Treatment of Ozonated Tannery Wastewater in Sequential Batch Reactor

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Abstract

From the earlier studies carried out using reverse osmosis system, the main drawback observed in reverse osmosis is frequent fouling of membranes mainly due to the presence of residual organics in the treated tannery effluent. In order to address this issue of reducing the residual organics in terms of colour and COD of the effluent, the secondary treated tannery effluent was subjected to ozonation in batch reactor of 5 liter capacity. The effect of pH on ozonation has also been carried out with three different pH values i.e., 3, 7 and 12. From the experiments, it was found that the maximum colour removal of 88% and a marginal COD reduction was possible. In addition, studies were carried with primary and secondary treated tannery wastewater with ozonation followed by aerobic biological using sequential batch reactor (SBR). From the studies carried out, maximum COD removal of 64% were observed for primary treated wastewater after combined treatment of ozonation and SBR whereas only 48% COD removal with SBR alone (without ozonation).

Keywords: Advanced oxidation process (AOP), sequential batch process (SBR), tanneries, wastewater, colour removal, COD removal

1. Introduction

Tannery is categorized as one of the highly polluting industries due to the presence of high organic and inorganic pollutants. Tanneries generate large quantities of wastes i.e., about 30 m^3 of wastewater per tonne of raw skin/hide processed. The effluent generated from tanneries has high concentration of BOD, COD, TDS and suspended solids. These effluents are also characterized by the high levels of colour caused by the residual dyes if finishing operations are carried out. The unit operations involved in the conventional tannery effluent treatment consist of bar screens, grit removal & chemical coagulation followed by primary settling tank. The secondary biological treatment can be carried out either by anaerobic treatment followed by extended aeration process or by two stage or single stage extended aeration process. In few units, tertiary treatment system mainly consisting of pressure sand filter (PSF) and activated carbon filter (ACF) were also provided. With this conventional system, the effluent discharge standards of SS-100 mg/L and BOD-30 mg/L are met except for Total Dissolved Solids (TDS) and chlorides (Discharge standard for TDS - 2100 mg/L; Chlorides – 1000 mg/L). TDS concentration after conventional treatment ranges between 6,000 and 16000 mg/L depending on the type of processing operation performed in tanneries (Semi-finished to finished leather or raw hides/skins to semi-finished/ finished leather). Discharge of effluent with high TDS levels leads to the

increase in TDS levels of the ground and surface water in the adjoining area making it unpalatable. The main objective of United Nations New Millennium Goal is to provide safe drinking water and sanitation to everyone in the world. Under these circumstances, regulatory authorities have directed tanneries in Tamilnadu to implement zero liquid discharge (ZLD) i.e., recovery of water from wastewater for reuse and prevention of discharge of any effluent outside their premises. ZLD can be achieved by two means i.e. desalination and reverse osmosis. In desalination, the water recovery of only 30 to 40% is possible leaving more percentage of rejects for evaporation. Whereas reverse osmosis systems have reported to recover more than 70% of water and the remaining portion of rejects with very high concentrations of TDS ranging from 20,000 to 50,000 mg/L depending on the inlet TDS levels. This reject needs to be evaporated in solar evaporation pans or mechanical evaporator systems to achieve zero liquid discharge.

With the strict implementation of zero liquid discharge, every industry is required to install zero liquid discharge (ZLD) system to meet the compliance for recovery and reuse-using membrane based reverse osmosis system. In addition to conventional biological treatments, effluents must be post-treated by physico-chemical processes such as chemical coagulation, sand filtration, adsorption using granular activated carbon, UV treatment, ozonation etc. to meet the feed quality requirements of reverse osmosis membrane system. From the pilot scale and a few commercial scale studies carried out with secondary treated tannery effluent, the main drawback observed in reverse osmosis system is membrane failure or fouling due to the presence of residual organics, dye molecules and other impurities in the effluent. In order to address this issue of reducing the residual organics in terms of colour and COD of the effluent, an attempt has been made using ozonation as advanced oxidation process alone and in combination with aerobic biological treatment using sequential batch reactor. The existing technologies widely used for decolorisation of colored effluents are adsorption, precipitation, membrane filtration, chemical degradation and photo degradation, which are expensive and commercially unattractive [Sarasa, 1998 and Konsowa, 2003]. Tertiary treatment using chemical coagulation/flocculation has major operational problems as huge amounts of sludge are generated. Adsorption technique is more expensive as it involves the use of powdered activated carbon as adsorbent and disposal of used activated carbon. Advanced oxidation process (AOP) like ozonation, Fenton and photo Fenton processes, ozone /UV radiation are the potential alternatives for decolorization of colored wastewater [Mehmet,2002, Mariana, 2004 and Marco, 2006]. Thus it is reported that oxidative degradation by AOP is effective one for decolorization of wastewater. AOP using ozone is very effective for decolorizing dye wastewater due to effective breakage of conjugated double bonds associated with the dye. One of the effective methods to remove color from wastewater is ozonation, which cleaves the unsaturated bonds in aromatic moieties found in humic substances, chromophores of dyes and other pigmented compounds, thereby reducing color [Idil, 2001 & 2002]. The mechanism of reaction of ozone follows two main pathways: a direct path corresponding to the action of molecular ozone and an indirect path corresponding to the action of free radicals species resulting from the decomposition of ozone in water.

Post treatment of biologically treated effluents from pulp and paper industry using ozonation and adsorption technique for COD, AOX & colour reductions have been studies [Kallas, 1994]. The capital and operating costs for both processes have been estimated and observed that for the same purification efficiency, adsorption incurred 10-20 times higher expense compared to ozonation.

Highly concentrated residual dye house liquors were decolorized and mineralized by a combined anoxic and biological–chemical treatment in a SBR and reported an overall COD elimination of 90% and complete decolorization [Krull , 1998].

The treatment of the industrial wastewater (particularly tannery wastewater) by SBR is preferred because of its several advantages over the continuous reactors i.e., a higher versatility and the possibility to work with higher loads (smaller volumes), by selecting, through the cyclic concentration gradients, a biomass resistant to the presence of inhibiting substances [Carucci, 1999]. Higher COD removal rates of 0.19 kgCOD/kgVSS.d and higher nitrogen removal rates of 0.02kgN/kgVSS.d were reported with organic loading rate of 0.21 kgCOD/kgMLSS.d for SBR when compared with full scale values of COD removal of 0.12 kgCOD/kgVSS.d and 0.009 kgN/kgVSS.d with organic loading of 0.088 kgCOD/kgMLSS.d.

Biological colour removal from simulated textile effluents containing dyes using a combination of anaerobic and aerobic periods in the operation cycle of a SBR have been reported [Lourenço, 2001]. The studied SBR system proved to be potentially efficient for colour removal from feeds containing azo dye when operated in optimized conditions and relative duration of anaerobic and aerobic reaction phases. Pena et al. 2003 reported that the colour removal from 71% to 93% and COD reduction from 15% to 25% were observed depending upon the applied ozone dosage, after 30 min. reaction time, while TOC values remained constant throughout ozonation for biologically treated molasses wastewater.

2. Material and methods

The wastewater for the study was collected from a tannery effluent treatment plant treating wastewater from tanneries processing mostly wet blue to finish operation. The characteristics of the primary and secondary treated effluents are analysed as per Standard Methods and are shown in Table 1 and 2 respectively. The ozone was generated from a laboratory ozone generator (Model No –SA001, India). Air was used to produce 3 g/h of ozone with flow rate of 30 L/min from the ozone generator. The effect of pH on ozonation of secondary treated effluent was investigated at 3 different pH values i.e., 3, 7 and 12. To maintain the required pH throughout the ozonation experiments, respective phosphate solutions or buffers were used. To maintain pH 3, 2.08 ml of ortho-phosphoric acid was required per litre of wastewater and for pH 12, 16.8 ml of 2N NaOH and 8 ml of 1 N di sodium di hydrogen phosphate (Na_2HPO_4) per litre were required.

3. Experimental set-up

Bubble column: Secondary treated tannery wastewater is subjected to ozone treatment in bubble column reactor. The dimensions of 5 L capacity reactors are 0.085 m diameter & 1.25 m height. The ozone containing gas is purged through ceramic diffusers in bubble column reactor.

Sequential batch reactor (SBR): The wastewater is subjected to ozone treatment in a bubble column reactor for 30 min. The effluent after ozonation is further treated in a sequential batch reactor for reduction of COD (aerobic biological treatment). The sequential steps carried out in SBR are filling (0.25 h), aeration (23 h), settling (0.5 h) and decanting (0.25 h). In this

experiment, SBR with a capacity of 5 l was operated with 24 h hydraulic retention time. In SBR, 3.5 l of ozonated secondary treated tannery wastewater was filled after decanting 3.5 l of supernatant. The seed sludge for sequential batch reactors was collected from the aeration tank of an operating treatment plant treating tannery wastewater. These experiments were carried out for both primary and secondary treated wastewater. Parallel experiments were also carried out without ozone treatment as control.

3. Results and Discussion

The characteristics of primary and secondary treated tannery effluent are shown in Table 1 and 2 respectively. The secondary treated effluent is characterized by dark brown colour and high residual organics.

Table 1 Characteristics of Primary treated Tannery effluent

Parameter	Range
pH	7.8-8.8
Colour (Pt-Co units)	650-1500
Total solids (mg/l)	6200-7300
Suspended solids (mg/l)	350-520
Total dissolved solids (mg/l)	5800-6700
BOD (mg/l)	300-600
COD (mg/l)	890-1500
Sulphate (mg/l)	2500-2700
Chloride (mg/l)	1250-1700

Table 2 Characteristics of Secondary treated Tannery effluent

Parameter	Range
pH	7.8-8.8
Colour (Pt-Co units)	450-540
Total solids (mg/l)	5900-6900
Suspended solids (mg/l)	60-100
Total dissolved solids (mg/l)	5800-6700
BOD (mg/l)	15-30
COD (mg/l)	300-700
Sulphate (mg/l)	2500-2700
Chloride (mg/l)	1250-1700

Treatment of secondary treated tannery effluent using ozonation alone

The secondary treated tannery wastewater is subjected to ozone treatment alone in a bubble column reactor with 5 L capacity. The samples were collected from the reactor at regular time intervals. The residual colour and COD were determined and the results are shown in Figure 1. The colour and COD removal efficiencies of 84.2% and 18.3 % were observed respectively. It is also reported that ozone oxidizes unsaturated bonds and leads to partial oxidation products,

causing wastewater decolorisation. However ozonation generates organic compounds that also contribute to COD and rarely produces complete mineralization of organic matter to CO2 and water [Pena, 2003].

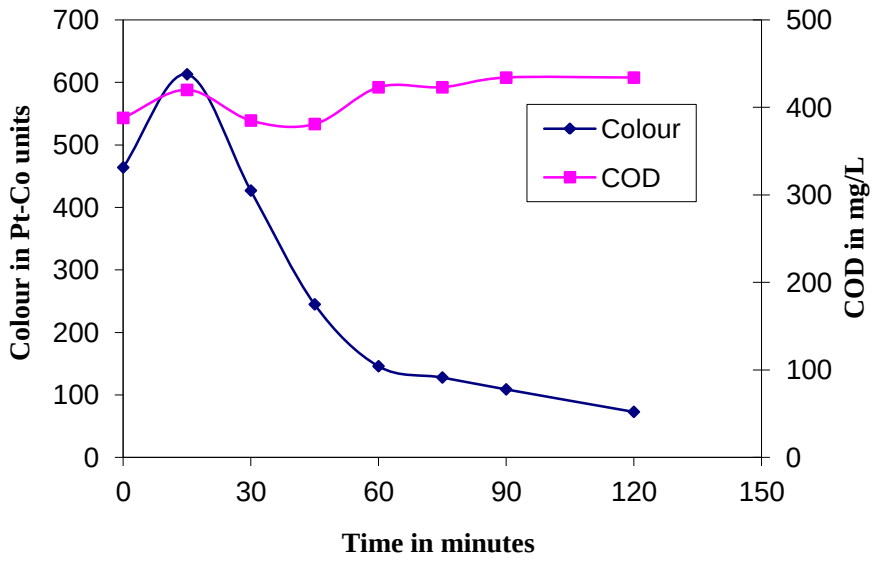

Figure 1 Colour and COD Reduction in secondary treated tannery effluent

The effect of various initial pH values (3, 7 and 12) on colour and COD reduction of secondary treated tannery wastewater has been carried out in bubble column reactor with 5 l capacity. The residual colour and COD of the samples at regular intervals were determined and shown in Fig 2 and 3 respectively. From the Figure 2, it is observed that the colour reduction is considerable in all the pH values studied. The maximum colour removal of 98% was observed at initial pH of 12 when compared with colour reduction of 76.5% and 84.3% at initial values of 3 and 7 respectively. From the Figure 3, the COD reduction showed varying nature for three different pH values. The maximum COD reduction of 34.9% was observed for pH 3 when compared with 33.9% for pH 12. For pH 7, there was no COD reduction in the effluent.

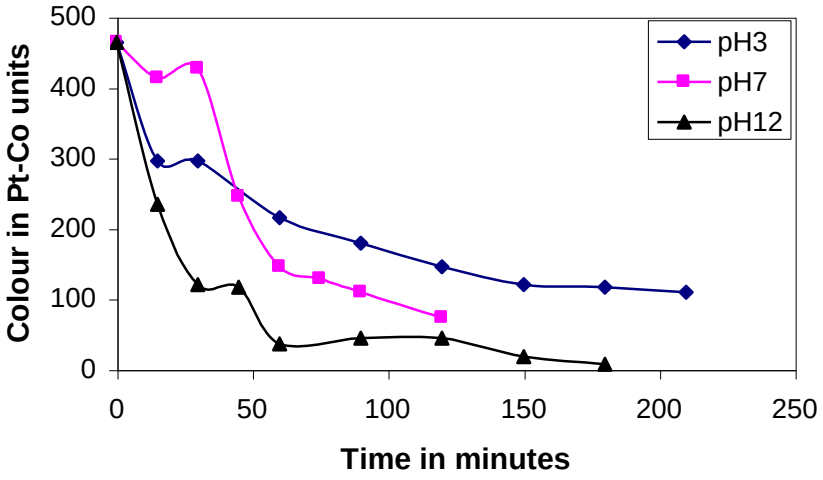

Fig 2. Colour reduction with different pH values

It is reported that in ozonation system, higher pH usually exerts a positive effect on the COD removal rate. This effect is due to two factors: the presence of dissociating compounds that react fast with ozone and in the absence of high concentrations of these compounds, the increase of ozone decomposition to generate hydroxyl radicals. Hence, any increase of COD removal during wastewater ozonation at increasing pH can be due to both the direct or indirect reactions of ozonation. In any case, a general rule of ozonation, relative to the pH value, is that at pH lower than 12, ozone will be consumed only through direct reactions in very concentrated wastewater when ozone fast-reacting compounds are present in high concentrations. In certain cases, pH effect is not as evident as might be expected i.e. pH might have no influence at all. But, generally, the increase in pH leads to an increase in the ozonation rate, and hence to an increase in colour / COD removal rate.

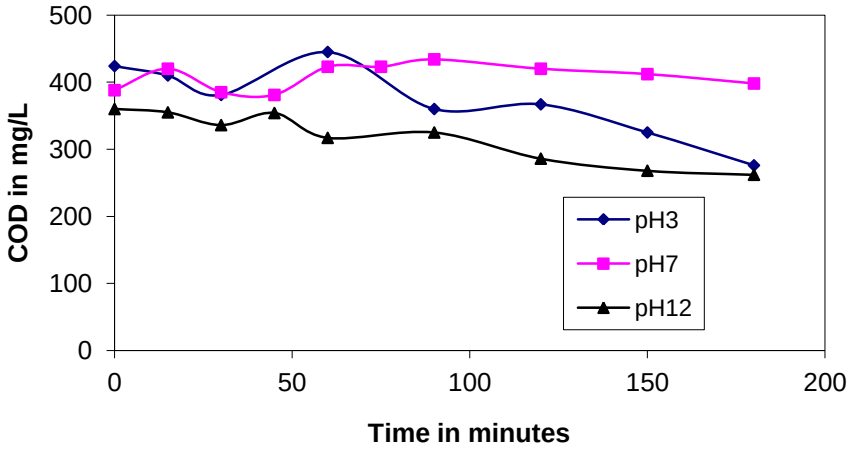

Fig 3. COD Reduction with time with different initial pH values

Effect of ozonation on biological treatment for secondary treated tannery effluent in SBR

The COD values of secondary treated tannery wastewater before ozonation, after ozonation and aerobic biological treatment in sequential batch reactor were determined after acclimatization and shown in Fig 4. From the Fig.4, it is observed that the COD values after ozonation was fluctuating and few occasion has increased over the initial COD values. However, COD of treated wastewater from sequential batch reactor was showing relatively lower COD values even lesser than 300 mg/L. The MLSS concentration of the SBR was also monitored and it was in the range of 500 to 800 mg/L. After 10 days of continuous operation, MLSS concentration of the SBR was constant. Further, experiments has to be discontinued, as MLSS concentration was not building more than 600 mg/L due to lower applied organic loading rate.

Effect of ozonation on biological treatment for primary treated tannery effluent in SBR

The primary treated effluent collected from CETP after primary treatment was having BOD and COD in the range of 300 – 600 mg/L and 900 –1500 mg/L respectively. The COD values of the effluent before & after ozonation and after treatment in SBR were determined after acclimatization and the results for 90 days of operation are shown in Fig. 5. From the Fig 5, it is observed that there was marginal COD reduction (4 - 20%) for primary treated effluent during ozonation. This marginal COD reduction during ozonation may be due to the easily oxidisable

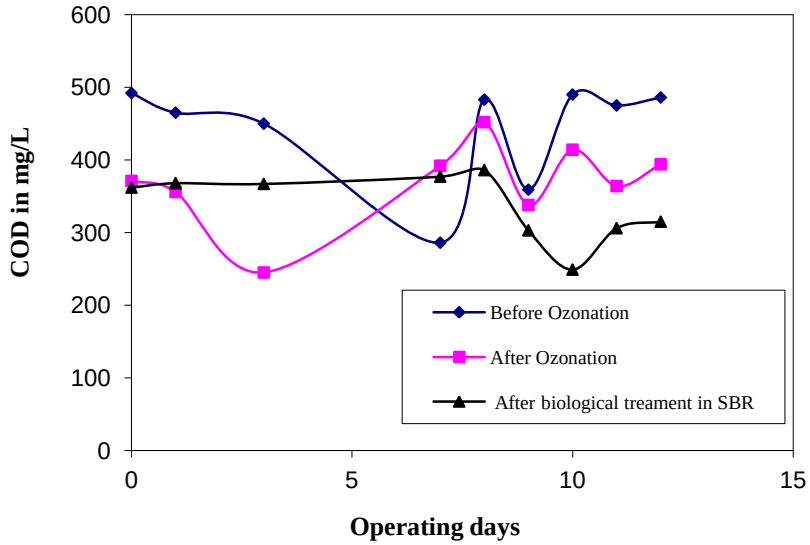

Fig. 4 COD reductions in secondary treated effluent using ozonation followed by biological treatment

compounds present in the primary treated effluent. The overall maximum COD reduction in SBR treating ozonated primary effluent was about 64% when compared 48% COD reduction in control SBR (without pre-treatment with ozone). The COD values after SBR using ozonated effluent was in the range of 450 to 650 mg/L. The MLSS concentration of the reactor was maintained in the range of 4000 to 6000 mg/L. In control SBR, which was run in similar conditions with out pre-treatment with ozonation showed 48% COD removal efficiency which

was lower than COD removal efficiency with pretreat with ozone. The COD values of the supernatant were in the range of 725 to 800 mg/L. The maximum COD reduction in control reactor without pretreatment
with ozone was only 48% and MLSS concentration in control SBR was in the range of 3000 to 4000 mg/L.

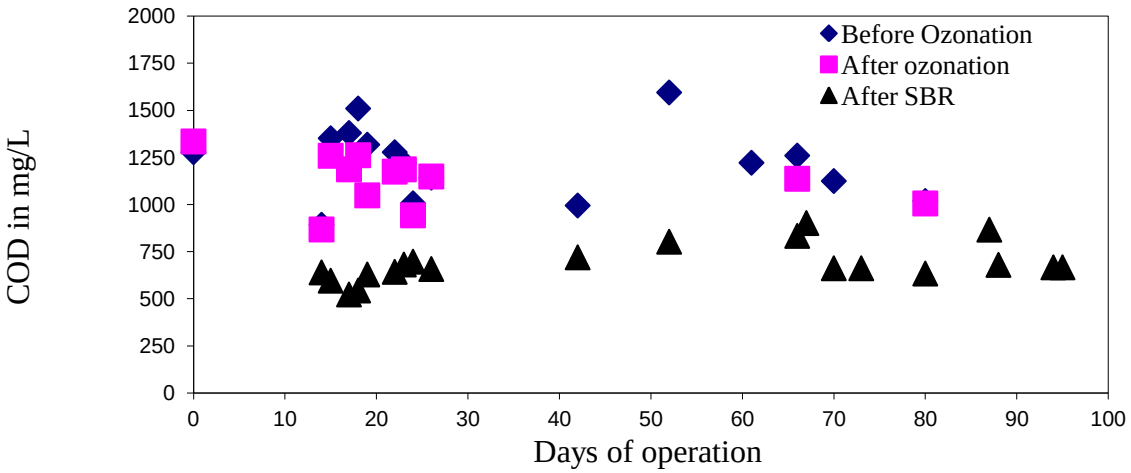

Fig 5. COD reduction in primary treated effluent after ozonation followed by SBR

4. Conclusions

The tannery effluents are subjected to ozonation studies alone and followed by biological treatment in Sequential batch reactor (SBR) for reduction of colour and COD. From experimental studies carried out, the following has been concluded:

- Maximum colour removal in secondary treated effluent is about 98% at pH 12 and 84% at neutral pH with ozone treatment alone in bubble column reactor.
- Reduction of COD was marginal in secondary treated effluent with ozone treatment alone in bubble column reactor.
- For primary treated effluent, it is concluded that ozonation followed by biological treatment in SBR showed higher COD reduction of 64% when compared with 48%
- COD reduction in control SBR (without ozone pre-treatment).

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