

# INVESTIGATION ON TREATMENT OF TANNERY EFFLUENT THROUGH OZONATION

by

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## ABSTRACT

Experiments were conducted on treatment of leather effluent by ozonation covering wide range in operating conditions. The influence of parameters such as influent pH, ozone flow rate and initial effluent concentration on ozonation efficiency has been critically examined. A maximum of COD removal efficiency of 92% has been achieved under optimum operating conditions. The ozonation of leather effluent has been modeled using pseudo first order kinetics. It has been observed from the present investigation that the biodegradability index of the tannery effluent has increased from an initial value of 0.18 to 0.49 due to ozonation indicating favorable adaptation of the technique as primer for biochemical methods.

## RESUMEN

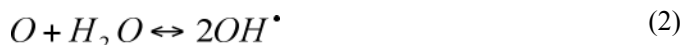
Experimentos fueron efectuados en tratamientos de los efluentes de curtición por ozonización abarcando una amplia gama en las condiciones de operación. El efecto de parámetros tales como el pH a la entrada, la tasa de flujo del ozono y como la concentración inicial del efluente afecta la eficiencia de ozonización han sido críticamente examinadas. Ha sido determinada en la presente investigación que un máximo de eficiencia del 92% del DQO es removible bajo condiciones de operación óptimas. La ozonización del efluente proveniente del cuero ha sido modelada cinéticamente por utilización de pseudo-primer orden. Ha sido observado en esta investigación que el índice de biodegradabilidad del efluente de las curtiembres ha sido aumentado de un valor inicial 0,18 hasta 0,49 debido al la ozonización indicando una favorable adaptabilidad de esta técnica como primer guía de métodos bioquímicos.

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## INTRODUCTION

The leather industry can be one of the more polluting industries in terms of volume and complexity of the effluent discharge.<sup>1</sup> The transformation of the raw hide into leather involves several processes, includes soaking, liming, bathing, pickling, tanning, etc. Each process in tannery industry often consumes large amount of water and generates significant quantity of wastewater. Tannery effluent is characterized to have high BOD, COD and strong in color,<sup>2</sup> which cannot be released into the environment without proper treatment.<sup>3,4</sup> Conventionally the tannery effluent is treated with primary treatment for removal of suspended solids, oil and fat followed by biological treatment (secondary treatment) for removal of colloidal organic matter and activated sludge process<sup>5</sup> for the removal of COD and color. Due to the large complexity of the leather effluent, most of the traditional methods are becoming inadequate. Several advanced oxidation processes (AOP) such as photochemical, ozonation, electrooxidation etc., have been experienced a widespread applications in the treatment of various industrial wastewater.<sup>6</sup> Among the advanced oxidation processes, ozonation has been receiving greater attention due its unique advantages such as complete degradation of pollutant, no generation of secondary pollutants, easy in scale-up and adaptability for large scale operations.<sup>7-9</sup>

Ozone is a powerful oxidant reacts with organic and inorganic compounds either by a direct reaction of molecular ozone ( $O_3$ ) or through a radical type reaction<sup>10</sup> involving the hydroxyl radical ( $OH^\bullet$ ), i.e.,



The above reactions occur simultaneously and the chromophor groups in leather effluent are broken into smaller molecules. Ozonation can also be used to improve the biodegradability and in turn the efficiency of biochemical processes.<sup>11</sup> The objective of this present investigation is to treat the tannery effluent by ozonation. The ozonation kinetics and the enhancement of biodegradability of the tannery effluent are also addressed.

## MATERIALS AND METHODS

The schematic representation of the experimental set-up shown in Figure 1 consists of an acrylic cylindrical column of 2.5cm internal diameter and 30cm height packed with glass beads of 5mm diameter. The oxygen/ozone mixture

was continuously introduced into the column through a porous diffuser plate placed at the bottom of the column. The tannery effluent has been collected from tannery department of Central Leather Research Institute (CLRI) and its characteristics are given Table 1. Experiments were carried in semi batch mode, i.e. continuous supply of ozone for a batch of liquid effluent. The effluent pH was adjusted using hydrochloric acid/sodium hydroxide. The un-reacted ozone leaving the column was scrubbed in 2% KI solution and titrated against standard thiosulfate. Effluent samples were withdrawn at regular intervals of time and analyzed for COD, color and BOD using standard estimation procedure. The UV scans of the samples were performed using UV-vis spectrophotometer [Shimadzu Model UV 160] at 200nm to 800nm. The percentage COD removal and the biodegradability index have been calculated for each experimental run. The biodegradability of the treated effluent has been calculated with BOD/COD ratio analysis.

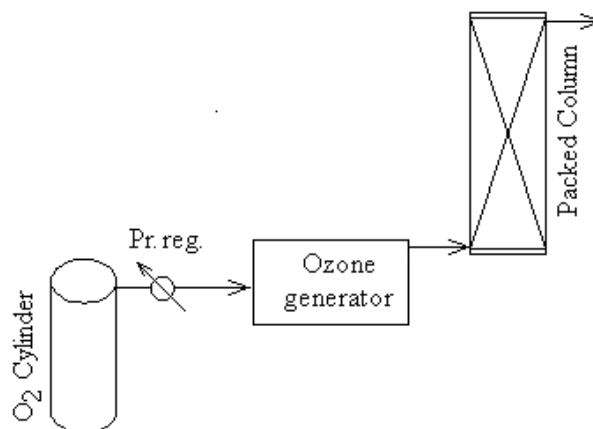


Figure 1. – Schematic representation of experimental set-up.

## RESULTS AND DISCUSSION

Experiments were carried out covering wide range in operating conditions and the results are presented in Figures 2-5. It can be ascertained from Figure 2a that the percentage COD removal is more or less linear with ozonation time and more than 70% of COD removal occurred within 90minutes. This is obvious that the ozone passes through the reactor containing batch of leather effluent where the ozone reacts with the effluent continuously resulting increased percentage COD with ozonation time. Further it can be ascertained from Figure 2a that the percentage COD removal decreases with an increase in initial effluent concentration. The percentage COD removal reduced from 60% to 20% when the effluent concentration increased from 2000ppm to 5000ppm for a given 80minutes of ozonation. Similar observation has been recorded for color removal [Figure 2b].

Wei and Chi-Wai reported<sup>12</sup> that hydroxyl radicals are formed from ozone decomposition at higher pH and molecular ozone remains as the main oxidant at low pH. The extent of decolourisation is favoured by the direct ozone attack, at low pH values, since molecular ozone is selective for the destruction of chromophore groups. The Figure 3 shows the influence of solution pH on the efficiency of ozonation. It can be ascertained that the maximum percentage of COD removal has been observed at pH value of 11 as the hydroxyl radicals (equation 2) have more oxidizing potential. Similar observation has been recorded for the color removal [Figure 3b].

**TABLE I**

**Characteristics of tannery effluent**

Characteristics	Value
pH	8.4
COD	5000 mg <sup>l</sup> <sup>-1</sup>
Suspended solids	4200 mg <sup>l</sup> <sup>-1</sup>
Dissolved solids	10000 mg <sup>l</sup> <sup>-1</sup>

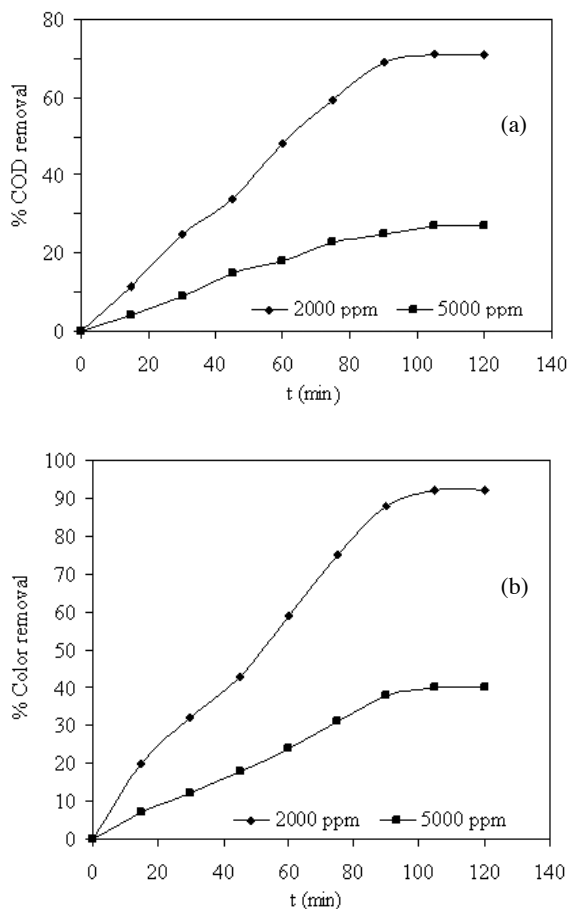


Figure 2. – Variation of percentage on (a) COD, (b) Color removal with ozonation time. Solution pH: 11; ozone flow rate: 6lpm.

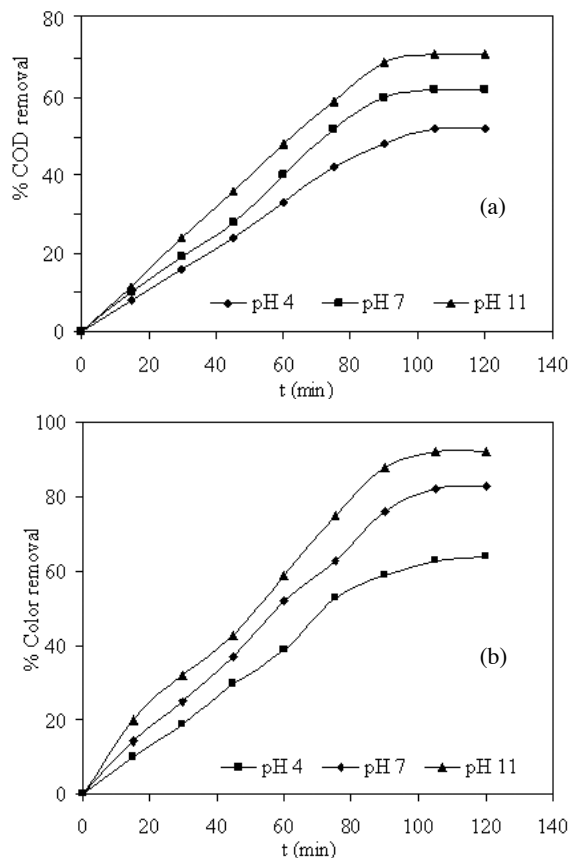


Figure 3. – Effect of initial effluent pH on percentage (a) COD, (b) Color removal. Initial effluent concentration: 2000ppm; ozone flow rate: 6lpm.

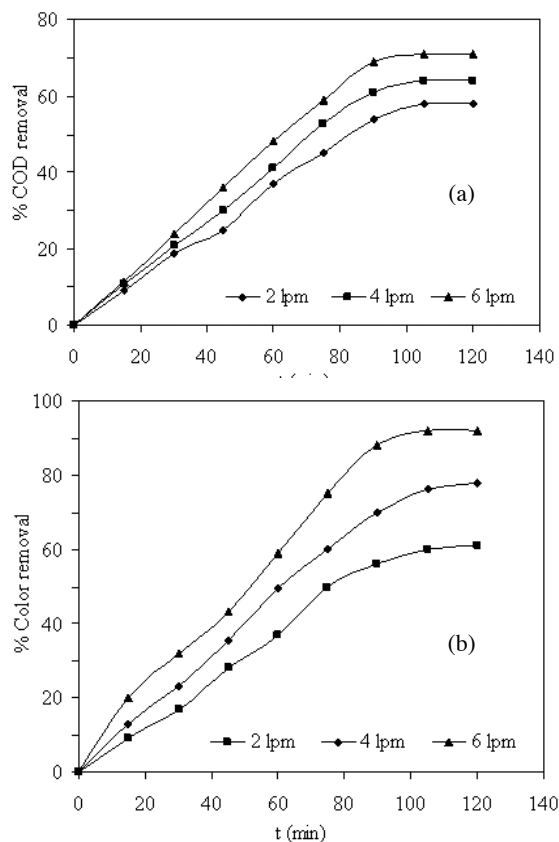


Figure 4. – Effect of ozone flow rate on (a) COD, (b) Color removal. Solution pH:11; initial effluent concentration:2000ppm.

The Figure 4 shows the effect of ozone flow rate on percentage COD removal. It can be noticed that the percentage COD removal significantly influenced by the ozone flow rate. This can be explained that the ratio of effluent volume to ozone availability decreases with an increase in the ozone flow rate resulting improved percentage COD reduction. It can be noticed from Figure 4a that the percentage COD removal increased from 50% to nearly 70% when the ozone flow rate increased from 2lpm to 6lpm. Similar observation has been recorded for the color removal [Figure 4b].

In ozonation, the rate of COD removal can be related to the pollutant concentration and the amount of ozone present in the solution, i.e.,

$$\frac{-d[COD]}{dt} = k[COD][O_3] \quad (3)$$

Since the generation of ozone is constant for a given experimental condition, the equation (3) can further be simplified to

$$\frac{-d[COD]}{dt} = k[COD] \quad (4)$$

The integration of equation (4) gives

$$\ln \frac{[COD]_o}{[COD]_t} = kt \quad (5)$$

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), i.e.,

$$RMSE = \left[ \frac{1}{n} \sum (\text{exp.} - \text{pred.})^2 \right]^{0.5} \quad (6)$$

The reaction rate constants have been estimated for each experimental run. The effect of individual parameters on reaction rate constant is given in Tables 2 and it can be ascertained that the reaction rate constant k is significantly influenced by the operating parameters.

It has been reported<sup>13,14</sup> that effluent having BOD/COD value of 0.4 and above can be treated efficiently by biological methods. The Bio-degradability index has been found to be

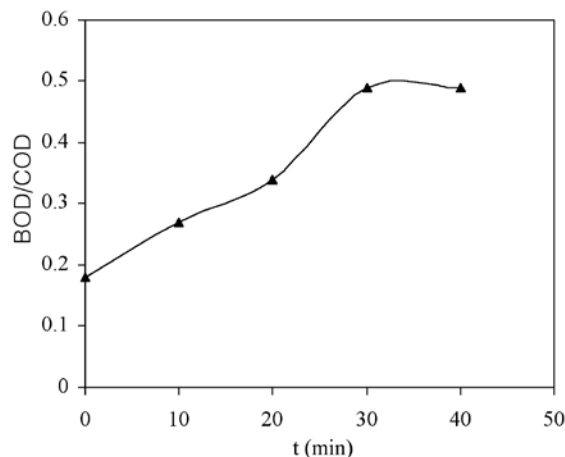


Figure 5. – Effect of ozonation on biodegradability for tannery effluent. The solution pH: pH=11; initial effluent concentration Ci: 2000ppm; ozone flow rate: 6lpm

0.18 for the tannery effluent used in the present investigation. The Bio-degradability index (BOD/COD) has been calculated for the ozonation process and given in Figure 5. It can be ascertained from Figure 5 that the Bio-degradability index increased to more than 0.4 within 30minutes of ozonation. Continuation of ozonation beyond 30 minutes did not show any significant improvement in Bio-degradability index. Aboulhassan *et al.*,<sup>15</sup> reported enhancement of biodegradability index of tannery effluent by conventional coagulant method. However, as stated earlier, this technique generate considerable solid sludge which itself needs further treatment. On the other hand, the ozonation improves the biodegradability within 30 minutes without generating any secondary pollutants. Hence the ozonation can be used as a primer to biochemical process to enhance the oxidation efficiency.

## CONCLUSION

Experiments were carried out on treatment of leather effluent using an ozonation covering a wide range of operating conditions. The influence of effluent initial concentration, pH and ozone flow rate on percentage COD removal has been critically examined. The following conclusions can be made from the present experimental observation

- The percentage COD removal is significantly influenced by the initial effluent concentration and ozone dosage.
- The biodegradability factor has been increased to more than 0.4 within 30 minutes of ozonation, which indicates the suitability of this method as a pretreatment for conventional biological method for effective degradation of color and COD.

TABLE II

Pseudo first order reaction rate constant for ozonation of tannery effluent.

Ozone Flow Rate	Effluent Concentration	Effluent pH	Rate Constant	RMSE
2	2000	4	0.0074	0.032
2	2000	7	0.0131	0.038
2	2000	11	0.0137	0.047
4	2000	4	0.0081	0.057
4	2000	7	0.0138	0.047
4	2000	11	0.0152	0.041
6	2000	4	0.0096	0.064
6	2000	7	0.0143	0.058
6	2000	11	0.0158	0.062
2	5000	4	0.0034	0.038
2	5000	7	0.0087	0.041
2	5000	11	0.0112	0.063
4	5000	4	0.0058	0.051
4	5000	7	0.009	0.046
4	5000	11	0.0112	0.047
6	5000	4	0.0068	0.047
6	5000	7	0.0113	0.037
6	5000	11	0.0124	0.066

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