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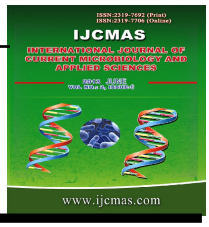

Original Research Article

Coupled ozonation with aerobic sequential batch reactor for treatment of distillery wastewater

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A B S T R A C T

Keywords
Distillery; spent wash; ozonation; wastewater; Advanced oxidation process (AOPs).

The present study details the treatment of distillery spent wash by ozonation followed by aerobic treatment in a sequential batch reactor. Ozonation was carried out in different stages by varying flow rate, contact time, addition of H_2O_2 and addition of Fenton's reagent. The ozonation at flow rate of 0.015 m^3/min and contact time of 1 h followed by reaction with Fenton's reagent for 1 h achieved 81% and 75% removal of colour and COD. This effluent from ozonation is carried over to sequential batch reactor which gave a removal efficiency of colour and COD at overall 90% and 88% respectively. Treatment of distillery spent wash with aerobic sequential batch reactor alone achieved only 13% COD removal.

Introduction

The wastewater released from distilleries is known as spent wash which contains huge quantity of dissolved organic matter, dissolved solids, suspended solids, colour along with other pollutants. Distillery spent wash is the unwanted residual liquid waste generated during alcohol production and pollution caused by it is one of the most critical environmental issue (Mohana *et al.*, 2009). In the year 1999 there were 285distilleries in India producing 2.7x 10^9 L of alcohol and generating 4x10^{10} L of wastewater annually. This number has raised to 319, producing 3.25x 10^9 L of alcohol and generating 40.4x10^{10} L of wastewater annually (Uppal 2004).

The contribution of distillery waste in India to organic pollution is approximately seven times more than that of the entire Indian population. Upon discharge into surface water, such a high value of organic contents are decomposed by microbial action leading to serious damage to aquatic life in consonance with depletion of dissolved oxygen (Nagaraj and Arvind kumar 2008). Also the highly coloured nature of spentwash can block out sunlight from rivers and streams thus reducing oxygenation of the water by photosynthesis and hence becomes detrimental to aquatic life (Radhika *et al.*, 2010). Because of using large quantities of

water in distillery industries it is necessary to treat and reuse the wastewater. In the most of time, the discharge standards applied for distilleries are often too stringent and below the level that can be achieved with appropriate biological treatment technologies (Radhika *et al.,* 2010).

The way of selecting the method depends on the characteristics of the wastewater, environmental regulations, cost and time. Nowadays among chemical technologies, a novel method that has been growing in decades is the advanced oxidation processes (AOPs) which are very potent in oxidation, decolorization, mineralization and degradation of organic pollutants (Christos *et al.,* 2008, Julia 2007). Satyawali and Balakrishnan (2008) reported physico-chemical treatment process effectively remove colour and COD in molasses distillery wastewater.

The problem with the advanced oxidation technologies is the operation cost compared to other conventional physiochemical or biological treatments. This can be solved by coupling AOP with other treatment methods (Beninez *et al.,* 2003, Masroor *et al.,* 2009,). The main advantages of AOPs include the lack of by-products of environmental concern, high process rate, efficiency and enhanced biodegradation. Rajesh *et al.,* (2008) reported integrated AOPs of anaerobic and solar photocatalytic treatment resulted in 95% of COD removal in dairy wastewater. Among AOPs ozone has proved a powerful oxidizing agent (Yasar *et al.,* 2007). In this study anaerobically digested wastewater is treated by a coupled Fenton, ozonation and aerobic treatment in a sequential batch reactor.

Materials and Methods

Sampling

Experiments were carried out on wastewater, collected from Dharani Sugars and Chemicals Ltd., Sivagiri, Tamil Nadu, India. The sample was taken from the outlet of thermophilic anaerobic digester. The sample was stored at 4^{o}C to prevent from any changes in the characteristics. The main characteristics of the wastewater sample is given in Table 1. Even after anaerobic digestion the COD is very high and the colour is very dark.

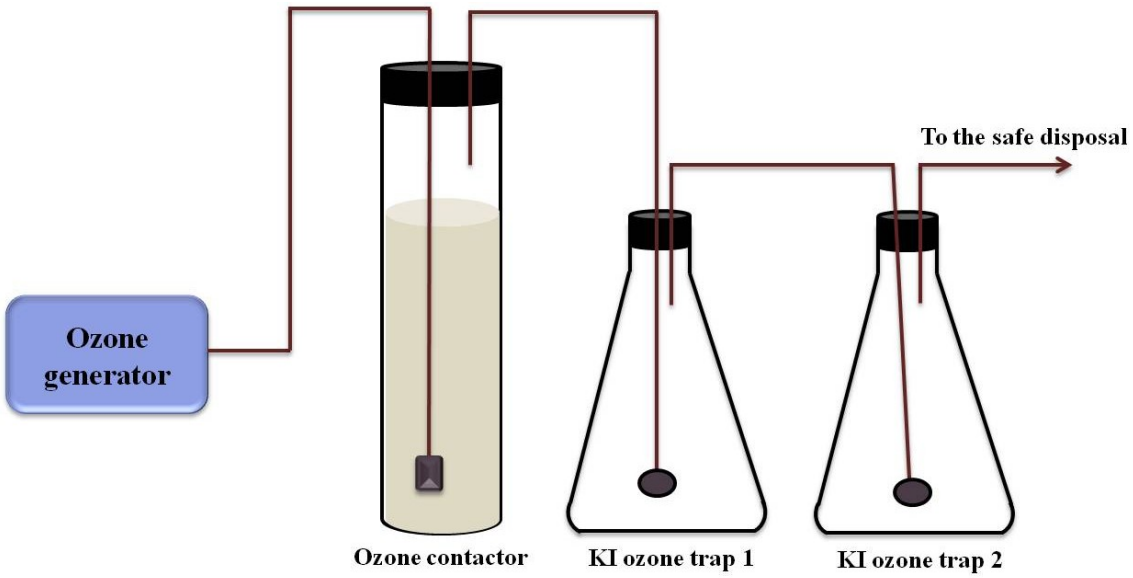
Table.1 Characteristics of the wastewater

Sl. No.	Parameter	Quantity
1.	pH	8.0
2.	Total solids (TS)	65,000 mg/L
3.	Total dissolved solids (TDS)	20,500 mg/L
4.	Total suspended solids (TSS)	46,600 mg/L
5.	BOD	5,000 mg/L
6.	COD	55,600 mg/L

Ozonation

The schematic of setup used in this experiment is given in figure 1. The experimental setup consisted of a reactor of pyrex glass bottle of overall capacity of 2L. A tubular cylindrical porous diffuser was at the bottom of the reactor to transfer input ozone gas. Teflon tubing line was used for the connection between the generator and the reactor. Flow rate was kept constant at $0.01m^3$/min and $0.015m^3$/min for different experiments. Various contact time was adopted for each

Figure.1 Schematic of the experimental set up



dosage of ozone. All experiments were performed at room temperature. After ozonation the sample was aerated for 5 min. to remove possible residual ozone. The ozone concentration in off gas was destroyed in two sequential wash bottles containing 250 ml of acidified 2% KI solution (Fig. 1).

Aerobic Sequential Batch Reactor (ASBR)

The reactor volume adopted was 5L, equipped with an air diffuser and mechanical agitator. A process was carried out to acclimatize the activated sludge taken from a municipal wastewater treatment plant to the distillery spent wash. In this process, the bioreactor was initially loaded with the above mentioned inoculum and the reaction medium was completed with a load of diluted spent wash containing an initial substrate concentration of 5000 mg COD/L and the bioreactor was aerated for 4 days. At the end of this process and after a settlement period, the biomass was separated by filtration from the supernatant liquid and charged again to the bioreactor. This procedure was repeated with successive additions of spent wash load to the biomass, each containing increasing concentrations of substrate from 5000-56,000 mg COD/L. The biomass acclimatization was considered to be achieved when a similar removal of substrate was obtained after experiments with the original sample. Once the acclimatization stage was finished, distillery spent wash treatment was conducted. The MLSS was maintained at 5000 mg/L. A 2L of the wastewater was introduced into the bioreactor which was inoculated with the previously acclimatized biomass to the required amount. Several samples were withdrawn at regular intervals to analyse the biomass and substrate concentrations.

Fenton's reagent

Treatment with Fenton's reagent was carried out in E_2 and E_4. In E_4 the contact time with Fenton was 30 minutes. In E_2, the contact time was 1 h. In both E_2 and E_4, 5 mg/L of H_2O_2 and 0.25 g/L of Fe^{2+} was kept as the optimum value.

Results and Discussion

The Experiments were carried out in different stages as E_1, E_2, E_3 and E_4. With ozonation alone (E_1), the results were not much satisfactory at lesser contact times. E_2 and E_4 are experiments done by treatment with Fenton followed by ozonation. E_2 was carried out with more contact time than E_4 with the same quantity of Fenton and at ozonation flow rate of $0.015m^3$/min. E_2 was able to achieve better result at half the contact time with ozone compared to E_4 which was carried out at a flow rate of $0.01m^3$/min. Moreover increasing the flow rate reduces the contact time for ozonation. The colour removal at 475 nm was nearly proportional to the COD removal. Ozonation is usually coupled with another oxidant such as hydrogen peroxide or UV irradiation to enhance the formation of hydroxyl radicals in aqueous phase (Mantzavinos and Psillakis 2004). The present study details about the coupled action of ozone with Fenton reaction to treat high strength distillery wastewater.

Effect of Ozonation on COD and Colour

Ozonation was carried out in the reactor with 1 L sample of wastewater at a flow rate of $0.01m^3$/min. The initial pH was 7.91. Samples were collected at every 15 minutes for 1 h. The efficiency of removal of colour and COD are in the range of 30% and 36% respectively. Ozonation was continued at a flow rate of $0.015m^3$/min. and samples collected at every 30 minutes for 1.5 h and the removal efficiency of colour and COD increased in the range of 58% and 62% respectively (Fig. 2a and 2b). pH after ozonation increased to 8.3. Sigge *et al.,* (2007) reported that even though low ozone concentration make effective biodegradation, but the treatment affected due to the presence of polyphenols and other recalcitrant compounds in the distillery wastewater. Pena *et al.,* (2003) also reported that oxidation by ozone could achieve 80% decolorization for biologically treated spentwash with simultaneous 15-25% COD reduction to improve biodegradability of the effluent.

Effect of H_2O_2 and Ozonation on COD and Colour

Ozonation at a flow rate of $0.01m^3$/min was carried out after reaction with H_2O_2 for 30 minutes. 1 L of wastewater sample was used for this treatment in a separate reactor. 5 ml/L was used as the optimum quantity of H_2O_2. During reaction with H_2O_2 fervent reaction took place forming brown coloured bubbles. Complete stirring was done to ensure complete reaction of H_2O_2 with wastewater. Then the mixture was allowed to settle for 15 minutes. The pH of the mixture before taken to ozonation reactor was 7.75. The supernatant was transferred to ozonation reactor. Samples were collected at every 30 minutes for 2 h. The pH after treatment with H_2O_2 was 7.75. The removal efficiency of colour and COD was in the range of 28% and 30% respectively (Fig. 3a and 3b). pH after ozonation increased to 8.15.

Figure.2a Effect of Ozonation and Fenton+Ozonation (1h) treatment on COD removal

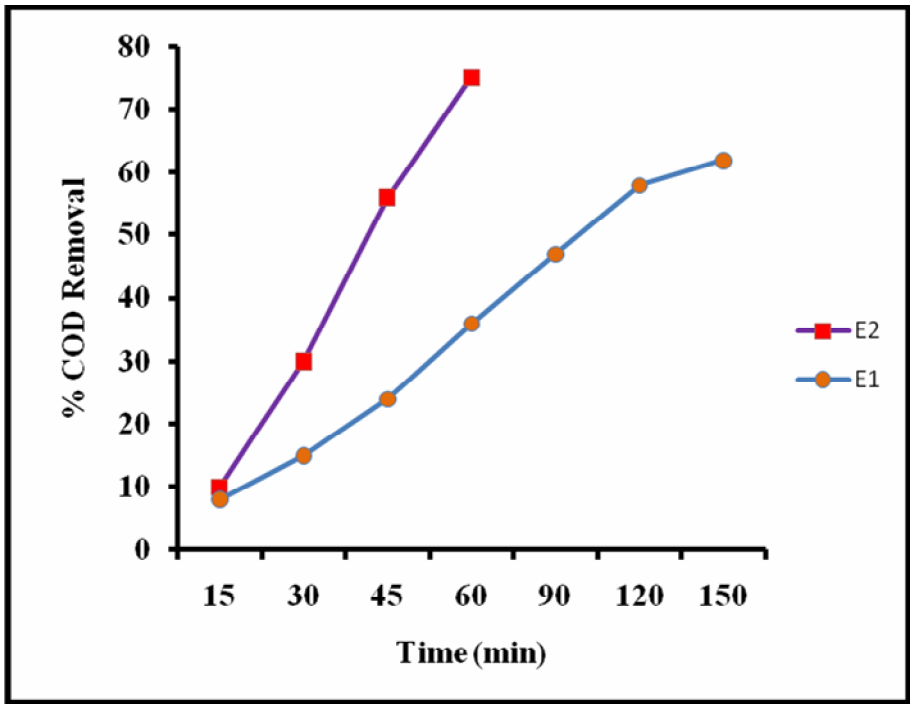


Figure.2b Effect of Ozonation and Fenton + Ozonation (1h) treatment on colour removal

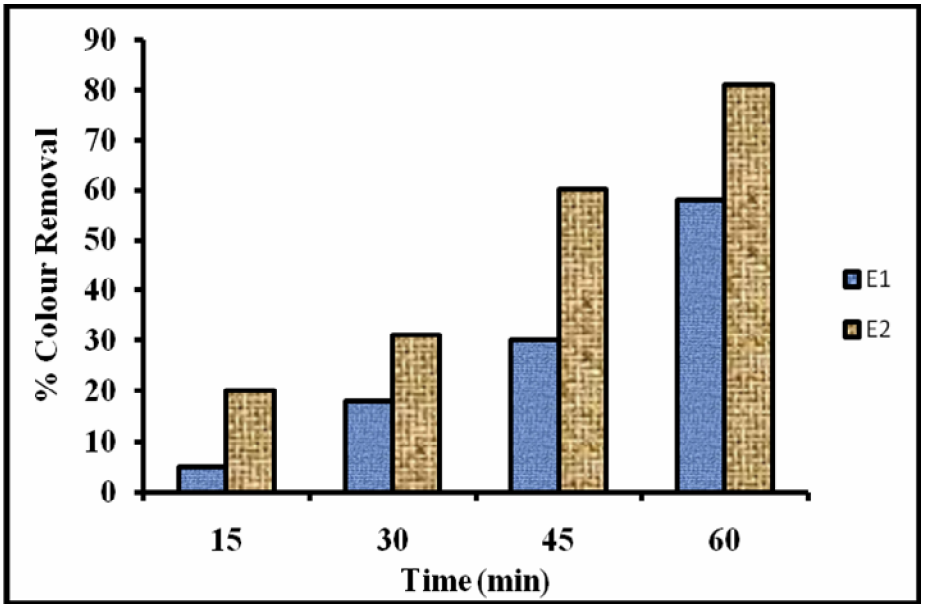


Figure.3a Effect of H_2O_2+Ozonation and Fenton (30min) + Ozonation (2 h) on COD removal

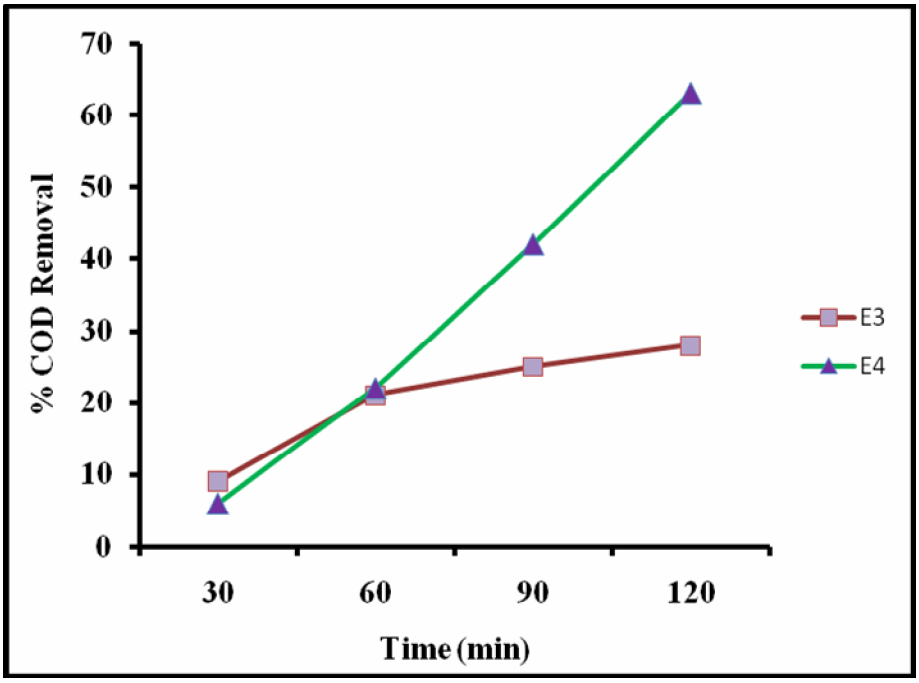
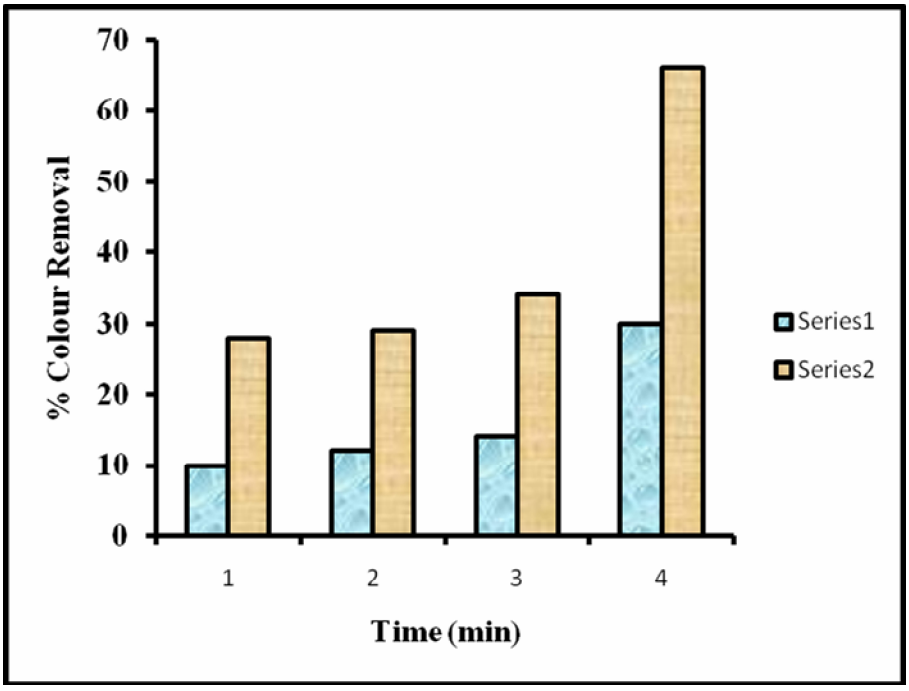


Figure.3b Effect of H_2O_2+Ozonation and Fenton (30min) + Ozonation (2 h) on colour removal



Effect of Fenton's reaction and Ozonation on COD and Colour

In this study, before the ozonation pretreatment the sample was treated with Fenton's reagent. 5ml/L of H_2O_2 and 0.25g/L of Fe^{2+} were added to the wastewater sample in a separate reactor of 2 L capacity and kept for 30 minutes. Complete stirring was carried out. Bubbles of the reaction raised certain millimeters above the wastewater surface. After 20 minutes the mixture was allowed to settle down. Then the pH of the mixture was noted. The supernatant was transferred to the ozonation reactor and ozonation carried out for 2 h at $0.01m^3$/min. Samples were collected at every 30 minutes for 2 h and the removal efficiency of colour and COD was in the range of 66% and 63% respectively (Fig. 3a and 3b). pH value increased from 7.43 and 8.95 during ozonation. When the treatment with the same concentration of Fenton's reagent for 1 h and the flow rate increased to $0.015m^3$/min the colour removal efficiency was 81% at 1 h and COD removal efficiency increased to 75% (Fig. 2a and 2b). An increase in colour was noticed after reaction with Fenton's reagent. This may be suspected as due to ferric ions (Munter 2001). In the present study, coupled ozone treatment plays vital role in treating distillery wastewater. Beltran *et al.,* (1999) also reported ozone dose is the key variable to treat a vinasse-domestic sewage effluent effectively with a combined chemical−biological system. Heredia *et al.,* (2005) showed addition of Fentons reagent oxidation process with aerobic biological treatment effectively removed 50 to 80% of COD in wine distillery wastewaters.

Thus the ozone contact time can be reduced by increasing the ozone flow rate from $0.01m^3$/min to $0.015m^3$/min. There is no notable reduction of colour and COD by addition of H_2O_2 alone. Addition of hydrogen peroxide could be increasing COD, which probably due to residual H_2O_2 that is not completely react with ozone to produce hydroxyl radical (Fahmi *et al.,* 2011). Since increasing the contact time is costly, the alternate method of treatment with Fenton influences the reduction of COD and colour at an lesser contact time of ozone. Thus the latter effect gives the better result at 1 h ozonation than the other ones with 2 h ozonation.

Biodegradability

Biodegradability of the ozonated effluent is calculated each time to ensure that the effluent be subsequently treated in the biological treatment (Sadeghi *et al.,* 2005). Thus the effluent after Fenton reaction for 1 h and ozonation for 60 minutes gave the satisfactory result of BOD/COD = 0.8 at an early stage. So the above pre-treated wastewater is used for treatment in the aerobic SBR.

Study on Aerobic Sequential Batch Reactor

2 L sample of spent wash was treated in the sequential batch reactor which was aerated and MLSS was maintained at the optimum value of 5,000 mg/L. Various samples were drawn at 4 h intervals for 2 days. There was no appreciable reduction of COD and colour. The treatment was continued for 13 days. The results showed overall process confirmed 88% of COD removal. SBR alone showed 13% COD removal. The present study clearly details about the efficiency of integrated ozone treatment along with SBR to treat high strength distillery wastewater with high COD level.

The feasibility of using ozone to reduce the COD and colour in distillery spent wash was studied. Increasing the contact time for the wastewater with Fenton's reagent gave comparably best result (75%). This reduces the contact time with ozone since this result is achieved in 1 h at 0.015m^3/min. Coupling this effluent with SBR gave the maximum removal efficiency of 88%. The effect of ozone dosage also increases the efficiency at early stage thus reducing the contact time with ozone. Coupled treatment with SBR was feasible only for 3 days due to practical difficulties during the process. Increase in HRT improved the treatment efficiency. Aerobic biological treatment yields large quantity of sludge. Pre-treatment with ozone helps to overcome this difficulty. Further studies on this coupled process may be economical and effective.

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