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Anaerobic digestion of tannery solid waste by mixing with different substrates

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Abstract

The tannery solid waste (fleshing) was collected from Hazaribagh, Dhaka. It has been found that fleshing contains 82.57% volatile matter. Further characterization of fleshing showed that it contains low C/N ratio of 2.64 and high pH of 10.99. These characteristics were not suitable for using fleshing as a substrate for anaerobic digestion. The study has been carried out in different ratio of waste fleshing, domestic sewage and cow dung at total solid 6% concentration. In all the reactors fleshing and domestic sewage were mixed at 1:1 ratio. On the basis of the performance of the reactors it was evident that the reactor which contains 75% fleshing with domestic sewage and 25% cow dung showed optimum result. Under optimum condition volatile solids destruction 52%, specific gas production 0.476 L/g volatile solids feed and methane yield 73% were achieved.

Keywords: Anaerbic digestion; Tannery solid waste; Biogas

Introduction

Leather and leather products have always been a part of our heritage and after the emergence of independent Bangladesh in 1971, the industry received a fresh momentum. Bangladesh started exporting crust and finished leather in early 80's and footwear and other manufactured leather goods during 90's. The contribution of leather industrial sector in the past decade was around.

US$ 250 million per year, accounting for around 3% of the country's export. Leather and leather goods are the third exportable item from Bangladesh according to Export Promotion Bureau (EPB) report. The leather industrial sector of Bangladesh has been almost entirely supported by local raw material resources. Based on UNIDO consultant's detailed interaction with the Hide and Skin Merchants Association in December 2005 as well as with a number of tanners and its own assessment, the weight of raw material processed in Bangladesh annually is estimated at present at about 85,000 t/y, with about 48,000 t/y (~56%) belonging to cows, 11,000 t/y (~13%) to buffalo and 26,000 t/y (~31%) to goats and sheep (Nemec, 2010). Peak season of the local tanning industry is the Qurbani or sacrifice of domestic animals (typically cows and goats) during the Eid-ul-Azha festival, which takes place each year. Accordingly the peak load during the Qurbani period is estimated at 450 t/d and the load during the rest of the year (225 days), at about 230 t/d (Nemec, 2010). Out of the total 206 tanneries in Bangladesh 192 of them are located in Hazaribagh area of Dhaka City.

The tanning industry of Bangladesh is primarily concentrated in Hazaribagh (25 ha of land within Dhaka City) as most of the operating tanneries are located there (Rahman, 1984). According to UNIDO report (Nemec, 2010) 15,000 m^3 of highly polluted wastewater generated everyday by tanneries in Hazaribagh area is discharged untreated into the open channel drains along the roadside passing through the area, which then eventually ends up in the Buriganga river. Often, the drains in the area spill over causing a highly unhealthy atmosphere. Leather manufacturing processes generate solid wastes varying in composition and quantity at various stages (Thangamani *et. al.,* 2009). Hence, the solid waste management systems of Hazaribagh area require special attention to reduce environmental hazards. A major portion of the solid wastes from leather industry is fleshing which contains mainly fat and protein and residual chemicals such as lime and sulphide used in the unhairing process of beam house operation (Thangamani *et. al.,* 2009). Anaerobic digestion of tannery waste has been studied by (Cirne *et. al.,* 1982; Thangamani *et. al.,* 2009; Seadi *et. al.,* 2008; Rahaman and Muyeed, 2010; Cirne *et. al.,* 2007; Deublein and Steinhauser, 2008; Oliveira *et. al.,* 2004). Research work for generation of biogas from Bangladesh tannery solid waste is yet to be done although the substrate has good potential for biogas generation. The main objective of the study is to generate biogas from tannery solid waste by mixing with sewage sludge and other wastes.

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Materials and Methods

Sample Collection

Different types of tannery waste were collected from 3 types of local tannery at different time. The waste was characterized by analyses, with Standard Methods (APHA, 1992). Substrates were collected at different time and stored at 4 ^{0}C, before analysis and other experiments. By examining the present management practices and the characteristics of waste, the fleshing portion of tannery solid waste was chosen as a substrate for biogas generation.

Preparation of substrates

The limed fleshing used as substrate was grounded to less than 6 mm diameter using a meat-grinding machine. To this, domestic sewage was added as diluent in different ratio to maintain the fleshing solids in suspension and to achieve the desired level of flowability in the feed mixture. Domestic sewage also act as a source of various microorganisms required for anaerobic digestion. The domestic sewage was collected from different locations of Elephant Road residential area. Cowdung was also used in different proportion as a substrate to maintain the C/N ratio. Sewage and Cowdung were also characterized by Standard Methods (APHA, 1992).

Inoculum

Pre-digested material consisting of all the essential microbes (hydrolyzing, fermentative, acetogenic and methanogenic bacterial consortium) was chosen as an inoculum for the study. The inoculum was synthesized in the laboratory using cow dung, limed fleshing and domestic sewage in equal proportions. After ceasation of gas production, the pre-digested material was tested for its activity with known quantity of sodium acetate as substrate for gas production, and later the digested residue was used as inoculum for the study.

Experimental setup

In order to examine the appropriate technology for the management of solid waste from tanning industry, anaerobic digestion process has been studied using batch reactors. A simple methanogenic activity test procedure was adopted (Jawed and Tare, 1996). The composition of limed fleshing, domestic sewage, cowdung and inoculum used in the batch experiments have been described in Table I. A known amount of substrate containing a mixture of waste was transferred into 2 L capacity wide mouth glass bottle. Different quantities of waste materials were mixed and added to the glass bottle to obtain an initial volume of 1 L in all the reactors, R1 to R4 (Table II). The total gas production was measured using a water displacement method at an interval of 24 h. Contents of the glass bottle were mixed manually, after every gas measurement. Daily gas production was recorded. The entire test was conducted at a temperature of 30 ± 3 ^{0}C for a period of 8 weeks.

In the month of September to November, 1st month was required for the preparation of inoculum. Room temperature, pH of the effluent were also monitored routinely. From second week volatile solids (VS) reduction and chemical oxygen demand (COD) reduction were monitored. Steady-state condition was identified when the COD value of the effluent and daily biogas production was same for two or three consecutive days.

Process parameters

Some of the commonly used anaerobic process indicators included pH, COD destruction, VS destruction, volatile fatty acid (VFA) concentration, gas production and gas composition. Most of the indicators listed above have been reported as appropriate for evaluating the effect of organic loading rate on the bioconversion of organic substrates and hence, these parameters have been chosen for assessing the decomposition of the substrate investigated in this study.

Analyses

Carbon and Nitrogen contents of the fleshing, domestic sewage were determined by C-H-N elemental analyzer (Thermo Fischer Scientific, FLASH-2000) with TCD detector. Helium gas was used as carrier gas at 250 kpa and 140 mL/m, furnace and oven temperature were 900^{0}C and 65^{0}C respectively. Its moisture and ash contents were estimated by gravimetric methods by drying at 105 ^{0}C and by complete combustion at 800 ^{0}C respectively. The protein content was estimated from the nitrogen content by multiplying with 6.25. Total solids (TS), VS, and VFA were estimated according to the procedures recommended in the standard methods for examination of water and waste water (APHA, 1992). Assay bottles were periodically analyzed for the above-mentioned parameters for a period of 8 weeks. Gas production from the reactors was monitored by means of water displacement method on daily basis. The volume of water displaced from the bottle was equivalent to the volume of gas generated at the temperature and pressure that prevailed during the study period. Gas chromatograph (Thermo Fischer Scientific, Trace GC Ultra) with TCD detector was used to measure methane content and carbon dioxide in the biogas composition. Helium gas was used as carrier gas at 900 kpa and 10.5 mL/m, oven and detector temperature were 80^{0}C and 180^{0}C respectively.

Experimental procedures and sampling schedules

A known quantity of wastes was added in a 2 L bottle as an initial experiment. On the basis of the result of the experiment four biogas digesters were taken for biogas generation from the substrate by mixing with domestic sewage in different proportions. The digested slurry from initial experiment was used as inoculum for the test reactors. Thus, the test reactors for four different organic loading were constructed. The TS concentration of all reactors was 6%. At the end of every week, one bottle for each VS load was analyzed for various parameters.

Table I. Characteristics of substrates

Constituents	Limed Fleshing	Domestic Sewage	Cowdung	Inoculum
pH	10.99	6.15	6.21	6.43
TS (%)	13.38	5.00	17.00	6.00
VS (%)	82.57	82.00	89.00	88.60
Oil (%)	9.50	2.32	1.56	-
Protein (%)	44.16	25.32	7.89	-
Moisture Content (%)	86.62	95	83.00	94.00
COD (mg/L)	-	1329	-	-
Calorific Value (kcal/kg)	4323.06	4010.04	4658.07	-
C/N Ratio	2.64	20	24.00	-

Table II. Quantity of lime fleshing, domestic sewage, cowdung and inoculums and the initial VS concentration in the reactors

Reactors Name	Fleshing (g)	Domestic Sewage (mL)	Cowdung (g)	Inoculum (mL)	Tap water	Initial VS Concentration (g/L)
R1	125.00	300.00	180.00	100.00	295.00	55.33
R2	170.00	450.00	90.00	100.00	190.00	52.45
R3	225.00	600.00	0.00	100.00	75.00	50.80
R4	195.00	525.00	45.00	100.00	135.00	51.56

Table III. Refractory fraction, biodegradable fraction and total VS destruction observed in the reactors

Reactor	Refractory fraction of VS	Biodegradable fraction of VS	% Biodegradable fraction of VS (calculated)	% VS destruction based on total VS (experimental)
R1	0.484	0.516	51.6	52.06
R2	0.499	0.501	50.1	51.94
R3	0.623	0.377	37.7	41.37
R4	0.562	0.438	43.8	45.04

Results and Discussion

Characteristics of raw materials

General characteristics of tannery waste fleshing are given in Table I. The fleshing contains 82.57 % VS and considerable amount (9.50%, dry basis). It also contains protein of about 44.16%. The C/N ratio of fleshing was 2.64, which were quite low for optimum biogas generation (Rouf *et. al.*, 2010) and that low C/N value increased by mixing with cowdung and domestic sewage. The pH of the fleshing was extremely high (10.99), which is not favourable to biogas generation. Buffering capacity of cowdung is very good and the domestic sewage would also act as a source of various micro organisms required for anaerobic digestion (Thangamani *et. al.,* 2009).

Biogas generation

Daily gas production

Fig. 1. to Fig. 4 represents the volumes of daily gas accumulation with varying amount of fleshing. Here substrate fleshing, sewage sludge and cowdung were used. In the mixture initially few days were required for biogas generation. After 5 days biogas generation was started properly and then gas generation per day was increased. Then after 45 days food concentration of bacteria was decreased and biogas generation was also decreased significantly. The irregularities of gas production are due to changes of temperature and also for scum formation on the surfaces of the slurry of the biogas digester. So, after breaking of scum by pressure of the biogas inside the digester, sometimes amount of biogas increased abnormally.

Fig. 1. shows the daily gas generation for reactor R1. It was observed that gas generation started at the very next day of charging the digesters with the slurry. The rate of gas generation gradually increased with increasing the digestion period. The graph also indicates that during the digestion period, most of the day gas production range was in between 200-600 mL. In this reactor, the peak gas production of 1100 mL was observed on the 34th day. It was observed that gas production rate declined after 54th days.

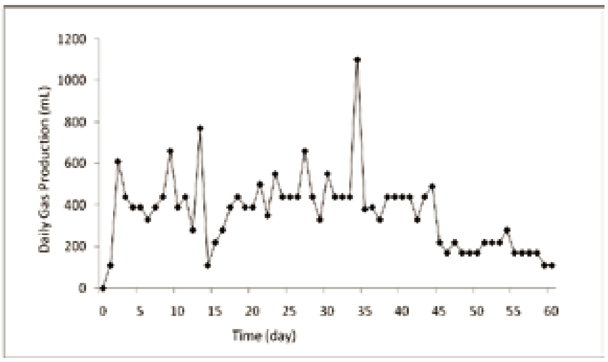

Fig. 1. Daily gas production in the reactor R1

Reactor R2 (Fig. 2) shows considerable amount of daily gas generation. In this reactor also the generation of gas started from the second day after recharging the reactor with slurry. The peak gas production was observed on the 28th day, the amount was 1100 mL. Here also the gas production range was in between 200-600 mL.

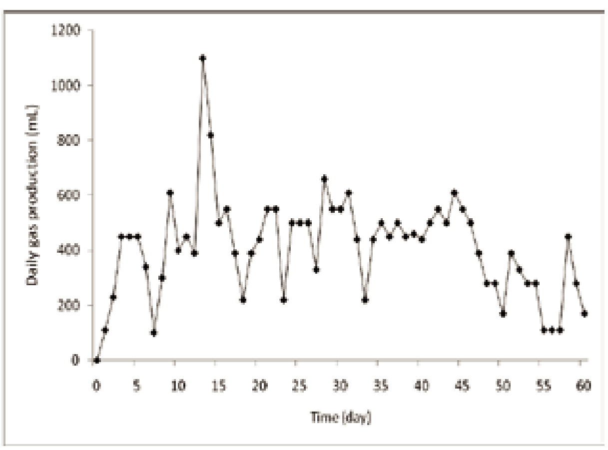

Fig. 2. Daily gas production in the reactor R2

Fig. 3. represents the daily gas production rate for reactor R3. This shows lower range of daily gas production (100-300 mL). In this digester, bacteria were taken four days for acclimatization as there was no cowdung in the slurry. The peak gas production was observed 550 mL at the 23rd day of digestion period.

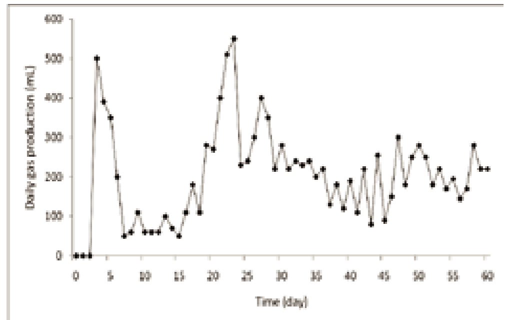

Fig. 3. Daily gas production in the reactor R3

Fig. 4. shows the daily gas production in the reactor R4. In this reactor also the generation of gas starts at the second day after charging the reactor. The peak gas was 780 mL which was observed at the 26th day. The gas generation also ceased at the 60th day of digestion period. A gradual shift was observed in the period of peak gas production with increasing VS concentration. One GC chromatogram of a biogas sample has shown in Fig. 5.

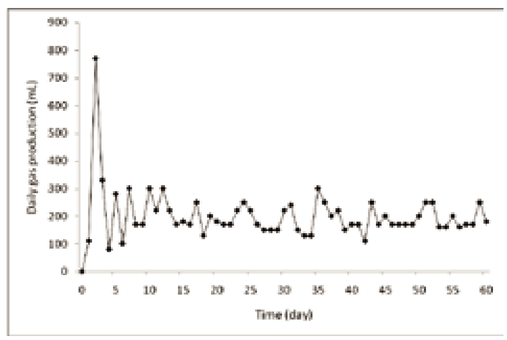

Fig. 4. Daily gas production in the reactor R4

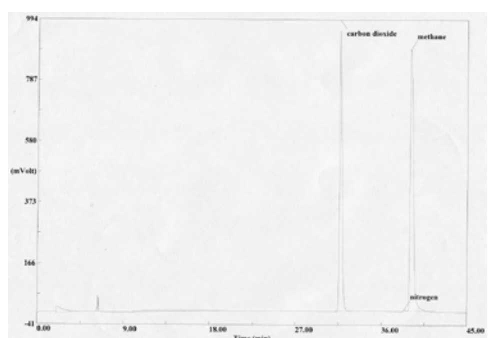

Fig. 5. GC chromatogram of a biogas sample.

Cumulative gas production

The cumulative gas production from each of the test reactors operating at various organic loading of tannery solid waste, domestic sewage and cowdung are shown in Fig. 6. A cumulative gas production from test reactor R1 was 22,200 mL at the end of the eighth week of the study period. A cumulative gas production from the test reactor R2 was 24,960 mL, while a cumulative gas production of 12,145 mL was observed in test reactor R3. In the last and fourth reactor R4 cumulative gas production was observed 14,850 mL. In the four reactors R1, R2, R3 and R4 specific gas production in terms of VS fed were 0.401, 0.476, 0.239 and 0.288 L/g respectively. Fig. 6 shows that the lag phase prevailed upto 5 to 6 days of digestion period. This was due to microbe limiting at the initial stage of fermentation. The peak generation of gas is delayed as the lag phase was longer. After the lag period, the cumulative volume of gas increased sharply and continued upto 50 to 55 days of fermentation period. After which the rate of gas generation decreased and this declination continues until the gas generation almost ceased. At the end of eighth week gas generation in all the reactors almost ceased.

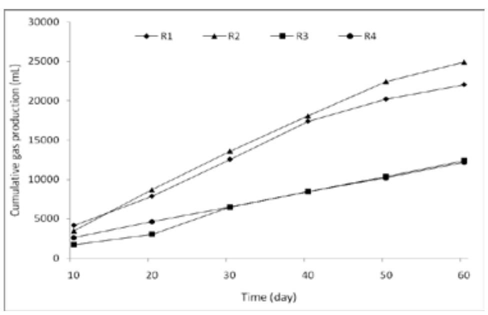

Fig. 6. Cumulative gas production in different reactors (R1, R2, R3, R4)

VS destruction in batch reactor

During anaerobic digestion of solid waste, biogas generation is more specifically related to the reduction of biodegradable fraction of VS in the digester. VS reduction in the test reactors was observed in the range of 41.37-52.06%. These values are comparable with the VS reductions reported in the literature for various substrates (Rouf *et. al.,* 2010 and Thangamani *et. al.,* 2009). The percentages of VS of slurry decreased with increasing digestion period. The VS concentration is decreased with time as the part of VS consumed by bacteria for biogas generation (Fig. 7). The percentages of the solids are correlated with the digestion time as the values of R^2 are about 0.99 in all cases. The tendencies of concentrations for solids are decreasing with time. But the degree of reduction depends on the initial volatile solids concentration of the slurry (Bosu, 1993). Biogas generation is a biological process and bacteria consume carbon for cell building and energy source extracting from solids which causes solid reduction.

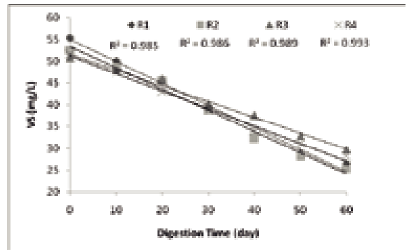

Fig. 7. Volatile Solids with digestion time for different reactors (R1, R2, R3, R4)

COD value reduction

COD of the slurry was considerably reduced by anaerobic digestion treatment .The reduction of COD value means the reduction of pollution load from any substrate by the treatment process. The COD value curves for four different reactors are shown in Fig. 8. The trend line shows that good correlation exist between digestion time and COD value as the R^2 value is above 0.95 for all the reactors.

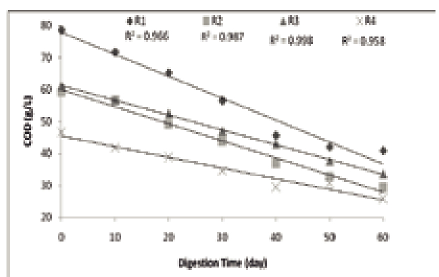

Fig. 8. COD value with digestion time for different reactors (R1, R2, R3, R4)

For reactors R1, R2, R3 and R4 COD reduction rates were 48.02, 50.67, 44.80 and 44.61% respectively. Maximum COD reduction was achieved from reactor R2 where maximum gas was produced. COD reduction value is comparable with the reference value given by Rahman and Muyeed, 2010.

C/N ratio

The C/N ratio of 2.64 for fleshing materials was very low. Therefore cowdung and domestic sewage were used as co-substrate. The reactors were operated at C/N ratio of 18, 17, 15 and 16 respectively which were low from standard value (20 to 30) (Rahman and Muyeed, 2010). But in this range reactors operated without any setback even at lowest C/N value R3 reactor has been given considerable amount of gas. Optimum gas production was obtained at C/N ratio 17 of reactor R2.

Biodegradability of feed mixture

The refractory fraction in the feed mixture is an indicator of the extent of biodegradability of the substrate. It is the portion of initial VS that remains in the digester as solid retention time

(SRT) approaches infinity (Borja, 1995). The refractory fraction and biodegradability were determined graphically from the intercept of the plot (Fig. 9) drawn between (S_i/S_0) and $(S_0*t)^{-1}$ where S_i = substrate concentration (g/L), S_0 = initial VS concentration (g/L) and t = retention time (d). It was in the range of 37.7–51.6% of the influent volatile solids concentration (Table III). The biodegradability factor indicates the presence of resistant volatile matter in the major portion of volatile solids in the digester. This reasonably conforms to the experimentally determined VS destruction efficiency of 41.37–52.06% in Table III (Parawira *et. al.,* 2004). Hence, it is essential to monitor the biodegradable fraction of VS in the feed to have better operational control over the process.

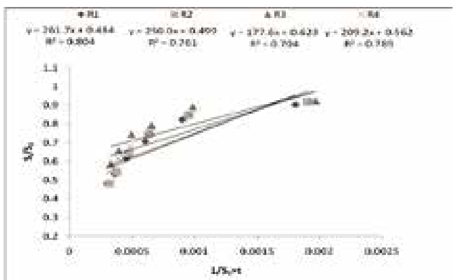

Fig. 9. Refractory fraction of feed mixture for different reactors (R1, R2, R3, R4)

Conclusion

The present practices of disposal of tannery waste are not environmentally friendly and cause great concern for Dhaka City. The solid waste fleshing contains about 82% VS which are amenable to biodegradation. The C/N ratio of fleshing is too low and alone is not suitable for biodegradation but mixing with other substrates with fleshing the generation of biogas is very satisfactory. The composition of reactor R2 gives the best performance for specific gas production, reduction of COD and VS reduction. In addition to this the mixing of other substrate improves the environmental condition of the biogas reactor for better anaerobic digestion. The methane content of biogas from the substrate is very satisfactory. The fleshing waste can be used as a complementary substrate part of small scale biogas plants. Use of fleshing will also reduce the cow dung requirement in a biogas plant which is also an important point, because very often cow dung scarcity turns off the biogas plants. The generation of biogas from the substrate is environmentally friendly, hygienic and it will reduce pollution.

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