



Potential of Biogas in Waste Activated Tannery Sludge by Anaerobic Co-Digestion

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In present study the possible management of waste activated tannery sludge through their simultaneous digestion with cow dung has been investigated. The anaerobic co-digestion of activated sludge can be helpful for recovery of energy and high quality of bio-solid product that can be used as soil conditioner. The accumulative biogas production of tannery sludge and cow dung (TSCD-2) in an ratio of 30:70, TSCD-3 in an ratio of 70:30 and tannery sludge (TS-4, 100 %) were measured as 208, 481 and 70 mL, respectively at temperature ranging from 25-37 °C. The waste activated tannery sludge can be used for biogas production with the help of co-digestion by utilizing suitable co-substrate that improve the digestibility as concluded in the results of TSCD-2 and TSCD-3 samples.

Keywords: Anaerobic digestion, Tannery sludge, Biogas and co-substrate.

INTRODUCTION

The whole tannery industrial activities are causing severe environmental degradation due to the disposal of untreated effluent and sludge on land and in water bodies. The operation of tanneries produce all types of waste that is wastewater, solid waste and air emission which pose threats to the ambient environment and health of working people. The high environmental impact of tannery effluents makes its treatment as an essential fact, mainly due to its high volume, nature and concentration of pollutants such as tanning agents, colour, organic matter and other pollutants¹.

The untreated waste from tanneries produces number of problems to local community, spoil the civic beauty of area and pollute water bodies. The levels of chromium in soil near tannery areas were found beyond the safe limits². Customarily, tannery sludge is disposed off in landfills, ocean dumping and incineration or solidification³. Landfills and ocean dumping of tannery sludge is under increasing pressure in many countries because of environmental considerations. When the sludge was incinerated, the gases and soluble toxic chemicals were generated, which can cause serious environmental problems such as air, soil and water pollution. When tannery sludge is solidified, chromium can be immobilized in the ceramic materials. However, sulfur compounds, zinc and chlorine are released to the air⁴. Tannery industries are producing tons of sludge on the daily basis. It must therefore be treated before disposal or reuse in order to protect our environment. In recent

time different kinds of waste mixture that obtained various sources have been used for the production of biogas through anaerobic co-digestion by many workers⁵⁻⁸.

Implementation of cleaner technologies in the leather sector considerably reduces the pollution load generated from tanneries. In tannery Waste Management Anaerobic co-digestion with mixed waste has been suggested as an effective method. Co-digestion is the simultaneous digestion of more than one type of waste in the same unit. Advantages include improve biodegradation rate, better digestibility, enhanced biogas production due to availability of additional nutrients, as well as a more efficient utilization of equipment and cost sharing⁹⁻¹¹. This biological method reduce the quantity of sludge to be disposed, destruction of many pollutants, efficient odour reduction, production of high-quality biosolids for land application and production of methane gas¹².

The present research work is focussed on proper treatment of tannery sludge to manage it into environment benign ways. The anaerobic digestion of waste activated tannery sludge will be done by utilizing cow dung as co-substrate in different experiments.

EXPERIMENTAL

Representative samples of tannery sludge were collected from Kasur treatment plant. The sample A was collected from secondary clarifier that contains activated sludge; B and C were collected from primary and secondary lagoon sludge respec-

tively. Sample D was collected from solid waste dumping site of Kasur treatment plant. The cow dung (04 Kg approx.) was collected from a dairy farm located near district Lahore, Punjab and subsequently was used freshly without drying.

Experimental set up: A set of four Buchner flasks (1000 mL) was used as digesters for this research, that is, one digester for each sample. All apparatus were properly washed with detergent solution and rinsed with double distilled water and dried in oven at 70 °C for approximately for 1 h. Another set of 4 Buchner flasks (500 mL) was used containing brine solution for the measurement of biogas that was produced in the digester. The biogas produced in the digester by the anaerobic digestion process passed through the connecting tube to the Buchner flask containing brine solution. The weighing balance was used to determine the mass of tannery sludge and cow dung that made up the total solid for particular digestion slurry. The digester was operated at temperature ranging from 25-37 °C. A digital pH meter (JANCO 6173) was used to determine the pH of the slurry (sample) during the experiment.

Total solid and water content: Four proportions of tannery sludge and cow dung (CD-1, TSCD-2, TSCD-3 and TS-4) were utilized on a weight percent basis to investigate the efficiency of biogas production. These proportions were as follows: Sample CD-1; 0:100, TSCD-2; 30:70, TSCD-3; 70:30, TS-4; 100:0 (Table-1). The fermentation slurry represents 8 percent of total solid (TS) for each sample to enhance biogas production as reported in literature¹³. The proportion of total solid to water was the same in all the fermentation slurry samples regarding their weight (Table-2).

Sample	% of Tannery sludge	% of Cow dung
CD-1	0	100
TSCD-2	30	70
TSCD-3	70	30
TS-4	100	0

Abbreviation CD (Cow dung sample), TSCD (Tannery sludge and cow dung) and TS (Tannery sludge)

Operating conditions: pH values of samples CD-1, TSCD-2, TSCD-3 and TS-4 were 7.09, 7.22, 7.39 and 7.51, respectively. The whole experiment was carried out at room temperature that varied between 25-37 °C representing mesophilic conditions.

Parameters	Methods	A (waste activated sludge)	B (Primary lagoon Sludge)	C (Secondary lagoon sludge)	D (tannery solid Waste)
pH value at 25 °C	4500-H+-B (APHA)	7.37 ± 0.05	7.98 ± 0.02	7.99 ± 0.04	7.57 ± 0.02
Ammonia (%)	4500-B,C (APHA)	0.062 ± 0.01	0.016 ± 0.003	0.0202 ± 0.001	0.021 ± 0.003
Sulfate (%)	4500-E (APHA)	0.004 ± 0.001	0.007 ± 0.001	0.001 ± 0.00	0.002 ± 0.00
TKN (%)	4500-N-B (APHA)	1.42 ± 0.15	1.45 ± 0.10	1.35 ± 0.13	1.32 ± 0.15
Organic matter (%)	D-2974 (ASTM)	36.87 ± 1.05	24.45 ± 1.34	25.6 ± 0.95	51.84 ± 1.65
TOC (%)	-	21.44 ± 0.50	14.192 ± 0.40	14.88 ± 0.63	13.78 ± 0.53
Ash (%)	E-830 (ASTM)	63.12 ± 1.75	75.58 ± 1.15	74.39 ± 1.24	70.39 ± 2.24
C/N	-	15.09 ± 0.45	9.72 ± 0.35	11.01 ± 0.20	8.01 ± 0.40
Nitrate (%)	-	0.091 ± 0.004	0.06 ± 0.001	0.072 ± 0.005	0.092 ± 0.004
Na (g/Kg)	5300 Na-B (APHA)	12.45 ± 0.45	11.05 ± 0.25	12.6 ± 0.40	27.95 ± 0.85
K (g/Kg)	5300 K-B (APHA)	0.60 ± 0.30	0.68 ± 0.20	0.70 ± 0.35	2.2 ± 0.67
Chromium (%)	-	0.342 ± 0.06	1.01 ± 0.03	1.04 ± 0.02	1.577 ± 0.01

Sample	Mass of W (g)	Mass of X (g)	Mass of Y (g)	Mass of Z (g)
CD-1	80	0	80	220
TSCD-2	80	20	60	220
TSCD-3	80	40	40	220
TS-4	80	80	0	220

W represents the sum of the tannery sludge and cow dung; X represents tannery sludge; Y represents the cow dung and Z represents the amount of water needed for any given mass of WL

Physico-chemical analysis: Physico-chemical analysis such as analysis of sulphate, nitrate, ammonia, total Kjeldhal nitrogen and pH were carried out by using standard methods¹⁴. The proximate analysis including moisture, ash and organic matter were carried out by using ASTM methods. Estimation of chromium was carried out on flame Atomic Absorption Spectrophotometer (Polarized Zeeman Hitachi 2000). Analysis of Na and K were analyzed on flame photometer (Jenway PFP-7). Results obtained from the experiments (n = 3) were expressed as mean values ± SD (Standard deviation).

Volume of biogas measurements: An acidified brine solution was prepared by adding few drops of sulphuric acid to prevent the dissolution of biogas in the water. The volume of biogas has been measured by the amount of water being displaced in collecting flask¹⁵.

RESULTS AND DISCUSSION

Different parameters of collected samples of sludge from Kasur tannery treatment plant has been depicted in Table-3. The C/N ratio of waste activated tannery sludge (15.01) was higher as compared to primary lagoon sludge (9.72) secondary lagoon sludge (11.01) and tannery solid waste (8.01). The study of Sievers and Burne reported that maximum biogas production will be obtained at carbon nitrogen ratio of 19.9¹⁶. The higher values of selected parameter such as organic matter (36.87 %), carbon nitrogen ratio (15.09), total nitrogen (1.42 %) sodium (12.45 g/Kg) and potassium (0.60 g/Kg) contents of waste activated sludge sample may be considered for biogas production as compared to other collected sludge samples. The waste activated sludge sample was used for biogas production in experiment with different compositions of cow dung as co-substrate. Characterization of cow dung sample used in

experiment was shown in Table-4. The result shows that it is feasible for biogas production.

Any carbon-based material that is organic in nature has a potential source of biomass feedstock to produce biogas. The commonly biomass that are used as feedstock to produce biogas include garden waste, sewage, manure (e.g., dairy, pig, cattle), organic fraction of municipal solid waste, forestry wastes, agricultural wastes, tannery wastewater sludge and industrial food processing wastes¹⁷.

Parameters	Methods	Results
pH value at 25 °C	4500-H ⁺ -B	6.77 ± 0.02
Sulphur (%)	E-776	0.05 ± 0.01
Organic matter (%)	D-2974	88.75 ± 2.25
TOC (%)	-	47.0 ± 1.45
Volatile matter (%)	E-897	19.83 ± 1.05
C/N	-	11.7 ± 0.45
Ash (%)	E-830	9.98 ± 1.65
Total Solids	-	31.93 ± 1.35
Na (g/Kg)	5300 Na-B	0.14 ± 0.02
K (g/Kg)	5300 K-B	0.45 ± 0.03

The anaerobic decomposition process is used for producing biogas and the residue after dewatering can be used as high quality biosolids (fertilizer). It occurs in the absence of oxygen with the following steps^{18,19}.

Hydrolysis → Acid formation → Methane formation

The experiment was carried out at 25-37 °C at laboratory conditions and was run for 7 weeks. There is a close relationship between biogas fermentation and temperature. The experiment shows that high temperature is not appropriate for biogas fermentation²⁰. The amount of gas evolved was recorded only when the gas became flammable. The daily biogas production was measure as a result of water displacement. The result of CD-1 sample (cow dung 100 %) was shown in Fig. 1. The data in Table-3 reveals that production start at 3rd day reaches at maximum value at day 10 (180 mL) of biogas produced then it decrease with passing days. The main objective of this experiment was to verify laboratory conditions that either these are suitable or not for biogas production.

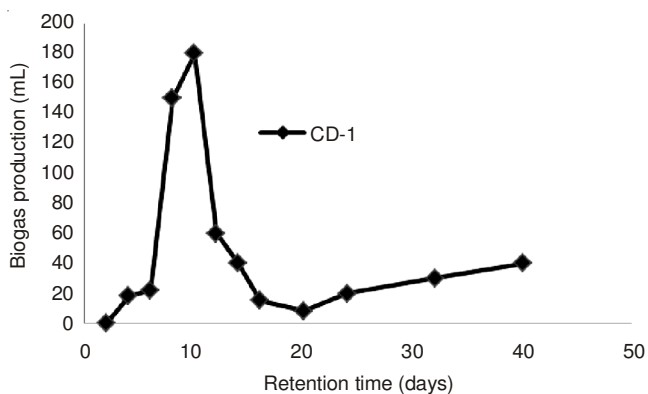


Fig. 1. Biogas production of CD-1 (cow dung) sample during experiment

In TSCD-2 sample (tannery sludge 30 % and cow dung 70 %) the gas production start at day 4 (5 mL) and at day 10 recorded its maximum value (70 mL) and then gradually decrease shown

in Fig. 2. In TSCD-3 (70 % tannery sludge and 30 % cow dung) and in TS-4 hundred percent of tannery sludge were used. The result of TSCD-3 sample was found to be good as compared to TS-4 shown in Fig. 3. The biogas production in TSCD-3 sample was recorded maximum at day 8 (200 mL) whereas TS-4 sample only 30 mL. The cumulative biogas production of TSCD-3 sample was measured 481 mL where in case of TS-4 only 70 mL. The result of TSCD-3 shows good result which means that the waste activated sludge produced from tannery treatment plant can be used for biogas production by using suitable substrate by anaerobic co-digestion. It is well known that the composition of biogas as well as biogas yields depend on the co-substrates owing to differences in material characterization in each feed material²¹⁻²³. The accumulative gas production was represented in Table-5. The result of CD-1 sample was higher as compared to TSCD-2, TSCD-3 and TS-4 samples shown in Fig. 4.

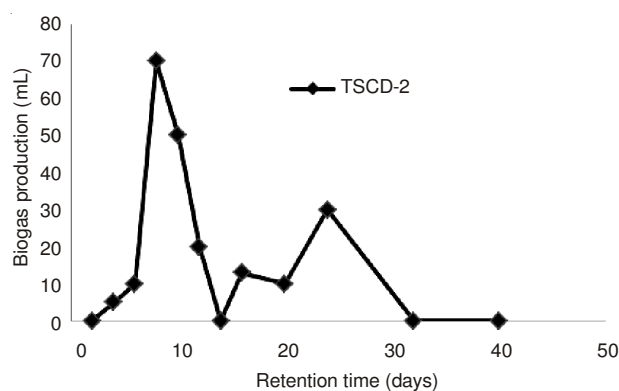


Fig. 2. Biogas production of TSCD-2 (tannery sludge and cow dung, 30:70) sample during experiment

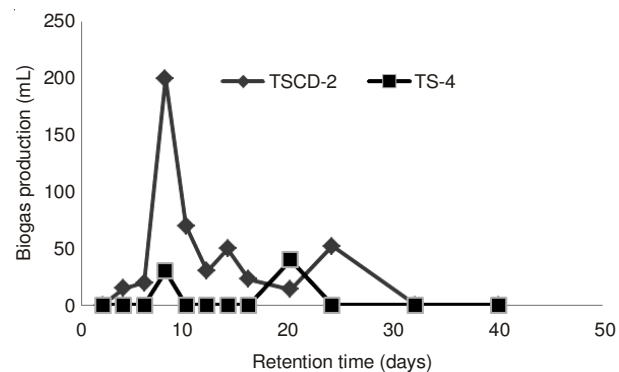


Fig. 3. Biogas production of TSCD-3 (tannery sludge and cow dung, 70:30) and TS-4 sample with time

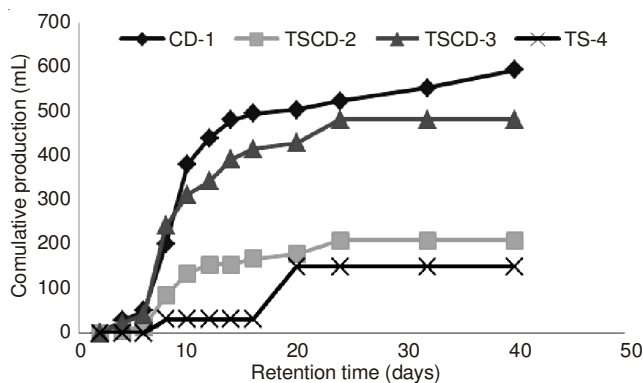


Fig. 4. Cumulative biogas production of CD-1, TSCD-2, TSCD-3 and TS-4 samples

TABLE-5
CUMULATIVE DAILY BIOGAS PRODUCTION FROM WASTE ACTIVATED TANNERY SLUDGE AND COW DUNG

Days	Sample CD-1 (mL)		Sample TSCD-2 (mL)		Sample TSCD-3 (mL)		Sample TS-4 (mL)	
	Daily production	Cumulative production	Daily production	Cumulative production	Daily production	Cumulative production	Daily production	Cumulative production
1	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-
3	10	10	-	-	7	7	-	-
4	18	28	5	5	15	22	-	-
6	22	50	10	15	20	42	-	-
8	150	200	70	85	200	242	30	30
10	180	380	50	135	70	312	-	30
12	60	440	20	155	30	342	-	30
14	40	480	-	155	50	392	-	30
16	15	495	13	168	23	415	-	30
20	8	503	10	178	14	429	40	70
24	20	523	30	208	52	481	-	70
28-32	30	553	-	208	-	481	-	70
32-40	40	593	-	208	-	481	-	70

The volume of biogas produced by this sample was very small. The result of TS-4 sample (100 % tannery sludge) produces very less quantity of biogas throughout the period of experiment. The reason is that the pure sludge contains toxic substance like NH_3 (0.062 %), nitrate (0.091 %) and sulfate (0.004 %).

Conclusions

The disposal of organic waste and energy production anaerobic co-digestion is an efficient process. The outcome of this research suggests that waste activated tannery sludge (TS-4) does not have the potential for biogas production at the temperature range of 25-37 °C but with the help of co-digestion by utilizing suitable co-substrate (biomass) can increase the digestibility for biogas production. Moreover, co-digestion has following advantages,

- Co-digesting improves nutrient balance and enhances pH buffer capacity
- Possible gateway for waste treatment
- Additional biogas production and digestion rate
- Production of high quality bio-fertilizer
- Co-digestion has economically better for anaerobic digestion due to shared equipment and easier handling of feedstock

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