Treatment of distillery wastewater in UASBR and its post treatment by MFC

SYNOPSIS

Managing the wastewater coming out from the heavy industrialization is the crucial problem facing by the world. It has become very costly and difficult. In India 17 Industries are rated as most pollution producing industries. Alcohol distillery industry is one of that. About 90% of the molasses produced in cane sugar manufacture is consumed in ethanol production (Billore et al., 2001). 13 billion liters/ annum alcohol is produced from cane molasses in the world. In India more than 319 distilleries are present; whose installed capacity is 3.25 billion liters of alcohol. These industries are generating 40.4 billion liters of distillery spentwash annually (Mohana et al., 2009; Chandra et al., 2014).

The effluent generated from distillery is called spent wash. The spent wash generated having volume of 12-15 times more than the volume of alcohol produced. Spentwash is considered as a high strength wastewater having high COD and BOD with low pH and dark brown color (Goel and Chandra, 2003). This dark brown coloured effluent, when discharged into water bodies without proper treatment, defiles the natural ecosystem (FitzGibbon et al., 1998).

There are 76 distilleries in Maharashtra, India. A large number of setups are by Co-operative Sugar Mills, which are producing more than 920 million liters of alcohol. Due to such a high production of alcohol, spentwash generated is more than 10000 million liters/ year (Jog, 2010). In general, anaerobic digestion is given to distillery wastewater due to energy recovery in terms of methane. But still, the COD, BOD of anaerobically treated distillery effluents are ranged in between 45,000 to 50,000 mg/L and 8000 to 10,000 mg/L respectively; which are far above the discharge standards in India as per Central Pollution Control Board.

Based on the literature survey, it was found that for high strength wastewaters like distillery, performance of the full scale UASB reactors was evaluated describing overall efficiency in terms of COD, BOD, Solids, etc. with inlet and outlet parameters. There was an utmost requirement of a thorough study of full scale plant dealing with such a high organic load.

Therefore, in this thesis; the performance of a full scale UASB reactor dealing with spentwash was evaluated in terms of (i) overall performance, (ii) sludge and COD profiles at various sludge ports of UASBR, (iii) COD mass balance and (iv) monitoring of different phases of anaerobic digestion in UASBR i.e. hydrolysis, acidogenesis, methanogenesis and biodegradability.

Based on the findings and limitations of full scale UASBR; a benchscale study was performed for finding optimum values for the best performance. The overall benchscale study was focused on (i) performance of UASBR, (ii) stability and efficiency of the reactor (iii) sludge profiling and morphology, (iv) COD mass balance, and (v) reactor performance in terms of hydrolysis, acidification and methanogenesis.

In next phase, Microbial Fuel Cell (MFC) was evaluated as a post treatment unit for UASBR based on the requirements as suggested by various literatures. Its applicability was studied based on COD removal and electricity generation. After that UASBR was operated at thermophilic range for getting maximum efficiency for distillery wastewater and its economic viability was evaluated.

Next two phases present the results of bench scale UASB results operated in thermophelic conditions and the comparison among mesophelic and thermophelic digestion along with energy pattern at full scale wastewater treatment plant.

For the ease of presentation of the subject matter of the flow of thesis has been divided in to following chapters:

1. **Introduction**
2. **Literature Review**
3. **Justification of Problem and Objectives of the Research**
4. **Material and Methodology**
5. **Result and Discussion**
6. **Conclusion**
7. **Scope of Future Work**

References are given at the end. Data generated during the work has been incorporated as appendix.

Chapter -1: **Introduction** describes scenario of the distillery wastewater regarding world and India.

Chapter-2: **Literature review** deals with the manufacturing process and sources of wastewater in distillery industry along with different treatment methods which are adopted now a day for the treatment of distillery wastewater.

Chapter-3: **Justification of problem and objectives of the research** the problem justification and the objectives of the research work are clearly defined in this chapter.

Chapter-4: **Material and methodology;** for the convenience and understanding, the overall study was conducted in four concurrent/sequential phases as given below:

Phase 1: Study of full scale UASB based distillery wastewater treatment plant: In order to investigate the performance of full scale UASB (450 m^3 per day capacity) based wastewater treatment plant for distillery (Latitude: 19.75148, Longitude: 75.713888) was selected for the study. Weekly sampling was performed for the period of 15 weeks duration. Samples of raw spentwash, before buffer tank, UASB influent and UASB effluent were collected. For sludge analysis; sludge samples were collected from sludge ports of UASB reactor.

Phase 2: Study of bench-scale up-flow anaerobic sludge blanket reactor (UASBR) (mesophilic condition): Bench scale UASB reactor was fabricated with a capacity of 5 liters for this study. Water jacket was having inlet and outlet at the bottom and top of the reactor respectively to circulate the hot water for maintaining the temperature of 37°C inside the reactor. Six sampling ports were installed along the height of the reactor to collect the sludge samples for analysis. Biogas was collected from the head space on the top of the reactor and passed to biogas collection assembly, having capacity to collect biogas 47.32 liter. The biogas was measured by the liquid displacement method. Distillery spentwash was continuously fed to the reactor from the inlet provided at the bottom of the reactor with the help of peristaltic pump to maintain uniform flow. The UASBR effluent was collected in the effluent tank.

Hot spent wash without dilution was collected from the outlet of a distillery industry, Ahemadnagar, India in polyethylene carboys, cooled by sprinkling cool water over the carboys and transported to the laboratory safely. Sludge from the same UASBR of distillery wastewater treatment plant was used as inoculum.

The UASB reactor was operated in continuous mode for more than 600 days. 2 days HRT was maintained throughout the study period. Initial four days the OLR was maintained to 1.76 kg COD/m^{3}day. OLR was increased gradually to 8 kg COD/m^{3}day in initial 75 days. From day 75 to 141 average OLR maintained was 8.07 kg COD/ m^{3}day. From 142 to 230 days it was 10.18 kg COD/m^{3}day and from 231 to 322 days it was 12.75 kg COD/m^{3}day. Similarly from day 323 to 453; OLR was changed to 15.34 kg COD/m^{3}day and finally up to days 581, 591, 616 and 634 OLR was increased to 17.83, 18.95, 22.94 and 25.88 kg COD/m^{3}day respectively. OLR was increased in a stepwise manner after getting stable performance of the reactor. Analyses of the samples were performed as per the Standard Methods of APHA. COD and BOD were analyzed as total, soluble and in particulate phases. Performance monitoring parameters like DO, ORP, solids, conductivity, temperature, pH, VFA, alkanity and chlorides were measured as per Standard methods. Percentage of hydrolysis (H), acidification (A), methanogenesis (M), and biodegradability in the UASBR were calculated for inside performance of UASBR.

Phase 3: Study of microbial fuel cell (MFC) as the post treatment unit for UASB effluent:

A dual chambered microbial fuel cell (MFC) was fabricated in the laboratory based on the concept given by Logan (2005). The dimensions of each chamber were 11 cm x 7.5 cm x 7.5 cm with a volume of 1000 mL. The anode compartment was air tight with the help of plastic cover and pasted with the help of silicone gel to maintain anaerobic conditions. The cathode chamber was kept open to atmosphere. Oxygen was continuously sparged from bottom of the compartment with the help of air pump. Pure carbon electrodes were used in both the chambers. Each carbon rod had a diameter of 15 mm and 15 cm length. The surface area of each electrode in anode and cathode chamber was 74.22 cm^2. Effective area of each electrode was 50.60 cm^2. Electrodes were placed equidistance from the membrane. The terminal of each electrode were connected with copper conceal wires. Both the compartments were connected with Proton Exchange Membrane. The anode and cathode electrodes were connected by copper wires with variable resistance. The MFC anode unit was inoculated with 500 ml anaerobic sludge collected from the same treatment plant as stated above. The MFC efficiency was evaluated in terms of COD and power generation.

Phase 4: Study of bench-scale up-flow anaerobic sludge blanket reactor (UASBR) performance at thermophilic conditions: For comparision of UASB reactor performance in mesophilic and thermophilic temperature conditions; phase 4 was proposed. 55ºC temperature of the reactor was maintained for thermophilic condition with the help of water jacket provided in the reactor. Other parameters and analysis were the same as per the phase 2.

Phase 5: Energy pattern of mesophelic and thermophelic temperature condition: Energy pattern was evaluated at the full scale plant discussed in Phase 1 and accordingly energy recovery was evaluated in terms of biogas. It was also compared with the energy recovery based on thermophelic conditions.

Chapter-5: **Results and Discussion** pertaining to different experiments performed in different phases have been organized in this chapter.

The full scale UASB based distillery wastewater treatment plant gave the overall COD removal of 60 – 87 %. The maximum removal occurred only in UASB reactor was 64% with an average value of 32% during this period. The percentage hydrolysis, acidification and methanogenesis in the UASB reactor were 60.48%, 49.55% and 33.82% respectively. COD mass balance analysis for the distribution of the influent COD through a UASB reactor was 57.62 % in effluent, 32.42 % gas recovery, 0.20% gas dissolved in the effluent, 4.47% in sludge, 5.16% in sulfate reduction and the incoming COD which could not be accounted was -8.78%. The removal efficiency of UASB reactor was found dependent on the active sludge concentration in the reactor. Removal efficiency in reactor was found increased with the increase in sludge concentration. Due to sludge washout, efficiency was found decreased. Therefore, UASB sludge needs to be monitored effectively.

Bench-scale UASBR was evaluated under mesophilic condition under various OLRs. The distillery spent wash characteristics showed high organic content and acidic nature. The COD_t removal was about 68.47 % at OLR of 12.75 kg COD/ m^3 day. COD_p removal was more than COD_s for maximum period of operation. BOD removal was found increasing on increasing OLR.

Percentage BOD removal was ranging from 35% to 89%. The optimum OLR range for UASB reactor could be 12.75 to 15.34 kg COD/ m^3day, in that 15.34 kg COD/ m^3 day OLR was considered as optimum because of maximum BOD removal (89%). UASB reactor performance got deteriorated after exceeding the OLR from 15.34 kg COD/ m^3 day. The average biogas produced was 0.38 m^3/ kg COD removed. The reactor process calculations showed acidification and the methanogenesis were the dominating processes in the UASB reactor. The sludge profile shows high concentrations of TSS and VSS in the bottom three ports, which was obvious based on the availability of sludge blanket in the lower portion of the reactor. FEG-SEM of sludge granules showed cavities for the escape of biogas as well as various colonies of cocci and rods, filamentous bacterium of Methanosaeta. ICP-AES showed that Ca and Fe play important role in the microbial aggregation. FTIR analysis showed alcohols O-H bond, infrared spectrum of ethanol, and CH_3CH_2OH. COD mass balance calculations showed utilization of influent COD as: COD converted in to methane (gas phase) > COD as effluent > COD converted in to sludge > COD converted in sulfate reduction > COD as CH_4 in the effluent (aqueous phase). The percentage of incoming COD converted in to CH_4 was 51.32% (gas phase) and 0.24% (aqueous phase).

Post treatment of Up-flow anaerobic sludge blanket reactor effluents by a duel chambered Microbial fuel cell (MFC) showed the maximum COD removal (73.79%) and open circuit voltage (1.1 V) at 20,600 mg/L of COD. At maximum COD concentration, MFC showed maximum power density, substrate degradation rate and power yield as 61.61mW/m^2, 1.086 kgCOD/m^3day and 0.041 W/kgCOD$_R$ respectively. UASB-MFC combinedly gave maximum COD removal of 90%. The experimental data revealed the potential of MFC as a post treatment unit feasible, economical (cost saving) and sustainable option.

UASB reactor was operated in thermophilic condition and compared with mesophilic condition. In thermophilic condition maximum COD and BOD removals were 75.31% and 92.66% respectively at average OLR of 15.58 kg COD/m^3day. Average biogas produced was 20.33 lit/ day which was 14.34% higher than the mesophilic condition at the same OLR. In thermophilic condition, methanogenesis was found higher and acidification was lesser compare to mesophilic condition. Biodegradability was also found more compared to mesophilic condition. The VFA/ Alkalinity ratio was found more stable in thermophilic condition.

Total energy consumed by the WWTP was 2.10 kWh/m^3 including mechanical, electrical and manual energy in mesophilic temperature condition in which electrical energy input was 2.07 kWh/m^3 and energy recovery in the form of biogas was 185 kWh/m^3. In the thermophilic condition, energy recovery in the form of biogas was 211 kWh/m^3.

The **conclusions** derived from the present study from the subject matter of Chapter-6.

Chapter -7: presents **Limitations and Scope of future work**.