Methane Production by Anaerobic Digestion of Spent Wash in **Continuous Stirred Tank Reactor**

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ABSTRACT

DSW (Distillery Spent Wash) is superfluous residual liquid waste produced during the process of alcohol production. It is one of the most critical environmental issues which cause pollution. Despite strictness of standards imposed on effluent quality, partially or untreated effluent very often finds access to surface and groundwater. The distillery wastewater becomes a serious risk to the water quality in several regions around the globe. The ever-increasing generation of DSW lead to take an attempt to investigate a few aspects of anaerobic digestion of spent wash collected from a distillery. In the present study CSTR (Continuous Stirred Tank Reactor) was used at laboratory scale. The study was carried out to evaluate the performance of CSTR after the effective startup and the gradual increment in the OLR (Organic Loading Rate). The maximum methane gas (CH₂) of 71.68 ml at the OLR of 1.0g of COD (Chemical Oxygen Demand)/L was observed. The optimum COD removal efficiency of the CSTR was 91% corresponding to OLR of 1g of COD/L. The pH ranges from 7.1-7.3 gave better performance and maximum stability of the process. By increasing the ORL, the VFA (Volatile Fatty Acids) content was also increased and reached to the 1.5g COD/L. However, the removal efficiency of TS (Total Solids) increased at an accelerated rate of OLR.

Key Words: Distillery Spent Wash, Methane Gas, Continuous Stirred Tank Reactor, Matiari Sugar Mill.

1. **INTRODUCTION**

he DSW has been considered as a pollutant liquid generated during the process of alcohol production and is undesirable residual waste which poses threat to the environment [1]. Sugarcane is a main cash crop in Pakistan which results in uplifting the economics of farmers, furthermore the feeding of ever growing sugar industries totally relies on cultivation of sugar cane [2-3]. The DSW is a very viscous and dark

brown liquid, which contains high concentration of COD and BOD (Biochemical Oxygen Demand). DSW contains about 2% melanoidin formed by Maillard reaction between the sugar and amino acid but the high molecular weight melanoidin cannot be degraded easily [4-5]. At present, there are sixteen distillery plants/units in Pakistan which have been producing 506.33 million liters of alcohol by using 1.687 million tons of molasses. Whereas, molasses

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is the byproduct of sugar industries and distillery industries are responsible to treat it in Pakistan [6]. The sugar manufacturing process generates the molasses at an average rate of 4% by weight on the total weight of cane. In Pakistan it is estimated that distillery industry generally operates for 250 days per years with alcohol production efficiency of 240 kg (250 liters) per ton of molasses [7]. DSW contains high concentration of organic compounds in the form of alcohol, which make it dangerous and source of water pollution. It is acidic in nature with high concentrations of BOD, COD and mineral salt contents [8-9]. The CSTRs are the simplest form of sealed reactors with conventional digesters having facility of gas storage. These reactors have revealed a great potential to remove COD from 80-90% at 10-15 days of retention from the distillery effluent [10].

The biogas and digestate are two end products which are found during the anaerobic digestion carried out in the presence of different types of micro-organisms. Combustible gas known as biogas is collectively formed by the combination of various types of gases such as CH₄ (Methane), CO₂ (Carbon Dioxide), and the traces of other gases like CO (Carbon Monoxide), NO, (Nitrogen Oxide), H₂ (Hydrogen) and H₂S (Hydrogen Sulfide) [11]. The anaerobic digestion contains the breakdown of carbon constructed materials in the atmosphere of molecular free oxygen and with the results of creation of CO₂ CH₄, ammonia (NH₃) and carbon based acids, also other trace gases [12]. Methane is a colorless, odorless and flammable gas, generated 50-60% through the anaerobic digestion and gives the energy value of 37.3 MJ/m³ [13]. The generation of methane gas through anaerobic digestion (bio-methane) is a clean for renewable energy source. This process also reduces the environmental pollution such as global warming, acid rain and can be potential substitute of the fossil fuels [14].

The main purpose of this study was to increase the effluent COD of the spent wash by simultaneously producing the methane from it. The present study includes the characterization of spent wash, inoculums for anaerobic digestion into the CSTR and the operation for different OLRs.

2. METHODOLOGY

For the present study spent wash was collected from Matiari Sugar Mills, District Matiari, Sindh, Pakistan. Polyethylene bottles as recommended by Shojaosadati et. al. [15] were used to transport spent wash samples from source to the laboratory. A mixture of substances was taken as inoculums consisting of effluents of a lab scale anaerobic digester and buffalo dung obtained from animal farm located near National Highway, Hyderabad, Sindh, Pakistan. Then, the effluent and buffalo substances in the volume ratio of 90:10 were used. In order to achieve the maximum methane production, the inoculums and different organic loads of spent wash were mixed as: 0.5, 1, 1.5 and 2g of COD/L/d. Then the effluent was analyzed for COD, MC (Moisture Content), TS, pH, TA (Total Alkalinity), and VFA attuned by mixing 6M of sodium hydrogen carbonate and Sodium Hydro oxide (NaOH). The spent wash was characterized for: MC, TS, TA, pH, VFA and COD according to APHA (American Population Health Association) standards. However, the spent wash was charged and discharged in different loads of inoculums on daily basis; their characteristics are shown in Table 1. In this study, the biogas was measured by water volumetric displacement method using the lab scale CSTR apparatus.

WASH	
Parameters	Values
Chemical Oxygen Demand (mg/L)	26727-41224
pH	3.8-4.4
Total Solids (mg/L)	16010-28082
Color	Dark Brown
Temperature	65-750C

TABLE 1. CHARACTERISTICS OF DISTILLERY SPENT

3. **RESULTS AND DISCUSSION**

The different physio-chemical characteristics of distillery effluent of spent wash were examined to accomplish the lower organic load. Clean water (neutral value of pH) was added into the distillery effluent for applicable dilution and 01M of NaOH.

3.1 Reactor startup and Acclimatization Phase

The CSTR was operated in the temperature range of 27-38°C and charged with 1 liter of mixture of water and fresh buffalo dung for a period of 28 days intended for inoculum acclimatization. During whole acclimatization phase this charging and discharging rate was kept on daily basis and production of biogas and pH were also monitored. It was observed that day by day production of biogas increased and also pH increased from 4.2-4.9 up to end of the phase. Pictorial views of modified CSTR and CSTR along with aspirator are given in Figs. 1-2, respectively. The biogas generated form the CSTR was first accumulated in the gas measuring jar, which was working on the similar principle of the Sahito et. al. [16]. The gas measuring jar contains the high concentrated solution of sodium hydroxide, which absorb the CO₂ contained in the biogas, and only methane gas was measured.

3.2 Treatment Phase

This study revealed that the acclimation phase was accomplished in the reported time period of 58 days. Initially the experiments started with an OLR of 0.5 g COD/ L to the treatment phase. Gradually the OLR was increased from 0, 5-2 g COD/L following the experiment method. Over a period of 30 days. The applied loading arrangement of treatment phase is described in to be added unit measure for OLR in Fig. 3. The initial period of reactor was 28 days for its stabilization. However, after that period, the trend of methane production was observed up to 30 days.

3.3 Influence of Moisture Content

During treatment phase, the influence of OLR on MC (Moisture Content) is demonstrated in Fig. 4. The addition of MC in the effluent under stable conditions up to OLR of 2g of COD/L was in the range of about 90-96.42%. During treatment phase no any remarkable changes occurred but very few changes were observed on increasing the OLR.



FIG. 1. MODIFIED CSTR



FIG. 2. CSTR WITH METHANE MEASURING JAR

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3.4 Influence of Total Solids

During the experimental study, it was observed that like other parameters, TS decreased at increased OLR and TS removal remained in the range of 4.94-3.58% up to an OLR of 1g of COD/L. It was noticed that only a few amount of TS was removed from the spent wash used. The influence of TS during variation of OLR is shown in Fig. 5.

3.5 Influence of pH

Regarding pH monitoring during the experimental study, it was observed that pH values variated from 6.9-7.1 at an OLR of 1g of COD/L but pH value remained in the range of 7.2-7.3 at an OLR of 2g of COD/L. Anaerobic digestion in CSTR is negatively affected by mass pH for values less than 6.8 and higher than 8.3 [17]. The influence of pH at pH value on the variation of the OLR is shown in Fig. 6.

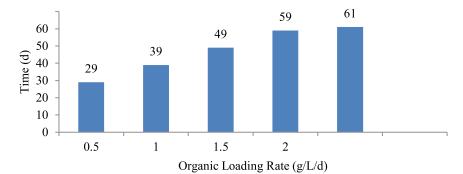


FIG. 3. LOADING PATTERN DURING EFFLUENT TREATMENT USING CST REACTOR

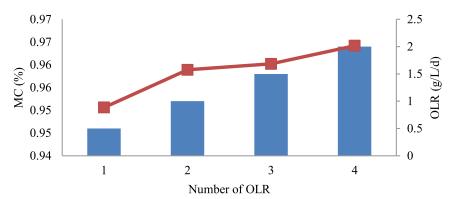
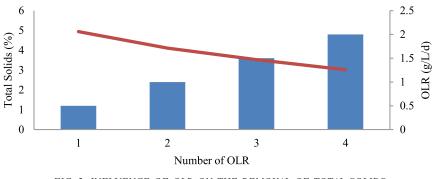
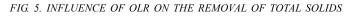


FIG. 4. INFLUENCE OF OLR ON THE MOISTURE CONTENT





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3.6 The Volatile Fatty Acids

During treatment phase, the digestion process stepped up as VFA increased till the maximum value of 36 mg/L at an OLR of 1g of COD/L. Throughout the total treatment phase, VFA values variated in the range of 24-36 mg/L during the stable operational phase at OLR of 0.5-2 g of COD/L. It was also acknowledged that during anaerobic digestion, VFA is considered as an essential parameter [18] and it is also a key parameter for the process stability [19]. The influence of OLR on concentration of VFA is graphically shown in Fig. 7.

3.7 Chemical Oxygen Demand

During treatment phase, the removal of COD was affected by OLR which is shown in Fig. 8. The influent COD was 100000 mg/L, whereas the effluent COD ant the different OLR is shown in Fig. 8. It was observed that 87% COD was removed at an OLR of 0.5 g COD/L. It was also observed that by increasing OLR, COD extraction increases gradually at an OLR of 1.0g COD/L while the removal of COD was observed as 91%. But removal of COD became stable in the range of 89-91% up to OLR of 1.5g COD/L Fig. 8.

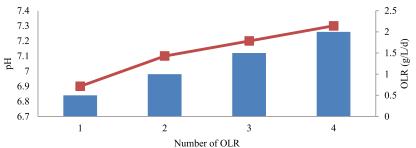


FIG. 6. THE INFLUENCE OF ORGANIC LOADING RATE ON PH VALUES

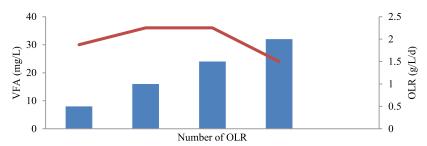


FIG. 7. INFLUENCE OF ORGANIC LOADING RATE ON VOLATILE FATTY ACIDS CONCENTRATION

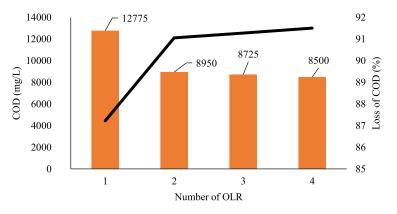


FIG. 8. INFLUENCE OF ORGANIC LOADING RATE ON CHEMICAL OXYGEN DEMAND REMOVAL

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3.8 Methane Generation

The efficiency of methane production was improved at increased rate of an OLR with 1.0g of OLR and achieved 71.68L of COD/L gas production. Afterward, the biogas production decreased for OLR rate up to 2g COD/L, as illustrated in Fig. 9. The gas produced from the loss of the COD was biogas, which comprises of methane and carbon dioxide. In the present study setup only the methane is measured through the gas measuring jar as stated already in the section 3.1. Up to the OLR of 1 g/L/d, the biogas and methane both increases but beyond it the biogas increases but it contains less quantity of the methane. As in the present study only the methane is measure, thus it reflects that the increasing the OLR beyond 1 g/L/d increase the biogas and carbon dioxide but not the methane.

3.9 Efficiency of Methane Production

During treatment phase, the efficiency of methane production at OLR of 0.5 g and 1 g COD/L was observed as 69.6 and 77.6% respectively. However, at OLR of 1.5 and 2 g COD/L, the efficiency of methane production was observed as 6.2 and 57.4% respectively. Graphical representation of methane production is described in Fig. 10.

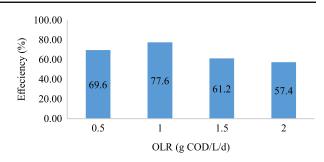


FIG. 10. THE EFFICIENCY OF METHANE PRODUCTION AT DIFFERENT OLR

4. CONCLUSIONS

The results of the study demonstrated that the CSTR has been modified and worked for the treatment of DSW. The different organic loads such as 0.5, 1.0, 1.5 and 2.0g of COD/L/day were applied to the used CSTR, in order to achieve the maximum production of methane. The efficiency of methane production was assessed for different OLR values selected in range of 0.5-2g COD/L but the OLR of 1g COD/L allowed the highest biogas production of 71.68 liters. The COD removal efficiency of the CSTR was found as 91% consistent to optimum OLR of 1g of COD/L and it remained almost constant up to OLR of 2g COD/L.

The treatment of distillery effluent in CSTR was tested in single operations resulting a COD diminution of 80-90% for the time length of 10-15 days. It was observed that the performance of reactor was higher for the mass pH in range of 7.1-7.3. The effect of OLR on VFA

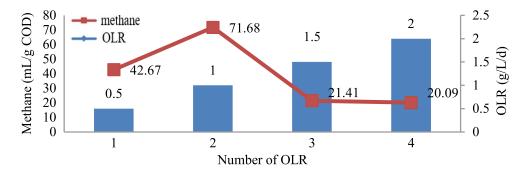


FIG. 9. INFLUENCE OF ORGANIC LOADING RATE ON THE METHANE PRODUCTION

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concentration was increased by increasing loads up to 1.5g COD/liter then reduced for higher OLR. When removal efficiency of TS increased then OLR was also stepped up.

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