Solar Detoxification of Distillery Waste

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Introduction

Pollution occurs through different mediums, however water and air are the two major resources, which get polluted in one way or other. Most of the water from natural sources gets polluted due to wastewater (WW) emerging from chemical industries. Distillery industry is one of the major chemical industries in India. Today there are about 295 distilleries in India with an installed capacity of 3198 million liters (L) of alcohol production per annum. About 15 L of WW is produced per L of alcohol production. This means that for a 30,000 liters/day (LPD) distillery about 4.5 lakh liters of WW is produced daily. Some distilleries even produce about 6-7 lakh L of WW daily and dump it into the water bodies. This distillery WW has very high biological and chemical oxygen demand (COD), dark brown color, high solid content and bad odor. Typical characteristics of the anaerobically digested WW are noted in table 1.1 below :

Table 1.1: Typical Characteristics of Anaerobically Digested Wastewater

Parameter	Value
Chemical Oxygen Demand (mg/L)	30000 – 40000
Transmittance (%)	0
pH	8.31 – 8.35
Total Solids (mg/L)	46000 – 61000
Total Dissolved Solids (mg/L)	44000 – 59000
Biological Oxygen Demand (mg/L)	3620 - 4780

Such a highly polluted WW, when dumped in water bodies, adversely affects the ecosystem. Hence there is a need to treat this WW so that its COD loading can be reduced down to a certain minimum level i.e. 250 mg/L, set by Indian pollution control board. Research is going on at various places in the world to solve this problem, but yet no effective solution has been found out. Photocatalysis can prove to be a solution to this problem. Photocatalysis uses the photon energy from solar radiation to activate the semiconductor oxide i.e. photocatalyst and results in formation of hydroxyl radicals which remove organic matter in WW and thus reduces the COD load. TiO_2 is the catalyst that has been mostly used for this purpose up till now.

The research work on the project, titled “Solar Catalyzed Chemo-Oxidation of Distillery Wastewater” has been going on at the Nimbkar Agricultural Research Institute (NARI), Phaltan since 2001.

Objectives of this project were

(i) To set up a continuous reactor for treatment of 100 liters per day of anaerobically digested distillery effluent for removal of color and odor and reduction in COD.

(ii) The aim of the oxidation reaction to be focussed:
(a) To minimize requirement of water for treatment;
(b) To minimize detention period for treatment preferably to few hours;
(c) To use the treated distillery wastewater at any stage of treatment.

(iii) To evaluate different reactor designs and materials of construction for the plant.

(iv) To develop a strategy for recycling the catalyst used for detoxification.

(v) To test the treated effluent on various crops and assess its usefulness for irrigation purpose.

(vi) To do a detailed techno-economic evaluation of scaling up this technology.

Pilot Plant Process Description :

Based on the laboratory and bench scale experiments carried out earlier, a pilot plant with a capacity of treating 200 L/day of five times diluted anaerobically digested distillery wastewater (DADW) was set up and various experimental runs were carried out on it. Fig. 1 shows the schematic of the plant and Fig. 2 is the photograph.

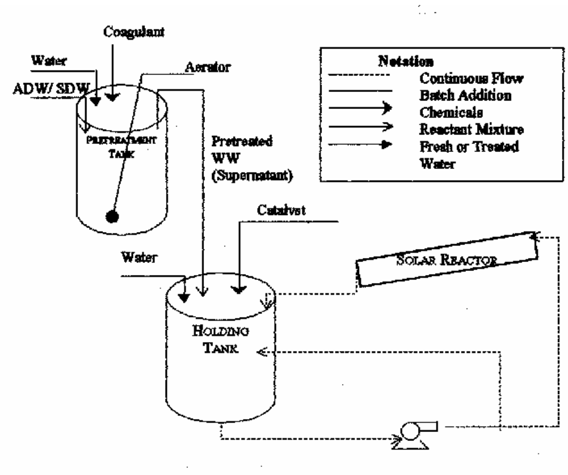

Fig1. Schematic of the pilot plant

Fig 2. Pilot plant

The treatment process consisted of two steps. First the anaerobically digested wastewater (ADW) was diluted five times with tap water and pretreated using selected coagulants and aeration and then allowed to settle. In the second step the supernatant of this pretreated effluent was solar detoxified in the presence of a suitable catalyst. After solar detoxification (SD), the effluent – catalyst mixture was settled and clear supernatant was separated, which is nothing but treated effluent. The catalyst separated as above was sun dried and reformed in a muffle furnace at high temperature (650-800 ^{0}C), and was thus ready to be recycled again. This treatment reduced COD load by 95-98% and increased the transmittance by about 90%.

Experimental Work and its Results

During this project period, various experiments, in order to achieve the objectives, were carried out on laboratory-scale, bench-scale as well as pilot plant-scale. In brief the experiments are described below :

Laboratory-scale experiments :

The laboratory scale experiments were done so as to help in designing a pilot plant. These experiments were carried out in the laboratory using petri dishes and conical flasks. For this an indoor UV lamp array having a total area of ~ 0.55 m^2 and producing UV radiation of intensity 22-25 w/m^2 on a horizontal surface was set up. The experiments carried out are given below :

Pretreatment experiments

As initial transmittance of ADW was zero, the penetration of solar radiation in it was very poor. To improve the transmittance and thus penetration of solar radiation as well as to reduce the initial COD, the pretreatment experiments were carried out using suitable coagulants.

Using these coagulants experiments were also carried out on pilot plant scale. The pretreatment reduced the initial COD load by about 87% and increased the transmittance by about 3 %.

Use of TiO_2 as a photocatalyst for treatment

The effect of using Titanium dioxide (TiO_2) as a photocatalyst for the process in its rutile, anatase and GR (mixed) forms was studied. It proved to be unsatisfactory when it was used alone. But pretreatment with a coagulant followed by treatment with TiO_2 was found to be better as about 81% COD reduction was achieved. However, it takes a relatively long time of about four days to achieve the satisfactory results. Hence further use of TiO_2 was discontinued and use of our catalyst only was continued.

Bench-scale study

For bench-scale study, a small bench-scale reactor was designed in which 10 liters of DADW could be treated using a circulation pump. For this, a bench-scale reactor consisting of a sheet of galvanized iron of 0.15 m^2 and a holding tank of 10 L capacity was fabricated. The following experiments on post-solar treatment were carried out on bench-scale.

Post-solar treatment experiments

Exposure of ADW mixed with catalyst, to solar radiation, produced treated effluent with lower COD values and higher percent transmittance. However, during initial stages of the project, the time required for the process was about five days. So, in order to reduce the time required, experiments were carried out to re-treat the solar-exposed effluent. For these post-treatments, various suitable chemicals were used. The post-treatment increased the transmittance of two day solar-treated ADW by about 20-30%.

Pilot plant-scale study

A pilot plant-scale reactor having reactor plate area of 6.28 m^2 and a holding tank of 200-L capacity was set up (Fig. 2). The various experimental runs were carried out on pilot plant scale. Some important conclusions from the pilot plant study were:

- Solar detoxification of five times diluted ADW with the pretreatment with suitable catalyst and coagulants, was completed within two days. Here final transmittance of nearly 90% and COD down to 386 mg/L were achieved.
- Treated effluent having transmittance of about 85-90% was successfully utilized for the dilution of ADW instead of water. In this case final transmittance of nearly 87% and COD down to 415 mg/L were achieved.
- The transmittance and COD values of 78% and 540 mg/L respectively were achieved after one day SD, by carrying out SD continuously for 11-12 hours even without compensation for evaporation losses.
- The transmittance and COD values of 88% and 406 mg/L respectively were achieved after one and a half-day SD for about 13 hours i.e. about eight hours on the first day and five hours on the second day without compensation for evaporation losses.
- Even after reducing the concentration of the catalyst used from 1% to 0.75%, the final transmittance and COD values of 70-89% and 669-397 mg/L were achieved, making the use of catalyst more economical.
- Activity of the catalyst was found to be reduced after each reformation. It was found that after reusing the catalyst three times, i.e. after third reformation when the catalyst was used for the fourth time, transmittance up to 54% was achieved. However, further recycling of catalyst for seven times was found to be able to give a transmittance of only up to 35-40%. In each subsequent run, about 8% catalyst was lost.
- This particular SD process was found to have the first order reaction rate constant equal to 0.172 hr^{-1} .

Figure 3 shows the color of the water treated in the plant.

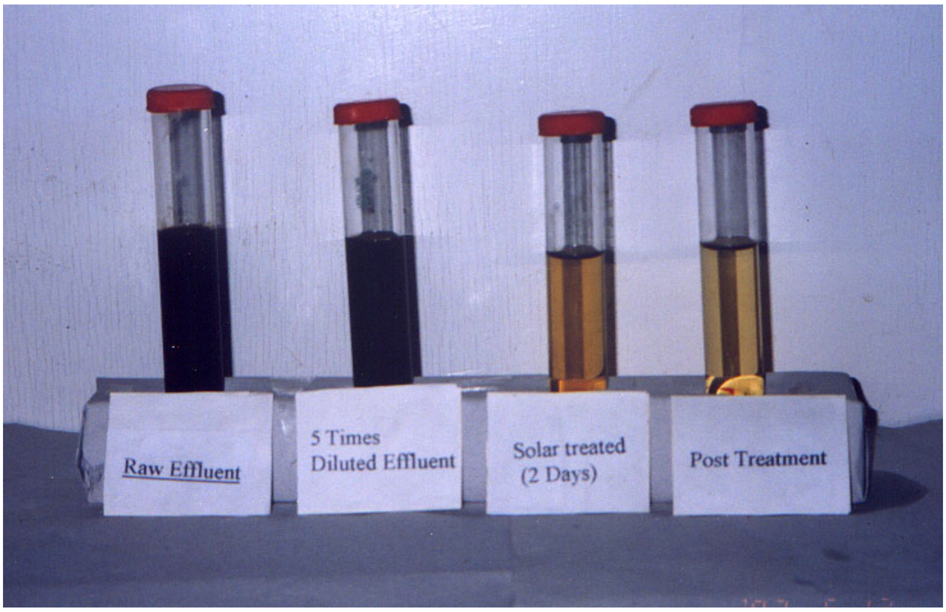

Fig. 3. Color of treated water

Catalyst Reformation

In order to reuse the catalyst for the SD process, it was necessary to reform it properly. Reformation removes the organic compounds that get deposited on the catalyst during SD and also opens the blocked pores on the catalyst surface. So a reformation strategy was developed, wherein catalyst separated from treated effluent after SD was first sun dried. Then it was reformed in the muffle furnace by heating it in the temperature range of 650-800^{o}C for about two and a half to three hours. This reformed catalyst can be reused for the SD process. After each reformation, about 90 - 92% catalyst is recovered. One batch of catalyst can thus be reformed and reused repeatedly for about 6-7 times.

Crop Trials – Application to Agriculture

Preliminary studies on the application of distillery WW to agriculture were conducted by cultivating cotton plants (in pots) using fresh water (FW), anaerobically digested wastewater (ADW), five times diluted anaerobically digested wastewater (DADW) and detoxified, diluted anaerobically digested wastewater (DDADW). Results of this study indicated that crops fed with DADW and DDADW fared better than those fed with FW and ADW, and gave greater plant height, tap root length, number of good bolls and seed cotton yield. The effect of water and DDADW on most soil parameters was comparable. In the case of ADW and DADW, most soil parameters showed an increase in value. The treatment of DDADW slightly increased the salinity of soil from 0.41 to 1.09 mmhos/cm, while treatment of ADW and DADW increased this value up to 6.37 and 1.39 mmhos/cm respectively. The potassium content of the soil increased vastly from initial value of 2000 Kg/ha to 13000 Kg/ha after the treatment of cotton plants with ADW, while treatment with DADW and DDADW increased the same value up to 2767 and 3700 Kg/ha respectively. DADW seemed to be the ideal treatment for replenishing the soil. However, environmental implications and long term effects on soil should be taken into consideration before recommendations are given. DDADW being much less contaminated than ADW and DADW could prove to be more environment-friendly in the long run. Two more pot trials with cotton and one with sugarcane were carried out with slightly modified treatments and were found to give similar results.

Economic Analysis

It was decided to carry out economic analysis for this treatment process at pilot plant and commercial scales. The running cost for the plant was calculated after taking into consideration various process requirements. It was found to be Rs. 0.33 and Rs. 1.67 for 1 L of DADW and ADW respectively.

It should be noted that, this cost is for pilot plant-scale process and is based on cost of chemicals, electricity etc., which was incurred during the project work. On commercial scale this cost will be far lower because commercial costs of different chemicals and other materials are much lower than the costs considered for present analysis. In addition, the large-scale plant will use much more efficient process equipment such as the furnace and separation equipment that will reduce the power and chemical consumption drastically. The losses in this large equipment will also be lower. The economic analysis on commercial scale will require information about various factors such as land requirement, sludge disposal arrangement, sludge handling system, large-scale plant development, depreciation cost, laborers required, commercial costs of chemicals and materials, material handling, land fill area requirement, dumping arrangement, etc. Thus doing a complete economic analysis is a long drawn process.

Therefore, as per the objectives set at the start of the project, the techno-economic analysis of pilot plant- scale process was carried out and simple costing for commercial plant-scale operation (i.e. for a distillery industry producing about 5 lakh L of ADW daily) was done. This included chemical cost, water cost and cost of catalyst reformation. The chemical cost (catalyst and coagulants) was found to be Rs. 0.23 for treatment of 1 L of ADW. Water cost was equal to Rs. 0.0002 per L of ADW, while the cost of catalyst reformation and pumping was Rs. 0.20 for 1 L of ADW. However, for large-scale treatment, the costs of chemicals may vary. Therefore, a sensitivity analysis for cost of treatment of ADW was done considering different costs of chemicals and catalyst.

Conclusions

With the experimental work carried out on laboratory scale, bench scale and finally on pilot plant scale, all the objectives set at the start of the project have been achieved. The achievements and conclusions drawn from this project are listed below :

- An effective treatment process consisting of two step i.e. pretreatment and solar detoxification (SD) for the treatment of anaerobically digested distillery wastewater (ADW) was developed.
- A pilot plant for the treatment of ADW was set up and tested successfully.
- Pretreatment with suitable coagulants alongwith aeration followed by two day SD after the addition of 1% catalyst was found effective for achieving an average COD reduction of about 95-98% and average increase in transmittance (%T) of about 85-90%.
- Post-solar treatment with suitable chemicals can be used to increase the transmittance of solar-treated effluent.
- Use of TiO_2 alone as a catalyst was found to be unsatisfactory for the process. However, along with coagulants, its effect was considerable, but it takes a relatively long time of about four days for satisfactory achievement of the results of SD.
- Effluent detention period for the process was decreased to two days. Also water consumption of the process was reduced considerably.
- Treated effluent (with % T in the range of 80-90) was successfully used for dilution of ADW.
- Strategy for catalyst reformation was developed. About 90% of the catalyst is recovered after the treatment. Catalyst can be reformed and recycled for at least 6-7 times. However, transmittance obtained on an average decreases after each recycle by about 5%.
- Treated effluent could be used for agricultural purpose. However, long term effects should be studied.
- A strong possible reason for deactivation of catalyst is pore blocking by ash content of the organic biomass. At high temperature in the furnace all of the organic mass gets evaporated but the inorganic ash gets deposited on the catalyst surface blocking the pores thereby reducing its effectiveness.
- A method to prevent pore blocking needs to be developed. The overall economics will improve once the catalyst can be re-used for more than eight times because the catalyst cost is a strong contributor to the total treatment cost of DADW.
- It costs Rs.0.33 and Rs. 1.67 for the treatment of 1 L of DADW and 1 L of ADW respectively. This costing is for pilot plant scale. However, simple costing carried out for

large scale revealed that it costs Rs. 0.23/- for chemicals and Rs. 0.20 for catalyst reformation plus pumping cost for the treatment of 1 L of ADW.

Achievements of the Project

Pollution is one of the major problems that the world is suffering from today. Chemical industries are one of the major contributors of water, air as well as soil pollution. Distillery industry, which is one of the major chemical industries, produces a huge amount of wastewater (approximately 4.5 lakh L of wastewater per day per distillery in India) and gives rise to high amount of water pollution. Such a highly polluted wastewater having very high chemical and biological oxygen demand (COD and BOD), dark brown color and obnoxious odor, when discharged into natural water bodies, causes severe water pollution. When such a highly polluted water is consumed by human beings it has adverse effects on health and existence. Water of such quality is dangerous to the whole ecosystem.

To solve this problem, research work is going on at various places in the world. However, no effective and feasible solution has been found yet.

Taking above into consideration, the research work was undertaken at the Nimbkar Agricultural Research Institute to develop effective treatment system for distillery wastewater, and based on it a pilot plant was set up and tested in this project titled, “Solar catalyzed chemo-oxidation of distillery waste”.

Solar energy, which is renewable and available free of cost was used here. Photocatalysis is the basis of this specific treatment system. The process was basically developed for the treatment of anaerobically digested distillery wastewater (ADW). The process system for ADW mainly involved two steps. First step is pretreatment, where, ADW was diluted five times using tap water and then treated with selected coagulants in presence of aeration. After about 90 minutes of aeration, it was terminated and the effluent was allowed to settle overnight. This was followed by second step i.e. solar detoxification (SD). During SD, supernatant of pretreated ADW was mixed with 1% catalyst and then it was detoxified in presence of solar radiation. SD was carried out for two consecutive days and comprised of 7-8 hours of operation on each day. Finally, this solar detoxified effluent-catalyst mixture was allowed to settle overnight and after settling, clear supernatant and catalyst were separated. This clear supernatant is nothing but the treated effluent. The treated effluent can further be drained into water bodies or can be effectively used for agricultural purpose. The process results in about 95 to 98% reduction in COD and increases the transmittance up to 90% from initial value of 0%. The catalyst used can be reformed and recycled for further treatment. For distilleries producing about five lakh L of ADW daily the treatment cost is expected to be Rs. 0.42 per liter of anaerobically digested wastewater.

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