Treatment technologies for distillery waste water a review

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Abstract: Distillery wastewater is big challenge to discharge in any water receiving body due to its high organic content hence its appropriate treatment is required. Present study is based on to provide critical and concise review of different technologies that are well applicable to treat distillery wastewater. Biological and physiochemical are most popular methods to treat this wastewater. Here adequate information is providing about aerobic and anaerobic method. In addition, detailed information of coagulation process is also provided.

Keywords: Distillery wastewater, Organics, Biological method, Coagulation, Waste Minimization

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INTRODUCTION

Alcohol is an important product to manufacture several types of chemicals and medicine. Recently government of India allowed 10% blending of ethanol with gasoline. Moreover, it is an important composition to prepare hand sanitizer that used in pandemic (i.e., Covid-19). Hence its demand increases day by day. Sugar cane molasses is major raw material for the ethanol production and around 60% alcohol is manufactured by this feedstock (Mikucka and Zielińska, 2020). Due to demand of ethanol increases rapidly, other raw material such as corn, rice, wheat, grapes etc. are also can be used for their manufacture. As India is big producer of and available throughout the year, it may be a good supplement of molasses. Additionally, lower grade rice grain can be also used as raw material for alcohol manufacture.

The production of alcohol is based on the fermentation of feedstock by fermentation broth. Liquor obtained after fermentation subjected to 10-15% of alcohol which is separated by distillation process. During the process alcohol is received from upper section of distillation column and further amount of liquid is exits from the bottom of distillation column. This liquid is called spent wash (SW) and it contains very high COD (40000-50000 mg/L) and color (1000-1200 PCU). However, the value of COD and color of SW depends on the feedstock used in process. For example, sugar cane molasses-based SW has much more COD (150000-200000 mg/L) and color (10000-15000 PCU) (Pant and Adholeya, 2007). Due to the very high organic content of SW, it is primary remediated in biodigester where near about 65% percent pollution load reduces. The treated water of the biodigester is called biodigester effluent (BDE) that still contains high COD (13000 – 16000 mg/L) and color (400-600 PCU). For production of one litre of ethanol sixteen litre fresh water is required. It means that medium or large-scale industry generated millions of wastewaters per day. If this untreated BDE is discharges in any water receiving body, then it can damage the aquatic system. In addition, BDE is dark brown in color because of presence of melanoidins that avoid frequent penetration of sunlight in water consequently photosynthesis reaction of water system does not work properly and water source being fully contaminated. Moreover, the pollution regulatory agency of India like Central Pollution Control Board (CPCB) published the norms to discharge of effluent into surface waters (COD < 0.1 g/dm^3, BOD < 0.03 g/dm^3) and sewers (COD < 0.3 g/dm^3, BOD < 0.1 kg/m3) (CPCB, 2006). Also, distillery wastewater generates unpleasant odor that spreads several kilometres around the distillery. Therefore, appropriate remediation of BDE is required before discharge in any water receiving body to avoid any environmental issue.

Present investigation aims to investigate and review of different technologies to treat the distillery wastewater.

PROCESS TECHNOLOGY OF DISTILLERY INDUSTRY

As earlier discussed, that in India, around 60% ethanol is produced by sugar cane molasses. But recently rice is also used as feedstock for ethanol production due to its availability throughout the year. Advantage of rice grain is that its crops available in both rainy (Kharif) and rabi season. Also, poor grade rice grain may also used as raw material for ethanol production. Hence it is easily available in open market for the distillers to procure the raw material. The production of ethanol is completed in several stages including preparation of rice grain, fermentation, rectification or distillation and packing. The flow sheet of the manufacturing process of ethanol is shown in Figure 1.

Feed Preparation: Rice is soaked in water and is kept for 48-72 h. Rice contains nearly 75% starch and 15% - 16% sugar (www.dietandfitnesstoday.com). The pH is maintained by addition of diluted acid or a base.

Fermentation: The prepared feed is passes in the fermentation tank where it is injected with *Saccharomyces cerevisiae* (10 % by volume). During the fermentation process sucrose is converted to glucose and fructose. Finally, glucose and fructose are converted into ethanol. The conversion reaction is as follows:

1. Conversion of sucrose to glucose and fructose

$$2C_{12}H_{22}O_{11} + 2\,H_2O \xrightarrow{\textit{Invertase}} 2\,C_6H_{12}O_6 + 2C_6H_{12}O_6 \qquad (1)$$

2. Fermentation of glucose to alcohol.

$$2C_{12}H_{12}O_6 + 2\,H_2O \xrightarrow{\textit{Zymase}} 4C_2H_5OH + 4CO_2 + 47\ k\mathit{cal} \qquad (2)$$

This is an exothermic reaction hence the fermenter is cooled upto 25-32^{o}C to maintain temperature of reaction. Fermentation process completed in 48 to 72 h. 10-15% ethanol is presented in resulting broth (product). Further, yeast is separated by settling and distillation is applied in cell-free broth.

Distillation: About 92^{o}C temperature is used to pre-heated the cell-free fermented broth and thereafter it is passes into the degasifying section of the analyzer column. Trapped gases such as CO_2 removes by the bubble cap distillation column from the liquor. Ultimately that is steam heated and fractionated with a yield of 40% ethanol. The effluent from the distillation column, collected from the bottom is known as spent wash (SW), distillery wastewater

(DWW) and stillage. The ethanol vapors from the analyzer column are finally taken to the rectifying section and 93-98% rectified ethanol is obtained after rectification.

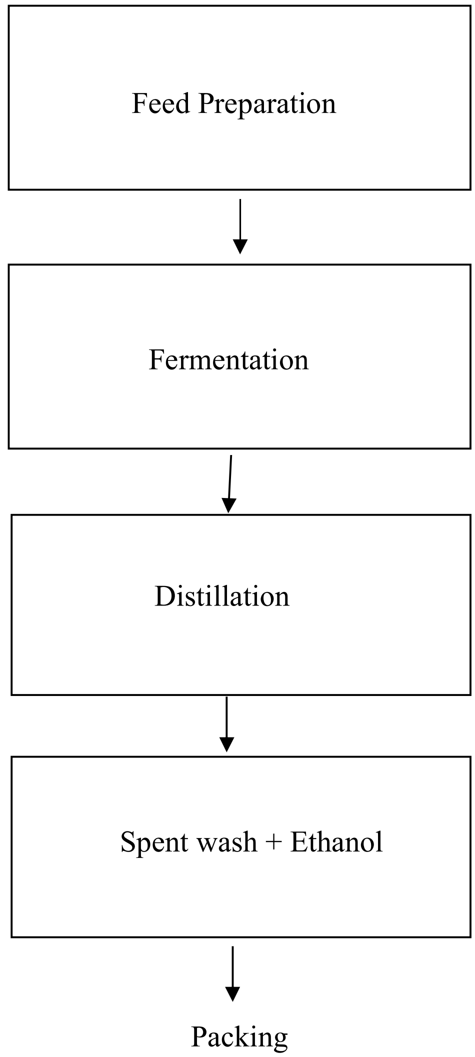

Figure 1. Process diagram for manufacturing of alcohol

Stillage Processing: Various processes are available to treat SW. In China it is sent into multi effect evaporator and is concentrated. This concentrated SW is used as fuel for the boiler to generate steam of high pressure. This steam is used for turbines, to produce electricity for its optimum use in the industry. In India SW is treated in an anaerobic biodigester, where the organic load is reduced and methane gas is produced. About 60-70 % COD and 70-80 % BOD is reduced in this process. The effluent from the biodigester is called biodigester effluent (BDE). The BDE is further treated by aerobic process. The methane gas is used as a fuel in a boiler to produce high pressure steam and further to run turbines for producing electricity.

Packing: Ethanol is directly marketed to manufacturer who used it to produce several useful chemicals including as acetic acid, acetone, oxalic acid, and absolute alcohol. The 99 % ethanol is now used as a motor fuel.

TREATMENT OF DISTILLERY WASTEWATER (DWW)

Several methods are available for the treatment of DWW. The brief description on common physical, chemical and biological pre treatment processes are given below

PHYSICAL, CHEMICAL AND THERMAL METHODS

- SW is concentrated in multi effect evaporators and this concentrated material is burned in the boiler where large amount of steam is generated.
- SW is concentrated and mixed with press mud and used for production of bio-fertilizer
- Physico-chemical remediation by coagulation/flocculation, electrocoagulation, sedimentation, membrane filtration for recycling of spent wash derived water for other application such as steam generation, heat transfer, etc. When water is separated from SW solid mass, the remaining solid mass can be used for different purpose such as composting for crops or incineration for energy recovery.
- SW is treated by electrical energy, later on water and the solid residues are separated. Water is used for industrial application and the solid residues are used for energy production.
- Thermolysis (catalytic/non-catalytic) is used for separation of dissolved solid form. The solid residue remaining are used for composting or drying and incineration for energy recovery
- Wet oxidation (catalytic/non-catalytic) is used for oxidation of the organics present in the effluent. Hydrogen is converted into H_2O and carbon into CO_2.

BIOLOGICAL TREATMENT

(i) Anaerobic treatment

Upflow Anaerobic Sludge Blanket (UASB) and its variants are effectively used in methane recovery. The sludge is separated by sedimentation and biodigester effluent is sent to further treatment from the anaerobic process. BDE is also used to sprinkle over press mud to make bio-fertilizer.

(ii) Aerobic Treatment

Various types of aerobic treatment process are used as below

- Air activated sludge process is an important suspended culture based aerobic process where bacteria generate biomass via consumption of organic content, nitrogen and oxygen that present in wastewater. Due to the mixing action of the air blown into the effluent, the bacteria are suspended in the aeration tank. High purity oxygen based activated sludge process and air activated sludge are almost similar except that pure oxygen injected in first condition while air is inserted in second condition.

- The aerated pond /lagoon is also suspended culture based an aerobic process where air is injected into wastewater using mechanical aerators to cause violent agitation of the wastewater and air in order to achieve oxygen transfer to the wastewater.
- Trickling filter is attached culture based aerobic process. In this process a tank is attached with media that involves a ratio of a high surface to volume. Sample passes from the upper section of the tank and permeates (trickles) down the media. Further, bacteria develop on the media that utilize organics and nitrogen as a food.
- Rotating biological contactor (RBC) is also attached culture based aerobic process where media are situated parallel across a tank of wastewater. Bacteria grow is rotated continues upon the media consequently it comes to the contact of the wastewater and the air.
- Oxidation ditch is very common process to treat wastewater that based on aerobic digestion. It is ring shaped with furnished mechanical aeration devices.

TREATMENT OF BIODIGESTER EFFLUENT (BDE)

The common process to treat BDE is a bio - aeration process. Almost no research work has been reported in the open literature for the treatment of rice grain-based BDE to make it suitable for discharge. A three-step treatment process has been suggested for molasses-based distillery BDE treatment (Dhale and Mahajani, 2000). In the process the BDE was thermally treated followed by flocculation and wet oxidation. The coagulation/flocculation process for the treatment of molasses-based distillery BDE has also been reported (Migo et al., 1993), wherein the considerable amount of organic load (COD) has been reduced. The flocculation/flocculation process has the major disadvantage,the poor settleability of the floc formed in the sedimentation tanks.

Indian distilleries still use traditional aerobic treatment in which the oxidation is done through either surface aerators or submerged high pressure bubblers. The cost of this system is very high and the COD and BOD of the treated effluent is 5000 to 20000 mg/dm^3 and 350-1500 mg/dm^3 respectively, and also it does not meet the effluent discharge quality standards. Therefore, effluent is properly diluted before being discharged either on land for fertiirrigation (fertilizer providing irrigation) or into the sewers and surface water bodies. The large volume of the sludge generated by this system is also clarified, dewatered and digested to use as manure.

AEROBIC TREATMENT/AERATION

Indian distilleries mostly use aeration process to treat BDE. The treatment is carried out in the aerobic lagoon. The effluent**,** activated sludge and nutrients to the microorganism is fed into the lagoon along with an increase amount of air (O_2). The BDE is oxygenated using either surface aerators or submerged high pressure aeration systems. Mostly, two or three-stage aeration system is applied to oxidize the organics. The treated effluent slurry is settled down in sedimentation tanks through the gravity settling process, where the sludge is removed, and a part is recycled to aeration lagoon. The remaining sludge is further treated for disposal. From the clarified effluent, the organic load are not removed completely, and it still contains high COD (5-15 kg/m^3) and BOD (0.5-2 kg/m^3). Therefore, further treatment or dilution with fresh raw water is done for discharge into sewers, land or surface water bodies.

COAGULATION/ FLOCCULATION

Coagulation/Flocculation process is used for the removal of colloidal and suspended particles present in water or wastewater. During the coagulation process small particles get agglomeration and settle down via sedimentation (Stephenson and Duff, 1996). Both industrial and surface water contains significant amount of colloidal and suspended particle causes undesired turbidity occurs in the water. The plain sedimentation is not suitable to remove very small particle from the wastewater. The particle settlement less than 50 μm cannot be expected by plain sedimentation. Coagulation is well effective to remove particle size less than 50 μm (Peavy and Row 1985).

The mechanism of coagulation is based on the agglomeration of particles. It is well known that colloidal particles passes net negative charges. Moreover, there are several type of organics present in the wastewater. All organics have own function group such as protein contains amino function groups that also releases negative ions. There are four type of theories involved in the mechanism of electrocoagulation namely (1) ionic layer compression (2) adsorption theory (3) sweep coagulation and (4) intraparticle bridging.

Metal ions are surrounded to the colloids particle with negative co-ions and compressed that cause it called ionic layer compression. When colloids are sufficiently compressed by metal ions there are two type of force work here one is the attractive/van der waals force and second is repulsive force. When the value of attractive force is greater than the repulsive force colloids are agglomerated and settle down through the gravity. Adsorption theory can be explained as in-situ production of metal ions occurs at the anode. On the other hand colloids passes net negative ions. In addition, effluent contained several types of organics and each organic have own function groups that passes negative ions. These negative ions added with the positive ions consequently effective size of the prticles increases and settle down. The typical reaction is given below when aluminium salt like $AlCl_3$ is

$$Al^{3+} + H_2O \rightarrow H^+ + Al(OH)^{2+} \quad (3)$$

$$Al(OH)^{2+} + H_2O \rightarrow H^+ + Al(OH)_2 \quad (4)$$

$$Al(OH)_2 + H_2O \rightarrow H^+ + Al(OH)_3 \quad (5)$$

In the above reaction metal hydroxide ($Al(OH)_3$) formed that may be amorphous in nature. Colloids and suspended are entrapped with metal hydroxide in sticky manner and settle down. The removal of suspension by this way is called sweep coagulation. In some cases, synthetic polymers are used as coagulant instead of metal ions. These polymers may be liner or branched in structure and offers very high surface reactive. Thus, several colloids may become attached to one polymer and several of the polymer colloid groups may be become enmeshed resulting in settable mass. This mechanism is known as intraparticle bridging.

Number of coagulants are used for the treatment of industrial/municipal wastewater. Inorganic coagulants are classified in three categories namely aluminum derivatives (such as Alum, $AlCl_3$), iron derivatives (such as $FeCl_3$, $FeSO_4$) and lime. Coagulants are acid salt hence initial pH of solution play very important role in coagulation process. During the coagulation process amount of metal ions releases by the coagulant that added with the negative ions passes by the colloids. The amount of pollutants removal depends on balance between the H+ ions that depends on pH, amount of metals ions releases by the coagulant and net negative ions passes by the colloids that present in the water/wastewater.

CONCLUSION

Number of treatment technologies available for the treatment of distillery wastewater including physical, chemical, physicochemical, biological and membrane technologies. But now a days biological and physicochemical methods are mostly used in practice due to their high efficiency and affordable budget. Present study showed that the aerobic and anaerobic both methods are well applicable to treat distillery wastewater even that have high organic content. Coagulation plays very important role to reduce the organics and color from the wastewater.

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