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# Combination of ozonation with conventional aerobic oxidation for distillery wastewater treatment

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**Abstract**

Laboratory-scale experiments were conducted in order to investigate the effect of ozone as pre-aerobic treatment and post-aerobic treatment for the treatment of the distillery wastewater. The degradation of the pollutants present in distillery spent wash was carried out by ozonation, aerobic biological degradation processes alone and by using the combinations of these two processes to investigate the synergism between the two modes of wastewater treatment and with the aim of reducing the overall treatment costs. Pollutant removal efficiency was followed by means of global parameters directly related to the concentration of organic compounds in those effluents: chemical oxygen demand (COD) and the color removal efficiency in terms of absorbance of the sample at 254 nm. Ozone was found to be effective in bringing down the COD (up to 27%) during the pretreatment step itself. In the combined process, pretreatment of the effluent led to enhanced rates of subsequent biological oxidation step, almost 2.5 times increase in the initial oxidation rate has been observed. Post-aerobic treatment with ozone led to further removal of COD along with the complete discoloration of the effluent. The integrated process (ozone–aerobic oxidation–ozone) achieved ~79% COD reduction along with decoloration of the effluent sample as compared to 34.9% COD reduction for non-ozonated sample, over a similar treatment period.


*Keywords:* Distillery wastewater; Ozonation; Discoloration; Biological treatment

## 1. Introduction

Biological treatment is often the least expensive and most cost effective process for eliminating the organic pollutants from the aqueous waste of chemical processing industries. Many pollutants can be fully biodegraded (mineralized) by the microorganisms in such processes, whereas many physical and chemical processes just concentrate the pollutants or transfer them from one medium to another (stripping from liquid to air), leaving their ultimate fate in the environment unclear. Unfortunately not all compounds are biodegradable. Treatment schemes combining chemical and biological processes are based on the finding that many oxidation products of biorefractory pollutants are easily biodegradable (Gottschalk et al., 2000; Gogate and Pandit, 2004).

Distilleries are amongst the most highly polluting industries with reference to the extent of water pollution both in terms of the quantity of the wastewater generated from the distilleries as well as the extent of pollution load in the effluent stream (Mall, 1995). In general about 6–15 l of spent wash is generated per liter of alcohol produced depending on the type of the process (Joshi, 1999; Beltran et al., 2001; Pant and Adholeya, 2006) thus creating enormous environmental problems. The characteristics of distillery wastewater vary considerably according to the fermentation feed stock, location and the fermentation process adopted (Pant and Adholeya, 2006). The wastewater is characterized by a high dissolved solid loading (of which 50% may be present as reducing sugars), high ash content, high temperature, low pH and high percentage of dissolved organic and inorganic matter (Beltran et al.,

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**Nomenclature**

| | |
|---|---|
| $S/S_0$ | residual substrate concentration, in terms of COD |
| $S$ | biodegradable COD fraction of the sample, $mg\,l^{-1}$ or mg |
| $S_t$ | total COD of the sample, $mg\,l^{-1}$ or mg |
| $S^*$ | non-biodegradable fraction of COD, $mg\,l^{-1}$ or mg |
| $X/X_0$ | increase in biomass fraction, $mg\,l^{-1}$ or mg |
| $U$ | specific substrate utilization rate, mg COD $mg\,MLSS^{-1}\,h^{-1}$ |
| $G/G_0$ | residual sugar concentration (as reducing sugars), $mg\,l^{-1}$ |
| $A_{254}$ | absorbance at 254 nm |
| BOD | biochemical oxygen demand, $mg\,l^{-1}$ |
| COD | chemical oxygen demand, $mg\,l^{-1}$ or mg |
| DO | dissolved oxygen, $mg\,l^{-1}$ |
| DNSA | dinitrosalicylic acid |
| MLSS | mixed liquor suspended solids, $mg\,l^{-1}$ |
| TDS | total dissolved solids, $mg\,l^{-1}$ |
| ASN6 | culture isolated from aeration tank of the effluent treatment plant of Asian Paints, Mumbai |
| ETP | effluent treatment plant |
| PTFE | polytetrafluoroethylene |
| AO | batch subjected to aerobic oxidation |
| GPC | gel permeation chromatography |
| EDOG | electric discharge ozone generator |

1999b). The biochemical oxygen demand (BOD) and chemical oxygen demand (COD), the index of its polluting character, typically range between 35000–50000 and 100000–150000 $mg\,l^{-1}$, respectively (Nandy et al., 2002). Due to stringent requirements being imposed by regulations concerning the discharge of the effluents, there is a growing interest in the development of new technologies and procedures for the treatment of distillery wastewater.

Moreover, distillery wastewaters often contain compounds, which are not readily decomposed by the microorganisms. Distillery spent wash does contain such compounds, viz., color pigments (melanoidins). Treating this highly colored spent wash has been the major problem encountered by this industry. The distillery spent wash contains nearly 2% of a dark brown recalcitrant pigment called melanoidin, an addition product of amino acid and carbohydrate due to Maillard reaction (Kalavathi et al., 2001). The reactions include the interaction of amino acids with reducing sugars as well as sugar dehydration and fragmentation of the reducing sugar with the formation of aldehydes, ketones, furans, pyrroles, quinolines and indoles. In the final stages of the Maillard browning reactions, brown pigments (melanoidins) are formed through aldol condensation and polymerization of carbonyl compounds. Melanoidins formed in amino acid reducing sugar system have a wide range of molecular weights, varying from about 290–14200 (Kitts et al., 1993). Melanoidins have conjugated carbon–carbon double bonds in their structure that are responsible for their brown color (Kim et al., 1985).

Currently, treatment processes such as chemical methods (Chandra and Singh, 1999), adsorption using activated charcoal (Chandra and Pandey, 2001) and flocculation (Migo et al., 1993) are used for the removal of melanoidins from the biologically treated wastewater. However, these processes still have disadvantages due to high operation cost, high consumption of chemical agents, and variations in the color removal efficiency and high volume of solid waste produced (Kumar and Chandra, 2006).

Peria et al. (2003) carried out molecular weight distribution measurement of the biologically pretreated molasses wastewater using gel permeation chromatography and reported that the high molecular weight compounds present in the wastewater could be divided into two groups of 60000 Da and 3000 Da fractions. Ozonation method was investigated as chemical means of oxidation and color removal from the wastewater. The evolution of COD and color for both synthetic melanoidins and real wastewater followed similar pattern. Ozone attacked compounds belonging to both the groups leading to a decrease in the concentration of chromophore groups.

Ozone has many properties desirable for the treatment of the wastewater. Firstly, it is a powerful oxidant capable of oxidative degradation of many organic compounds and also results in oxidation products which are more biodegradable (Heredia et al., 2000). Ozone also results in the formation of highly reactive hydroxyl radical in the system, which has higher oxidation potential as compared to ozone itself. Ozonation has been used for the disinfection, oxidation of inorganic and organic compounds, including taste, odor, color and particle removal (Gottschalk et al., 2000). Recent works have also demonstrated the combined use of ozone and aerobic oxidation for the treatment of synthetic and real distillery wastewater (Beltran et al., 1993; Beltran et al., 1999a,b; Beltran et al., 2001a,b; Peria et al., 2003; Benitez et al., 2003).

Accordingly, in the first phase of work, the biological degradation or aerobic oxidation by microorganisms and the chemical oxidation by ozone have been studied separately, with an aim of quantifying the color and COD removal efficiencies. In the second phase, the combined processes consisting of ozonation followed by aerobic oxidation was carried out to establish the COD removal efficiency achieved by these processes in series. In the third phase, ozonation was used as the method of choice to