Anaerobic Biological Treatment of Distillery Wastewater – Study on Continuous Stirred Tank Reactor

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Abstract. Various studies have verified that anaerobic treatment with the recovery of biogas appears to be the most promising technology for the treatment of distillery wastewater. The technologies currently used by distilleries for treatment of wastewater are bio-methanation followed by two-stage biological treatment and disposal in watercourses or for utilization on land for irrigation and composting with or without bio-methanation. These technologies treat the wastewater up to a certain extent. However, there are limitations posed by these technologies for full compliance with prescribed pollution control standards. For the better understand the performance of continuous stirred tank reactor (CSTR), anaerobic treatment of distillery effluent having very high chemical oxygen demand (COD) (110000–140000 mg/L) and biochemical oxygen demand (BOD) (55000–65000mg/L) was studied on CSTR. Under various organic loading rates (OLR), optimum conditions for maximum COD removal and biogas generation was found and are observed to be 0.09 kg COD/d to 0.12 kg COD/d OLR hydraulic retention time (HRT) of 14d and volatile fatty acids (VFA) to alkalinity ratio of around 0.2. Maximum COD removal efficiency was found to be around 72%. These performance figures are significant when operating the anaerobic bio digesters for the treatment of distillery effluent. Anaerobic CSTR can effectively be employed for the treatment of distillery effluent, but post-bio-methanation effluent still contains high organic concentration and needs to be treated further to meet the safe and acceptable pollution control limits for disposal into surface water or on land.

1. Introduction
The generation of wastewater from distillery is in the order of 12-15 times of the generation of alcohol [1]. The distillery effluent has very high values of biochemical oxygen demand (BOD) (40000-50000 mg per L) and chemical oxygen demand (COD) (100000-125000 mg per L) [2]. The distillery effluent is highly acidic (pH 4.0–4.3) with high suspended solids (2.0–2.5 kg per m³) [3]. This effluent is toxic to surrounding environment [4]. Besides high organic content, distillery wastewater also contains nutrients in the form of nitrogen (1660–4200 mg per L), phosphorus (225–3038 mg per L) and potassium (9600–17475 mg per L) [5].

The distillery industry is one of the heavily polluting industries identified by Ministry of Environment and Forests, Govt. of India [6]. There are around 400 distilleries are operating at present in different parts of the country, average generation of distillery effluent is up to 15L per litre of alcohol produced, depending on continuous or batch process and quality of molasses used, etc [7]. The secondary and tertiary treatments on their own are not technically and economically viable options for mitigating the problems associated with treatment and disposal of high strength distillery effluent.
[8]. Because of the high BOD and COD values, distillery effluent is having great potential to produce energy in the form of biogas. From the available technologies, anaerobic digestion of distillery effluent for energy recovery is reported to be the most effective way [9]. Anaerobic treatment of distillery effluent with biogas recovery is being adopted nowadays in India by many alcohol industries [10]. Various types of anaerobic bio digesters have been tried at both pilot scales as well as in full scale operations [11]. For distillery effluent in particular, anaerobic digestion is suitable [12]. The main focus of the present study was to assess the influence of organic loading rates on the performance of CSTR with respect to process parameters and biogas production in order to investigate the feasibility of Continuous Stirred Reactor (CSTR) for anaerobic bio digestion of distillery wastewater. Various factors affect the performance of CSTR digestion process. Parameters of importance relating activity of microorganisms, substrate utilization, and biogas formation on which operations of the reactor is based include Alkalinity, VFA, COD exertion, and TSS [13].

2. Material and Method

2.1 Substrate:
For the present study, effluent and seed culture were collected from the Lokmangal Sugar and distillery Industry located at Solapur, Maharashtra, India. Table 1 shows the characteristics of distillery effluent.

Table 1. Key Properties of Distillery Effluent

| Parameters                  | Values of Raw spent wash |
|-----------------------------|--------------------------|
| pH                          | 3.0–4.5                  |
| BOD5                        | 55000–65000 mg/L         |
| COD                         | 110000–140000 mg/L       |
| Total Solids (TS)           | 90000–140000 mg/L        |
| Total Volatile Solids (TVS) | 80000–100000 mg/L        |
| Total Suspended Solids (TSS)| 11000–14000 mg/L         |
| Total Dissolved Solids (TDS)| 80000–130000 mg/L        |
| Chlorides                   | 7000–8000 mg/L           |
| Phosphate                   | 2300–3000 mg/L           |
| Total Nitrogen              | 6000–8000 mg/L           |

2.2 Startup of CSTR:
In the present investigation, the plastic tank of 20 litres capacity was used as a reactor with 12 litres for liquid volume and 8 litres for gas volume, as shown in Figure 1. The reactor has provision for inlet, outlet, and overflow of effluent. The outlet of biogas was connected to the kerosene lamp, which was partially filled with water and used as a flare stack to burn the biogas produced. Mechanical stirrer with motor was mounted at the top of the bottle. The entire setup was checked for liquid as well as gas leakage, if any. Activated seed culture from full-scale digester was used as a seed material and fed into the reactor with dilution factor 3 to initiate the process. The key characteristics of activated seed were as shown in Table 2.
Continuous feeding of wastewater to the reactor was started at a very low rate of 0.01 kg COD per day with continuous stirring of reactor liquid. The steady-state condition refers to very little variation in COD of overflow effluent, Alkalinity, or VFA of digester sample [14]. Constant VFA to alkalinity also considered as the steady-state condition. It can also be examined by stable gas production [15]. The pH was tried maintained within the optimum range of 6.5 to 7.5 to enhance the growth and activity of anaerobic bacteria throughout the study. The performance of CSTR for different organic loading rates (OLRs) was assessed in terms of COD removal efficiency and corresponding biogas generation.

3. Results and Discussions
Characteristics of raw spent wash (RSW), Reactor effluent, and overflow effluent were analyzed as per the standard methods for the examination of water and wastewater [16]. The effluent was highly acidic, with a high concentration of TDS and TSS. The COD and BOD values were observed to be 126000 mg/L and 57000 mg/L, respectively, resulting in COD to BOD ratio 2.2, which indicated the effluent is highly suitable for biological digestion.

3.1 Organic and Hydraulic loading rates:
The anaerobic digestion of distillery spent wash was carried out with different organic loading rates from 0.01 kg COD per day to 0.16 kg COD per day with an increment of 0.01 kg COD. As the COD of influent wastewater was not content, hydraulic loading rate (HLR) (L/d) was varying as per the
required organic loading rate (OLR) (kg/d). The hydraulic loading rate and corresponding hydraulic retention time (HRT) (Days) for CSTR model were shown in Table 3.

**Table 3. Influent COD and OLR details**

| Influent COD (kg/L) | Hydraulic Loading Rate (L/d) | Organic Loading Rate COD (kg/d) | Hydraulic Retention Time (d) |
|---------------------|-----------------------------|--------------------------------|-----------------------------|
| 0.122               | 0.08                        | 0.01                           | 146.4                       |
| 0.122               | 0.16                        | 0.02                           | 73.2                        |
| 0.122               | 0.25                        | 0.03                           | 48.8                        |
| 0.122               | 0.33                        | 0.04                           | 36.6                        |
| 0.130               | 0.38                        | 0.05                           | 31.2                        |
| 0.130               | 0.46                        | 0.06                           | 26.0                        |
| 0.130               | 0.54                        | 0.07                           | 22.3                        |
| 0.130               | 0.62                        | 0.08                           | 19.5                        |
| 0.130               | 0.69                        | 0.09                           | 17.3                        |
| 0.128               | 0.78                        | 0.1                            | 15.4                        |
| 0.128               | 0.86                        | 0.11                           | 14.0                        |
| 0.128               | 0.94                        | 0.12                           | 12.8                        |
| 0.128               | 1.02                        | 0.13                           | 11.8                        |
| 0.119               | 1.18                        | 0.14                           | 10.2                        |
| 0.119               | 1.26                        | 0.15                           | 9.5                         |
| 0.119               | 1.34                        | 0.16                           | 8.9                         |

3.2 *Effect of OLRs on CSTR parameters:*

From the commencement of the process, the temperature of the reactor was observed as the stability and efficiency of the anaerobic treatment process is greatly influenced by temperature [17]. Temperature is one of the essential parameters in anaerobic digestion and, in most cases, correlates the biogas formation [18]. Reaction rate, biological reactions and activities are some of the areas known to be affected by temperature [19]. Hence, paying attention to the reactor temperature is important, since minor temperature changes can considerably influence the CSTR performance and the biogas yield [20].

![Figure 2. Effect of HRT on MLSS and Temperature.](image)

![Figure 3. Effect of OLR on Biogas formation and COD removal efficiency.](image)
The growth and decay rates are different at different temperatures; hence, mixed liquor suspended solids (MLSS) concentration was correlated to temperature variations (Figure 2). The steady growth of MLSS was observed for constant reactor temperatures, whereas higher growth in MLSS was recorded for the rise in CSTR temperature. Maximum COD removal efficiency (72%) was recorded at temperature $37 \pm 1^\circ C$ when MLSS was around 36000-44000 mg/L. This efficiency is slightly at lower side as comprised of membrane anaerobic bioreactor which results 76% COD removal efficiency at $37^\circ C$ [17]. Figure 2 summarizes the variation of MLSS and Temperature at steady-state conditions. Reactor temperature increased up to $37^\circ C$. Further, a decrease in HRT (up to 8 days), results in high COD in overflow effluent, this could be the combine effect of high substrate availability and low net biomass growth rate.

The optimum organic loading for maximum COD removal from the distillery effluent has been examined and shown in Figure 3. It was observed that COD removal reached a maximum of 72.66% when OLR is 0.11 kg COD per day, with 9.166 kg COD/m$^3$/d. Perez-Garcia et al. (2005) have reported hydraulic shock loading conditions would result with rapid drop in COD reduction activity in case of UASBR with fixed film [21]. In our study, the comparable performance was observed. CSTR performance was on the slightly lower side in terms of the percent removal of COD with respect to a similar range of OLRs. This may be because of a better reaction rate shown by fixed film reactors than the continuous stirring of matter. At higher ORRs more than 0.11 kg COD/d, it was observed and predicted that there is a gradual drop in COD reduction, unlike the fixed-film reactors, which shows a sharp drop in COD removal efficiency. Biogas production is the prime advantage in the anaerobic treatment of highly organic distillery wastewater. An increasing volume of biogas was observed during the treatment process, which indicated the presence of a growing number of methanogenic bacteria. Characterization of seed present in the digester at different stages of bio digestion is required to be done in order to understand the performance of CSTR towards biogas generation better. Generally, biogas production is due to the degradation of organic matter present in the activated sludge in digester and volume of biogas can be calculated as:

$$\text{Volume of biogas} = \alpha \times Q \times (S_{\text{in}} - S_{\text{out}})$$

Where $Q$, the feed-flow rate in m$^3$/d, $S_{\text{in}}$ and $S_{\text{out}}$ are the influent and effluent substrate concentration (kg/m$^3$), and $\alpha$ is the conversion coefficient of the substrate in biogas. For biogas produced by the degradation of COD as a substrate a conversion coefficient $\alpha = 0.45$ applies [22]. In our study, from the recorded biogas quantities from full-scale CSTR, the conversion coefficient was calculated, and it was found to be 0.405, and the same is used to calculate the biogas generation to get relevant results. It was observed that optimum biogas produced was in the range of 29L to 32L with maximum COD exertion of 72% to 73%. The anaerobic process is very sensitive to temperature as mentioned earlier; it was observed that temperature increases from $32^\circ C$ to $37^\circ C$ from the commencement of process study in order to produce maximum COD exertion of 72% for HRT of 14 days.

![Figure 4. Effect of OLR on HRT and COD removal efficiency.](image1)

![Figure 5. Effect of OLR on VFA and Alkalinity.](image2)
As indicated in Table 3, influent COD values are not constant, and variation in COD values of distillery effluent maybe because of the variation in the fermentation and distillation processes in the distillery. During the present study, COD variations observed between 119000 mg/l to 130000 mg/l. Figure 4 shows variation in HRT with OLRs and the corresponding removal of COD. It was observed that the maximum efficiency of COD removal (72.6%) occurred when OLR increased from 0.10 kg/d to 0.11 kg/d with the decrease in HRT from 15 d to 14 d. These observations are similar to the study conducted by T. Benabdallah El-Hadj et al. (2007) and were in accordance with the fundamentals of anaerobic mesophilic treatment. Further, it is observed that a decrease in HRT from 14 d to 8 d by increasing OLRs from 0.11 kg/d to 0.16 kg/d, COD removal efficiency decreased from 72.6% to 68%. Effluent shows higher value VFA, and VFA to alkalinity ratio at this stage was recorded as 0.34. For various organic loads, Volatile Fatty Acids and Alkalinity of CSTR samples were observed, and variations in the values are shown in Figure 5. The variation in pH of the reactor is very less during the study and it was well maintained in the favorable range. This indicates that the efficiency of the reactor decreased due to sulfide inhibition rather than VFA inhibition. Similar findings were reported by Gupta S.K. et al (2007) with the anaerobic hybrid reactor. This indicates biogas production is strongly correlated with the OLR [23]. VFA has been recognized as one of the important intermediates during anaerobic digestion and is considered a central parameter for anaerobic treatment. The impact of VFA accumulation was reflected in the decrease in COD removal.

![Figure 6. Effect of OLR on pH and VFA/Alkalinity ratio.](image)

Reactor operations were carried out by observing the pH between 6.5 and 7.5. During the operations, variation in VFA to alkalinity ratio was observed to be from 0.021 to 0.344 at all OLRs. VFA has been identified as one of the vital characteristics during anaerobic digestion and is considered a central parameter for anaerobic treatment [24]. The study shows that methano-genesis appears to be an alkalinizing process, as it consumes hydrogen and H3O+ ions [25]. Figure 6 shows the variation of pH and VFA to alkalinity ratio for all ranges of OLRs. It is extremely difficult to maintain the pH of the reactor constant as the reaction rate is variable in this phase. VFA production was found to increase with an increase in organic loading due to the high metabolic activity of acid-forming bacteria, and the Alkalinity of the digester is considerably affected by the organic loading rate. The decrease in alkalinity with the increase in OLR can be attributed to an increase in VFA concentration in the reactor effluent. Further, better results could be achieved by increasing the buffering capacity of the reactor.

4. Conclusions
CSTR can effectively be adopted for the treatment of distillery wastewater. The maximum COD removal efficiency of the CSTR was observed to be 72 to 73% when operated in the favorable pH and temperature ranges. Optimum conditions for COD removal and biogas generation were found to be for OLR 0.10 kg/d to 0.11 kg/d, 15d to 14d HRT, and for VFA to Alkalinity ration around 0.12. Optimum
biogas generation with a conversion coefficient of 0.405 was observed to be around 30 L/d for steady-state conditions. Post-methanation effluent still contains high COD and needs to be treated further. The performance towards COD reduction and Biogas formation can further be enhanced by increasing the buffering capacity of the reactor. Characterization of seed and or response of seed to micronutrients can also be required to focus in order to enhance the performance of CSTR.

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