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Research article

# Ozonation of tannery effluent for removal of cod and color

V. Preethi[a], K.S. Parama Kalyani[a], K. Iyappan[c], C. Srinivasakannan[b], N. Balasubramaniam[b,*], N. Vedaraman[c]

[a] Department of Chemical Engineering, A.C.Tech. Campus, Anna University-Chennai, Chennai 600 025, India
[b] School of Engineering, Monash University, Sunway Campus 46150, Malaysia
[c] Department of Chemical Engineering, Central Leather Research Institute, Adyar, Chennai 600 041, India

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ABSTRACT

Ozonation of leather dye effluent for removal of color and COD reduction covering wide range in operating parameters forms the scope of the present work. The influence of parameters such as influent pH, ozone flow rate and initial effluent concentration on ozonation efficiency has been critically examined. It has been observed from the present investigation that a maximum of COD removal efficiency of 92% has been achieved under optimum operating conditions. Further the biodegradability index of the tannery effluent has increased from an initial value of 0.18 to 0.49 during ozonation indicating favorable adaptation of ozonation as a primer to the biochemical technique to enhance the efficiency of biochemical treatment.


## 1. Introduction

Leather industry is one of the most polluting industries in terms of the volume and complexity of the effluent discharge. The transformation of the raw hide into leather product involves several processing steps consuming considerable of amount water in each processing step. The effluent from leather industries contains high organic and inorganic loadings, strong color, dissolved and suspended solids, salinity with specific pollutant such as chromium, etc. [1,2]. Conventionally tannery effluent is treated by physicochemical techniques such as adsorption, biological oxidation, coagulation, etc. Though the coagulation process effectively removes the pollutant present in the effluent, the generation of secondary pollutants, i.e. solid sludge becomes serious issue. The biological technique is time consuming with low removal efficiency. Further, the nature of effluent, contaminant type and fluctuating pH and the presence of biocides may inhibit the functional activity of biological system. Due to increased economic, social, legal, and environmental pressures industries are focusing on new technologies to meet their demand. In recent years, there has been special focus on advanced oxidation technologies such as such as photochemical, ozonation, electro oxidation, etc. [3].

Ozone ($O_3$) is a powerful oxidant has been extensively used in process industries at various levels to remove pollutant present in the effluent. Ozonation is a promising treatment process due to its unique features such as no sludge generation; has high potential for both color removal and organic reduction through a single step and easy decomposition of residual ozone. Ozone reacts with organic compounds present in the effluent through either direct ozone attack or indirect free radical attack. During the ozonation process, tannery effluent loses their color by the oxidative cleavage of the chromophores. The cleavage of carbon–carbon double bonds and other functional groups, which have high electron densities, will shift the absorption spectra of the molecule out of the visible region [4]. The objective of this present investigation is quantitative determination of oxidation tannery effluent by ozonation, which include: (1) to enhance the biodegradability of tannery effluent; (2) to study the ozonation kinetics of organic pollutants and (3) to check the influence of operating parameter on pollutant degradation.

## 2. Materials and methods

The schematic of the experimental set-up shown in Fig. 1 consists of an acrylic cylindrical column of 2.5 cm internal diameter and 30 cm height packed with glass beads of 5 mm diameter. The oxygen/ozone mixture was continuously introduced into the column through a porous diffuser plate placed at the bottom of the column. All the experiments were carried out at atmospheric temperature and in semi-batch mode with continuous supply of ozone

* Corresponding author. Tel.: +60 3 5514 46231; fax: +60 3 5514 6207.
*E-mail address:* n.balasubramanian@eng.monash.edu.my (N. Balasubramaniam).

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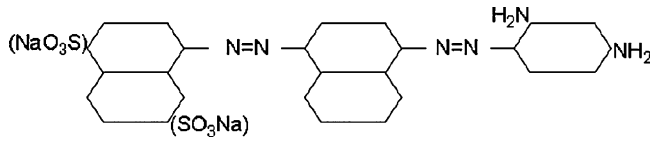


**Fig. 1.** The chemical structure of the direct brown diazo dye [CI. No. 26230].

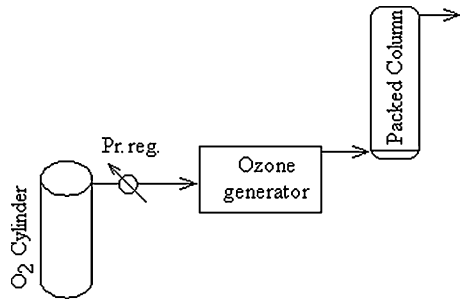


**Fig. 2.** A schematic representation of experimental set up.

**Table 1**
Characteristics of tannery effluent.

| Characteristics | Value |
|---|---|
| pH | 8.4 |
| COD | 5000 mg $l^{-1}$ |
| Suspended solids | 4200 mg $l^{-1}$ |
| Dissolved solids | 10,000 mg $l^{-1}$ |

for a batch of liquid effluent. Two different effluents were used in the present investigation: direct brown diazo dye [Fig. 2] and real tannery effluent from wet tanning process [Table 1]. The azo dye effluent was selected for investigation because it was frequently used in leather processing and usually non-degradable by the conventional process. The wet process tanning effluent was considered to test the ozonation process for real effluent. The un-reacted ozone leaving the column was scrubbed in 2% KI solution and was titrated against standard thiosulfate. Samples were withdrawn at regular intervals and analyzed for COD, color and BOD using standard estimation procedure [5]. The UV scans of the samples were performed using UV–vis spectrophotometer [Shimadzu Model UV 160] at 200 to 800 nm. The percentage color removal and the biodegradability index have been calculated for each experimental run.

## 3. Results and discussion

Experiments were carried out covering wide range in operating conditions and the results are critically examined in this section. Fig. 3 shows the percentage COD removal with ozonation time for the dye effluent. It can be ascertained from Fig. 3a, that the percentage COD removal increased with ozonation time. This is an expected behavior and can be explained that the ozone passed through the packed column reacts with the pollutants present in the effluent resulting in percentage COD removal. It can be noticed from Fig. 3a that the trend of percentage COD removal is more or less linear. It can further be observed from Fig. 3a, the percentage COD removal decreases with an increase in the initial effluent concentration. The percentage COD removal decreased from 65% to 45% when the initial effluent concentration increased from 300 to 500 mg $l^{-1}$ for a given ozonation time of 50 min. This can be attributed due to the increased ozone consumption with increased initial effluent for a given operating conditions as the ozone availability is fixed for a given ozone flow rate resulting in reduction of the percentage COD

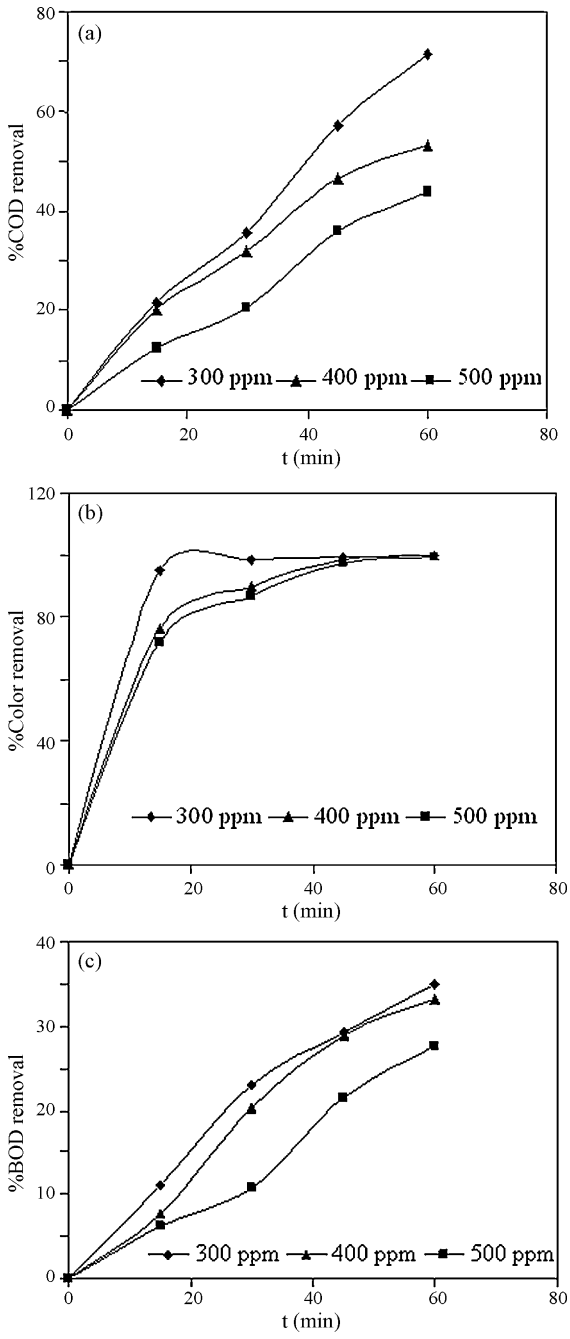


**Fig. 3.** Variation of percentage (a) COD, (b) color removal and (c) BOD of direct brown dye with ozonation time. Solution pH: 11; ozone flow rate: $6 \times 10^{-3}$ $m^3$ $min^{-1}$.

removal. Similar observation has been recorded for the percentage color removal [Fig. 3b]. Fig. 3c shows the percentage BOD reduction with ozonation time. It can be noticed that a maximum of 35 percentage of BOD reduction has been achieved during 60 min of ozonation.

Fig. 4 shows the variation percentage COD removal with ozonation time for tannery effluent. It can be noticed from Fig. 4a that the percentage COD removal increased gradually with process time and a maximum value of 70% has been obtained around 90 min of ozonation. Further continuation of ozonation did not yield any significant improvement in percentage COD reduction. It can be further ascertained from the figure that the initial effluent concentration has significant impact on the ozonation efficiency. For example, the percentage COD removal has reduced from 60%

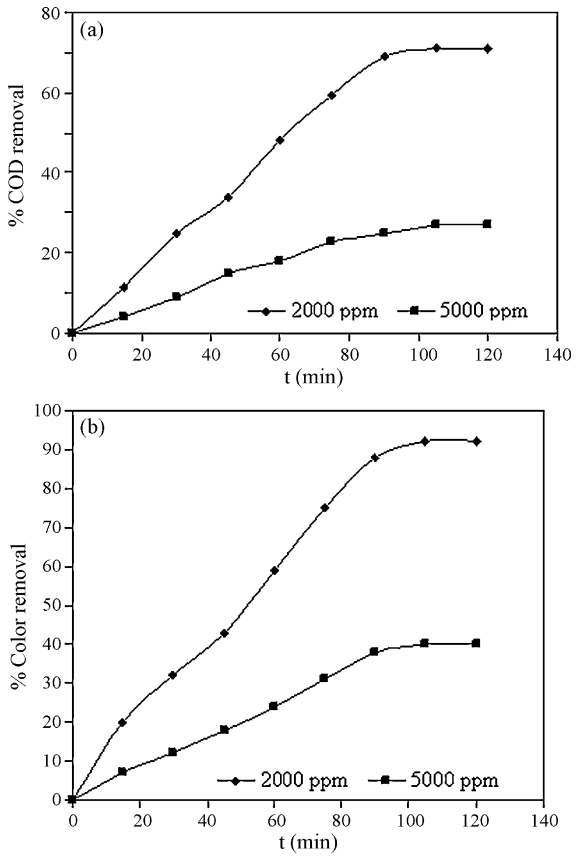


**Fig. 4.** Variation of percentage (a) COD, (b) color removal for tannery effluent with ozonation time. Solution pH: 11; ozone flow rate: $6 \times 10^{-3}$ m$^3$ min$^{-1}$.

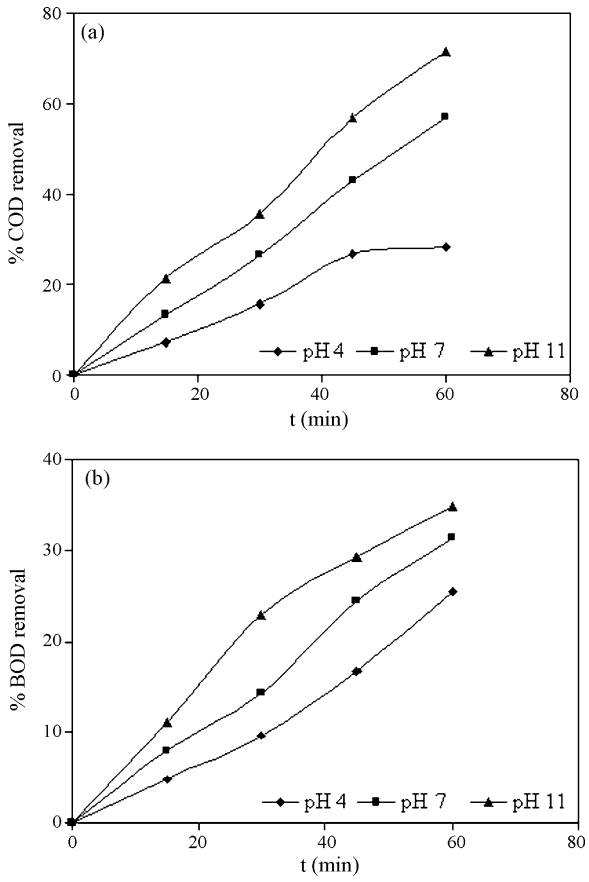


**Fig. 5.** Effect of effluent pH on percentage (a) COD, (b) BOD reduction for dye effluent. Initial effluent concentration: 300 mg l$^{-1}$; ozone flow rate: $6 \times 10^{-3}$ m$^3$ min$^{-1}$.

to 20% when the effluent concentration increased from 2000 to 5000 mg l$^{-1}$ for a given 80 min of ozonation. As explained earlier, this can be attributed due to the increased ozone consumption with an increase in the initial effluent for a given operating conditions, as the ozone availability is fixed for a given ozone flow rate resulting in reduction of the percentage COD removal.

To evaluate the effect of solution pH, experiments were conducted covering acid, neutral and basic conditions [Fig. 5]. It can be seen from Fig. 5a that the percentage COD removal increased with an increase in the solution pH and the maximum COD removal has been observed at a pH of 11. The ozone decomposition is directly affected by the solution pH. Hydroxyl radicals are formed from ozone decomposition at higher pH, while the molecular ozone remains as the main oxidant at low pH values. The extent of decolorisation is favored by the direct ozone attack, at low pH values, since molecular ozone is selective for the destruction of chromophore groups [6]. The hydroxyl radicals have a higher oxidizing potential and are less selective than molecular ozone, leading to a decrease in decolorisation an increased mineralization at higher pH. It can be ascertained from the figure that the percentage COD removal increased from 65% to 90% when the solution pH increased from 4 to 11. Similar observation has been recorded for percentage BOD reduction [Fig. 5b].

Fig. 6 shows the effect of ozone flow rate on percentage COD removal for dye effluent. It can be noticed from Fig. 6 that increasing the percentage COD removal increased significantly with an increase in the inlet ozone concentration. Noticed from Fig. 6 that the percentage COD removal increased from 50% to nearly 65% when the ozone flow rate increased from $2 \times 10^{-3}$ to $4 \times 10^{-3}$ m$^3$ min$^{-1}$ for a given ozonation time of 60 min. This can be explained that the volume of effluent to amount of ozone available for oxidation decreased with increase in the ozone flow rate for a given operating conditions resulting increased percentage COD reduction and color removal.

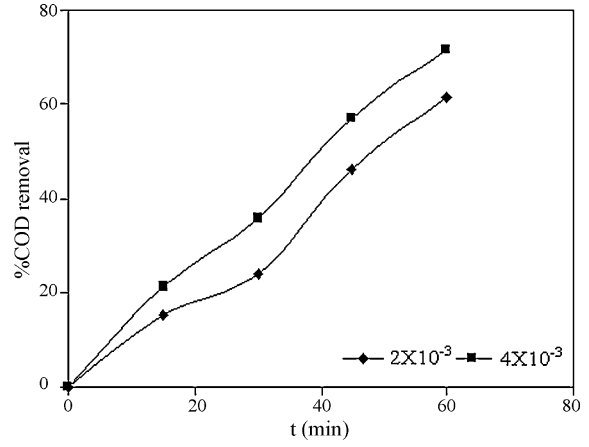


**Fig. 6.** Effect of ozone flow rate on percentage COD removal for dye effluent. The solution pH: 11; initial effluent concentration $C_i$: 300 mg l$^{-1}$.

## 4. Reaction kinetics of ozonation

The reaction kinetics of ozonation can be determined with the assumption that the resistance of the ozone transfer from gas phase to liquid phase is insignificant and the ozone consumption rate is determined solely by the rate of chemical reaction in the bulk [7].

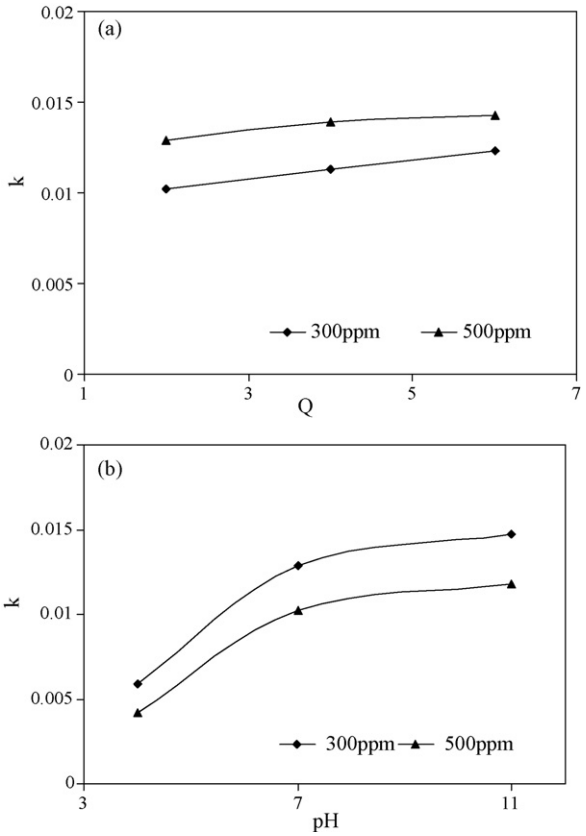


**Fig. 7.** Variation of pseudo-first order reaction kinetics with (a) ozone flow rate; (b) electrolyte pH for ozonation of direct brown dye effluent.

The reaction kinetics of dye ozonation can be related to the pollutant concentration and the amount of ozone present in the system,

$$\frac{-d[\mathrm{COD}]}{dt} = k[C][\mathrm{O_3}] \quad (1)$$

where '*C*' refers the effluent concentration. Since the generation of ozone is constant for a given condition, Eq. (1) can further be simplified to pseudo-first order kinetics as

$$\frac{-d[C]}{dt} = k[C] \quad (2)$$

The integration of Eq. (2) results

$$\ln\frac{[C]_o}{[C]_t} = kt \quad (3)$$

where $k$ refers the pseudo-first order rate constant. The rate constant $k$ was estimated by minimizing error between the experimental data and the model prediction by minimizing the Root Mean Square Error (RMSE), using the following equation:

$$\mathrm{RMSE} = \left[\frac{1}{n}\sum(\mathrm{exp.} - \mathrm{pred.})^2\right]^{0.5} \quad (4)$$

The reaction rate constants have been evaluated and the effect of individual parameters on reaction rate constant is given in Fig. 7. It can be noticed from Fig. 7a that the reaction rate constant increases with an increase in the solution pH. As stated earlier, the ozone oxidation of dye effluent occurs both by direct oxidation by generated ozone and radical oxidation by $OH^-$ radical. The direct oxidation by ozone is more selective and predominates in acidic conditions, while radical oxidation is less selective and predominates under basic conditions. However it can be noticed from Fig. 7a that the reaction rate constant increased significantly when the solution pH increased from 4 to 7 and a marginal increase in the rate constant when the solution increased from 7 to 11. The steep raise in reaction rate constant is due to contribution of both the ozone and $OH^-$ radicals from pH 4 to 7 while the marginal increase of reaction rate constant may be due to increased activity of solution pH alone.

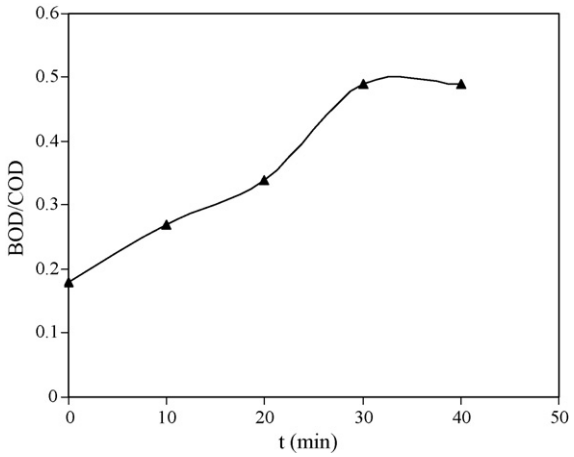


**Fig. 8.** Effect of ozonation on biodegradability for tannery effluent. The solution pH: 11; effluent concentration $C_i$: 2000 mg $l^{-1}$; $Q$: $\times 10^{-3}$ $m^3$ $min^{-1}$.

Fig. 7b shows the variation of reaction rate constant with ozone flow rate. It can be ascertained that the reaction rate constant increased with an increase in the ozone flow rate. This can be attributed due to the ratio of effluent to ozone decreased with an increase in the ozone flow rate resulting increased reaction rate constant. This can be further confirmed with the reduction in the reaction rate constant with an increase in the initial concentration of the effluent.

It has been reported that effluent having BOD/COD value of 0.4 and above can be treated efficiently by biological methods [8]. The bio-degradability index was found to be 0.18 for the tannery effluent. The bio-degradability index has been estimated during ozonation of tannery effluent and the variation of bio-degradability index with process time is shown Fig. 8. It can be noticed that the bio-degradability index increased to more than 0.4 within 30 min of ozonation. Continuation of ozonation beyond 30 min did not show any significant improvement in bio-degradability index. It has been reported that substances whose BOD/COD value of about 0.4 would be treated efficiently by biological methods. This observation shows that the ozonation can be used as a primer to biochemical process to enhance the oxidation efficiency.

## 5. Conclusion

The present study aimed to evaluate ozonation of dye and tannery effluent for removal of color and COD and enhance the biodegradability. Experiments were carried out using direct brown dye effluent and tanning wet process effluent covering wide range in the operating conditions. The following conclusions can be made based on the present investigation:

- The percentage COD removal is significantly influenced by the initial effluent concentration and ozone dosage on both dye and tannery effluent.
- The ozonation of dye and tannery effluent is found to follow pseudo-first order kinetics.
- The reaction rate constant is influenced by the operating initial effluent concentration, pH and ozone dosage.

- The biodegradability factor has been increased to more than 0.4 within 30 min of ozonation, which indicates the suitability of this method as a pretreatment for conventional biological method for effective degradation of color and COD.

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