Biogas Generation and Chemical Oxygen Demand Removal through Anaerobic Treatment of Spent wash Diluted with Grey Water under Mesophilic Condition

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Abstract: Spent wash is a highly toxic liquid wasted generated by distillation of molasses into alcohol containing high amounts of organic matters that cause the increase in high COD. Discharge of this waste has become the main problems of distilleries unless qualitative procedure is applied to treat it by degradation of organic matter. Anaerobic digestion is best suited treating process for spent wash as biological, environmental friendly and economical which also produces clean source of energy called as Biogas. Sample was collected from treated spent wash as outlet of anaerobic digestion plant as it contains still high COD. Grey water was used as innovation in research to dilute spent wash because of presence of microorganisms in it. Biogas production from co-digestion of chicken manure & buffalo dung with spent wash were used with a calculated ratio in all digesters. The ratio of dung slurry was prepared as 1:3 of buffalo & chicken. Total three formulations were prepared in this research. The batch was consisted of A, B & C digesters respectively. Anaerobic digestion for biogas generation and biogas quality analysis was evaluated under Mesophilic condition (35±2°C). The biomasses (substrates) of buffalo &chicken manures were characterized in terms of Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and pH before and after co-digestion process. The biogas production was measured on 24 hours basis by water displacement method for (60 days). The maximum Biogas was observed in digester C. Biogas production from digesters A & B were negligible or not sufficient. The generated biogas was sampled from digester-C and analysed through Gas Chromatograph (GC) for methane (CH_4) Carbon dioxide (CO_2) concentrations. The maximum methane concentration was found in digester "C" as 71% methane and 13.80% carbon dioxide. The significant removal was obtained in C.O.D reduction 80.84 % with the concentration value as 8140mg/l. Results of this research work from digester C showed positive findings as compared to literature outcomes. According to Unicol distillery's treatment, COD removal is approximately 60%. Whereas this research provides 20% increase in COD reduction and maximum amount of concentrated biogas in terms of Methane.

Keywords: *Spent Wash, Biogas, Anaerobic Treatment, Grey Water, Chemical Oxygen Demand*

1. Introduction

Spent wash is the toxic and most polluted effluent in terms of BOD and COD causing most dangerous environmental problem [1].Spent wash can be classified as a diluted liquid organic fertilizer having high potassium content [2]. It is a dark brown coloured effluent and characterized as one of the most contaminated wastes containing extremely high COD (82,000-100,000 mg/l), BOD (35,000-51,000 mg/l), inorganic solids, colour and low in pH(3.5-4.5) [3,4,5,6]. It is rich in organic matters and nutrients like Nitrogen (N), potassium (K), phosphorus (P), calcium (Ca) and sulphur (S), micronutrients (traces) viz iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) and traces of sugar are also contained. It can be used as source of energy and fertilizer as well if properly managed. Anaerobic digestion is acceptable prime treatment method for the effluent (spent wash) for reducing pollution contents and recovery of biogas [7, 8]. It can be used as source of energy and fertilizer as well if properly managed. Anaerobic digestion is acceptable prime treatment method for the effluent (spent wash) for reducing pollution contents and recovery of biogas [9]

Biogas is basically a type of bio fuel which is naturally produced from biodegradation of organic waste and this biodegradation occurs in the anaerobic digestion. The biogas production process is also known as anaerobic digestion [10]. Biogas comprises of 50-60% Methane (CH_4) and 30-40% Carbon-Dioxide (CO_2) and minor fraction of different gases like H_2S. Biogas possesses a calorific value up to 21-24 MJ/m^3. 1m^3 of biogas can produce energy (electrical) up to 2.5 KWh. The livestock sector annual growth rate is four percent in Pakistan and its dung can generate 35.625 million KWh of electricity per day. The livestock sector annual growth rate is four percent in Pakistan and its dung can generate 35.625 million KWh of electricity per day [11].

Anaerobic digestion is one of the most effective methods of treatment, in which bacteria in the absence of oxygen decompose and convert food organic matters. Anaerobic digestion process consists of several stages; major phases include hydrolysis, acidogenesis, acetogenesis, and methanogenesis shown in figure 1. Hydrolysis Phase converts insoluble organic matter and heavy molecules such as lipids, polysaccharides, and proteins into simple soluble substances such as amino acids and fatty Acids. In the second phase, acid-forming converts material into simpler compounds such as short chain fatty acids. In the third phase, acids and alcohols are degraded to acetic acid, hydrogen gas, and CO_2. In the final phase of methane forming two groups of methane-generating bacteria produce methane in two ways: 1) The first group degrades acetate to CH_4 and CO_2, 2) The second group uses hydrogen gas as an electron donor and CO_2 as an electron acceptor.

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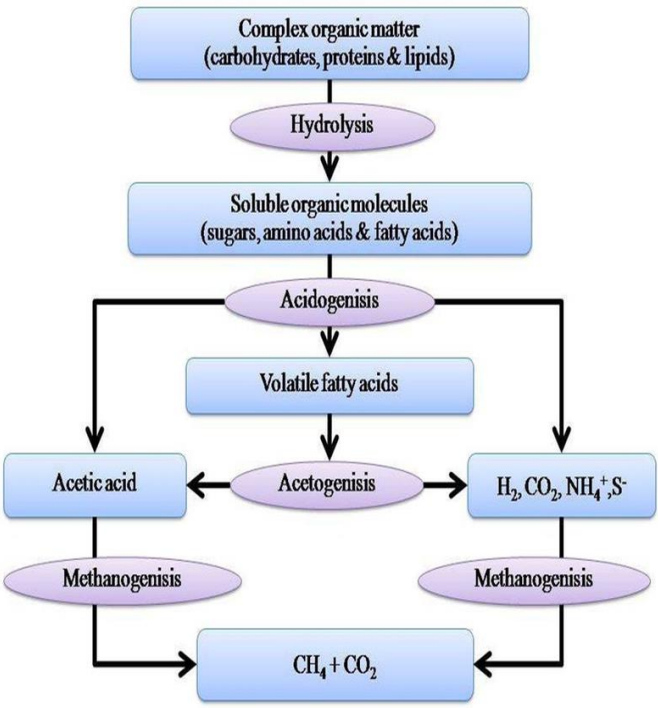

Grey water is defined as domestic wastewater produced from washbasins, bathroom and washing machines. Grey water participates up to 55-75% of the total household wastewater. Properly treated grey water can be reused for different applications like toilet flushing, car washing, home gardening etc. Moreover, treated grey water can also be used to irrigate the non-eatable crops. The nutrients present in the grey water like Phosphorus and Nitrogen deliver an excellent food source for these plants. Water coming from toilets having urine and faecal matter is said to be black water. [12]

2. Related Work

Dheeraj Rathore (2012) suggested that spent wash after the dilution treated under anaerobic digestion showed

Parameter	Two Third Dilution	One Third Dilution	Raw Spent Wash
Influent COD	30,800	62,000	82,000
Effluent COD	11,400(63%)	17,600(71%)	17,300(79%)
pH	8.18	8.54	8.45

positive response on growth parameters. Moreover, he further suggested that one-half dilution for spent wash is that the best fitted to the growing parameters.

Farid Ansari et al (2012) administered a study to understand the standard of distillery effluent to be treated and diluted properly for discharge within the water stream or in land. He observed high load of COD (chemical oxygen demand) and organic pollutants within the spent wash and PTDE (primary treated distillery effluent). But 50% and 75% dilution with water showed a decrease in physicochemical properties. The reduction in such values showed that toxicity of spent wash declined with increase within the dilution but the dissolved oxygen was also increased.

D. k. Veeral et al (2017) performed a laboratory experiment to analyse the pH of spent wash diluted with

Parameter	Value
pH	3.67
Total Solids	66,980 mg/l
Total Dissolved Solids	14,660 mg/l
Chemical Oxygen Demand (COD)	82,000 mg/l
Biochemical Oxygen Demand (BOD)	35,000 mg/l

water at several ratios of 1:0, 1:10, 1:20, 1:30, 1:40, 1:50. Water diluted spent wash at ratio 1:0 showed a pH of 4.2 that indicated as acidic in nature while at ratio 1:50 showed pH of 7.57 that was neutral and may be used as fertilizer in agriculture purposes. pH at ratio 1:10, 1:20, 1:30, 1:40 was found to be 5.13, 5.86, 6.35, 6.98 respectively. She also suggested it a simple way for the spent wash disposal without polluting the environment by diluting with water.

Lekshmi.S.R (2013) studied on spent wash treatment under hybrid anaerobic baffle reactor (HABR) in three steps i.e. (1) HABR, (2) Advanced Oxidation, (3) HABR which had following characteristics in table 1.

Operation was run for 60 days in two stages of 30 days each. Dilution factor was analyzed on two third and one third dilutions. COD removal efficiency was achieved up to 79% in 30 days and characteristics were checked as shown in table 2.

While at second stage COD value reduced to 6000 mg/l with an overall efficiency of 92% as given in the table 3.

Parameter	HABR
Influent COD	11,500
Effluent COD	6,000
pH	8.7

3. Methodology

- **3.1** Bench Scale study was conducted at Chemical Engineering Department, Mehran UET Jamshoro.
- **3.2** Three anaerobic digesters each containing capacity of 1000ml were used. The mesophilic condition (35-37ºC) was maintained for the treatment of spent wash.
- **3.3** Characterization of spent wash was performed at IEEM Mehran UET, Jamshoro.

Figure 1: Three Prepared Anaerobic Digesters

Figure 2: Batch under Anaerobic treatment in water bath

Samples Collection

Following samples shown in provided figures were collected from their particular resources and carried to MUET Jamshoro for research.

1) Poultry manure and Buffalo dung were collected from poultry farm and cattle farm respectively near Jamshoro.
2) Grey water was gathered from backside of the Afghan Hostel's drain source of MUET Jamshoro.

Figure 3, 4: Poultry manure and Buffalo dung collection

Figure 5, 6: Grey water collection from Afghan Hostel MUET Jamshoro

Figure 7: Spent wash collected from Unicol Distillery Limited Mirpurkhas, Sindh, Pakistan

Samples Preparation

- ✓ Initially substrates were collected from their particular resources and analyzed at Institute Environmental Engineering & Management, MUET Jamshoro.
- ✓ Samples were firstly prepared and stored in small 20ml plastic bottles as shown in figure 8.

Figure 8: Prepared samples of substrates for testing.

Batch Formulation for Treatment

Slurry was firstly prepared by blending the poultry manure and buffalo dung. The ratio of slurry was 300 grams of chicken and 100 grams of buffalo as 3:1 respectively as shown in table 4.

1. Digester A = 300 ml slurry, 50 gms wheat straw (powder form) and 150 ml spent wash (50% diluted)
2. Digester B = 300 ml slurry, 50 gms rice husk (powder form) and 150 ml spent wash (50% diluted)
3. Digester C = 300 ml slurry and 300 ml spent wash (50% diluted)

Substrates	Digester A	Digester B	Digester C
Slurry	300 ml	300 ml	300 ml
Spent wash (50% - Dil)	150 ml	150 ml	300 ml
Wheat Straw	50 gm	-	-
Rice Husk	-	50 gm	-
Total Volume	500 ml	500 ml	600 ml

Table 4: Batch formulation for anaerobic treatment

Figure 9, 10: Slurry preparation using blender (Poultry + Buffalo)

Figure 11, 12: Mixing of wheat straw and rice husk as inoculums

Figure 13: Batch containing three anaerobic digesters ready for operation at Mesophilic condition.

4. Results and Discussion

Characterization of Substrates

- ✓ Initial and final characterizations of substrates and digestate samples were tested at IEEM, MUET Jamshoro.
- ✓ Focused parameters in this for testing were pH, TSS and COD.
- ✓ Biogas generation was calculated on daily basis at HRT of 60 days applying mesophilic condition (35±2 ^{0}C).
- ✓ Biogas sample was analyzed through GC to observe the Methane (CH_4) and Carbon Dioxide (CO_2) concentrations.
- ✓ Following table 5 shows the production of biogas in the batch for 60 days.
- ✓ Initial and Final characterization are given in table 5 and 6

Following figure 1 describes the overall generation of biogas in all digesters regularly for 60 days HRT

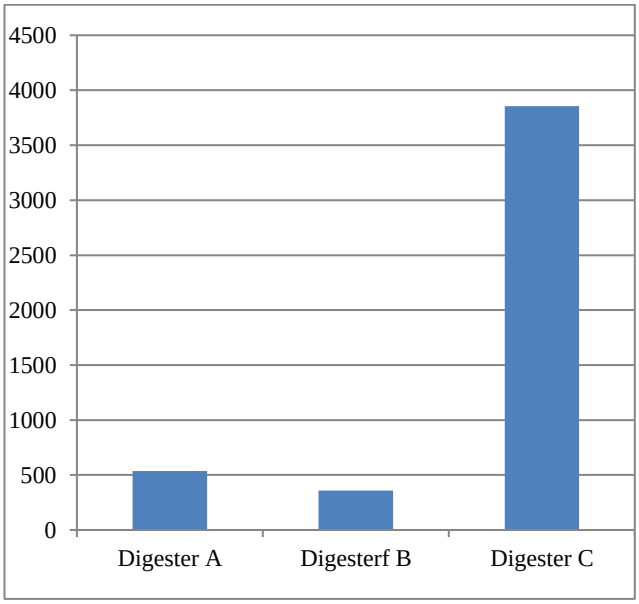

Figure 1: Overall Biogas production in the batch for 60 days

Sr. No.	Sample	pH	M.C (%)	T.S (%)	V.S (%)	TSS (mg/L)	COD (mg/L)
1	Buffalo dung	8.03	85.9	14.1	68	48000	-
2	Poultry manure	9.04	75	25	43.4	6000	-
3	Grey Water	8.25	99.8	0.2	33.33	35	317
5	Spent wash	8.84	93.4	6.6	39.9	10000	32000
6	Slurry	7.61	89.7	10.3	51.25	62500	42500

Table 5: initial characterization of substrates

Parameters	Digester-C
pH	7.95
TSS (mg/L)	9600
M.C (%)	97
T.S (%)	3
V.S (%)	42
COD (mg/ L)	8140

Table 6: Final characterization of Digestate

5. Conclusion

- Research work in this paper was mainly focused on the problem with treated spent wash of a distillery which further needed to be handled well and chemical oxygen demand may be reduced as much as possible.
- COD removal was found to be 80% in this research as compare to 60% removal by Unicol Limited. It was tremendous achievement of research work.
- Biogas generation could not occur in Digesters A and B but C gave sufficient readings day by day.
- GC analysis performed and was observed the concentrations of Methane and Carbon Dioxide as 71% and 13.8% respectively.
- Dilution of grey water in digester C without any addition of solid inoculums was examined and achieved to be the best one in this research work.

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