermal pretreatment in dewatered pig manure is not as significant as thermo-chemical pretreatment.

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