OZONE PRE-OXIDATION OF A TEXTILE INDUSTRY WASTEWATER FOR ACUTE TOXICITY REMOVAL

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ABSTRACT

In this work, pre-ozonation for degradation, decolourization and detoxicifying of a raw textile wastewater collected in a textile fininshing industry, Istanbul (Turkey) is investigated. Differing from the previous studies, a low ozone (O_3) flow rate (9.6 mg min^{-1}) was applied at original pH of the wastewater. The effect of pH varying from 5 to 11 and the H_2O_2 dose of 600 mg l^{-1} on ozone oxidation were also investigated. The acute toxicity of raw and treated wastewater samples were measured using 24 h newborn *Daphnia magna*. COD, colour in APHA Pt-Co (platin-cobalt) unit and absorbance at 450, 500 and 550 nm wave lengths which were coinciding the peak absorbance band of the raw wastewater were analyzed in treated samples.

A 60% of acute toxicity, 92% of and 50% of total COD removal were obtained at original pH of wastewater by applying ozone for 30 min. Absorbed ozone dose was 105 mg l^{-1} with a ozone transfer rate of 3.5 mg l^{-1}. Varying pH did not improve toxicity removal, however, soluble COD removal increased at 3 and 6% respectively for 9.0 and 11.0 values while colour removal increased (7%) only at 11.0 pH. Adding 600 mg l^{-1} of H_2O_2 increased COD removal at 10% after 20 min oxidation. Colour removal increase was more significant in O_3/H_2O_2 oxidation in parallel with the increase in absorbance kinetics.

All over results obtained this study are expected to contribute to control the textile industry wastewater pollution and to protect aquatic environment.

1. INTRODUCTION

Textile industry originates a complex wastewater containing various chemicals used in the process such as dyestuff, surface-active materials and textile additives. Many azo dyes which cause intensive colour in the wastewater [1-5] and textile industry effluent [6-8] have been found to mutagen/carcinogen/toxic to aquatic organisms. Many advanced oxidation processes (AOPs) such as photocatalytic oxidation [9], Fenton [8] and Photo-fenton oxidation [10] have been applied individually or combined with UV, H_2O_2 oxidants to decolourize, detoxicify and degradate textile wastewater and dyes.

Ozone (O_3) oxidationas has been extensively studied to decolourise dyes [11] or pre-oxidation to enhance the biodegradability [12-14] or to reduce inert COD fractions [15] and toxicity removal [8,9,16] and post treatment of textile industry wastewater [17].
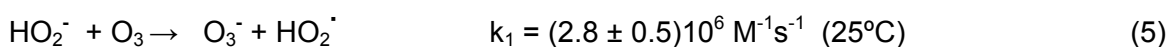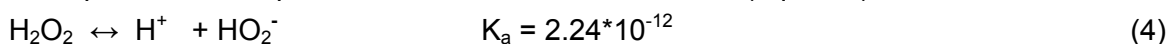
Both molecular ozone and especially hydroxyl radical (OH$^\bullet$) which is non selective oxidant forming decomposition of O_3 as explained by eqs (1-2), play an important role for the oxidation of organics [18]:

$$O_3 \leftrightarrow O + O_2 \tag{1}$$
$$O + H_2O \leftrightarrow 2OH^\bullet \tag{2}$$

These reactions occur simultaneously. The chromophor groups in textile dyes can be broken by ozone (directly or indirectly) forming smaller molecules resulting in colourless effluent [11]. The wastewater characteristics (i.e. pH, concentration of initiators, promoters and scavengers) play important role on the process efficiency, hence on the reaction kinetics. For instance, O_3 decomposes readily to $OH^\bullet$ radicals at high pH (11.0-12.0), while ozone reacts with OH^- and produces hydroperoxide radicals according to eq. 3:

$$O_3 + OH^- \quad \rightarrow \quad HO_2\bullet + O_2\bullet \qquad\qquad k = 70 \ M^{-1}s^{-1} \tag{3}$$

When ozone is used with H_2O_2 (weak acid), here ozone reacts both with H_2O_2 and HO_2^- which occurs much faster than H_2O_2. Thus, the reaction with H_2O_2 can be neglected and the eq. 5 and consequent reactions to form $OH^\bullet$ radicals (eqs. 6-7) are considered.

$$H_2O_2 \ \leftrightarrow \ H^+ \ + HO_2^- \qquad\qquad K_a = 2.24 \text{*} 10^{-12} \tag{4}$$

$$HO_2^- \ + O_3 \rightarrow \ O_3^- + HO_2^\bullet \qquad\qquad k_1 = (2.8 \pm 0.5)10^6 \ M^{-1}s^{-1} \ (25^oC) \tag{5}$$

$$O_3^- + \ H^+ \rightarrow OH + O_2 \tag{6}$$

$$HO_2^\bullet + O_3 \rightarrow OH^\bullet + 2O_2 \tag{7}$$

Because the reaction with $OH^\bullet$ radicals occurs much faster than that of O_3, the reaction with ozone is ignored for total reaction rate [13].

Although there exist intensive literature on O_3 oxidation of textile wastewater notated above, the toxicity removal by pre-ozonation, in particular, with the addition of H_2O_2 or pH varying has not been optimized due to wastewater characteristics in detail. In this study, pre-ozonation was attempted for detoxicifying, decolourizing and biodegradation of a textile finishing industry wastewater (Istanbul, Turkey). The effect of pH and H_2O_2 on ozone oxidation to remove toxicity was also investigated. *D. magna* as a standard and reliable toxicity testing method was used to optimize O_3 dose [4-6,8, 16,19].

2. MATERIALS AND METHODS
2.1. Sampling
Raw textile wastewater sample was taken from the process wastewater balancing tank of a textile industry in which cotton and polyester fabrics are dyed using reactive, dispersive dyes. The wastewater is originated from bleaching and dyeing processes. Total process wastewater originated from the industry is around 500 m^3 a day. The sample was delivered to the laboratory cooled and kept at 4 ^0C during experimental study. Toxicity tests were done within 1 day while chemical analyses were realized in 3 days after collection.

2.2. Ozonation (O_3)
O_3 was supplied by an air-ozone generator through a closed cylindrical pyrex glass reactor with a with a diameter of 40 mm and height of 1100 mm. A tubular cylindrical porous diffuser was replaced at the bottom of the reactor to transfer input O_3 gas into aqueous solution. Teflon tubing line was used for the connection between generator and the reactor (Figure 1). The appropriate O_3 concentrations were adjusted by changing the electrical current of the ozone generator. All experiments were performed at room temperature (25 ^oC) and at original pH of wastewater. After ozonation, the samples were aerated for 5 min to remove possible residual O_3. The O_3 concentrations in input and off-gas were destroyed by two sequential washing bottles containing 250 ml of acidified 2 % KI solution. Than, a sodium thyosulfite titration procedure in the presence of starch as the indicator was performed to measure O_3 concentration [20,21]. The transfered O_3 (TrO_3) was calculated as the following:

$$TrO_3 \ (mg \ l^{-1}) = \text{input } O_3 \text{ concentration} - O_3 \text{ concentration in off gas} \tag{8}$$

To avoid from the dilution errors during kinetics experiments, ozonation experiment repeated at time intervals under same conditions. The supernatants of the reactors were filtered

through 0.45 μm Millipore micro filter for COD, colour, absorbance and toxicity measurement. A low ozone dose (9.6 mg min^{-1}) was applied differing from the previous studies [8].

To evaluate the effect of pH which play important role in the process efficiency, in other terms, on the reaction kinetics [11,13], the original pH of wastewater adjusted to 5, 9 and 11.0 pH values and ozonated at the above described conditions for 10 min. Further, the effect of H_2O_2 addition to O_3 oxidation was investigated by adding 600 mg l^{-1} of H_2O_2 at original wastewater pH and the raw wastewater was ozonated for 20 min with the same O_3 flow rate.
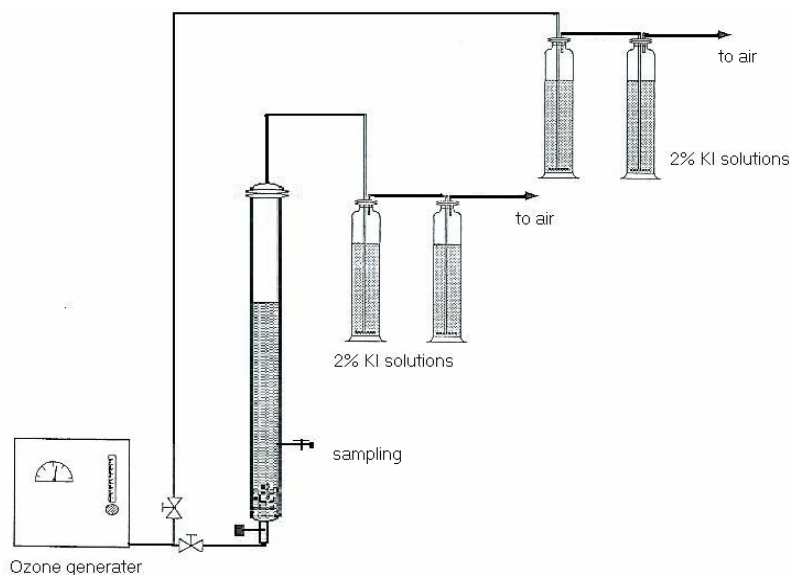

Figure 1. Ozonation set-up

2.3. Daphnia magna

The toxicity was measured using 24 h newborn *D. magna* at 50% dilution [22]. Raw and ozone pre-treated samples were tested within 2 h to avoid any effect of residual O_3 [23]. Daphnids were grown in the laboratory at 16 h day light and 8 h dark periods supplying a 3000 lux illumination [4,5,8]. They were fed with Selenastrum capricornutum (300.000 cell ml^{-1}) and baker's yeast (*Schizosaccharomyces cerevisiae*, 200.000 cells ml^{-1}). Room temperature was kept at 20°C $\pm$ 1°C and a minimum 6 mg l^{-1} of dissolved oxygen was supplied by air filtered through activated carbon. Experiments were carried out quadruplicate and 5 daphnids being used in each test beaker with 50 ml of effective volume. All solutions were prepared using bidistilled water at pH 8.0. Results were expressed as a percentage of immobilised animals after 24 h.

2.4. Analysis

COD was measured according to ISO6060 [24]. All other chemical parameters were measured according to Standard Methods [21]. Absorbance measurements were made using 1 cm cyristal cuvette in Pharmacia LKB-Novaspe II model spectrophotometer. HACH-Dr-B model spectrophotometer was used for colour measurements in Pt-Co unit. All chemicals used were of analytical grade. KI solution used for residual ozone titration was prepared daily.

3. RESULTS AND DISCUSSION
3.1. General

The characteristics of the raw wastewater are given in Table 1. The ammonia concentration was higher than 25 mg l^{-1}, was recorded 50% toxic to *D. magna* [25] for testing samples without dilutions. However, the raw water displayed 100% toxicity even at 50% dilution when the conductivity [6] and ammonia parameters were below the toxic limits. Therefore, the pre-ozone oxidation was considered to remove the toxic component such as dyes, were toxic on *D. magna* [4,5] or auxilaries, found toxic on *Vibrio fisheri* [7].

Table 1. Raw wastewater characteristics

Parameter		Unit	Value
Total COD		mg l^{-1}	1200
Soluble COD		mg l^{-1}	700
TSS		mg l^{-1}	250
TKN		mg l^{-1}	33
NH$_3$-N		mg l^{-1}	5
Total-P		mg l^{-1}	2
Conductivity		mS cm^{-1}	10000
Chloride		mg l^{-1}	1600
Sulphate		mg l^{-1}	590
Colour		Pt-Co unit	1060
Absorbance	450 nm	(m^{-1})	0.397
	500 nm	(m^{-1})	0.469
	550 nm	(m^{-1})	0,415
pH		--	7.8
Immobilization at 50% dilution		%	100

3.2. Ozone treatment and toxicity removal

As seen in Figure 1a, TrO$_3$ dose increased linearly during first 10 min and it was almost stable between 15 and 20 min than it continued to increase gradually up to 45 min. A cumulative TrO$_3$ concentration was found to be 140.6 mg l^{-1} at the end of 45 min. TrO$_3$ rate was 9.5 mg l^{-1} min^{-1} during first minutes tahn it decreased gradually up to 3.8 mg l^{-1} min^{-1} at the end of 20 min and to 3.125 mg l^{-1} min^{-1} at the end of the reaction (Figure 1b). Absorbances at 450, 500 and 550 nm were removed at a range of 90-95% during 25 min when 82.5 mg l^{-1} of ozone concentration was transferred. Absorbance removals at 450, 500 and 550 nm obeyed first order kinetic as seen in Figure 2. Absorbance removal rates (k) are given in Table 2.

Table 2. Absorbance kinetics for pre-ozonation

	450 nm	500 nm	550 nm
k (min^{-1})	0.103	0.158	0.206
R^2	0.94	0.92	0.81

Figure 3 illustrates the removal of soluble COD, colour (Pt-Co) and toxicity tested at 50% dilution of pre-ozonated wastewater. More than 90% of colour was removed during 10 min by 90 mg l^{-1} of TrO$_3$. Soluble COD removal fluctuated during oxidation. While a 40% of soluble COD removed during first 2.5 than it decreased to 5% at the end of 15 min. It increased again to 40% after 45 min. This fluctuation was observed in the previous study [16]. This phenomenon was attributed to rapid oxidation of suspended solids which contributed to the soluble COD by time. However, a gradual increase in toxicity removal was observed. Toxicity removal (60%) was lesser than color removal up to 25-30 min but i increased to 100% by soluble COD removal increase at the end of 35 min. This can be explained because the chromophor groups in textile dyes causing the effluent colour can be broken by ozone (directly or indirectly), forming smaller molecules resulting in colourless effluent [11] but the by-products which may be still toxic [8].
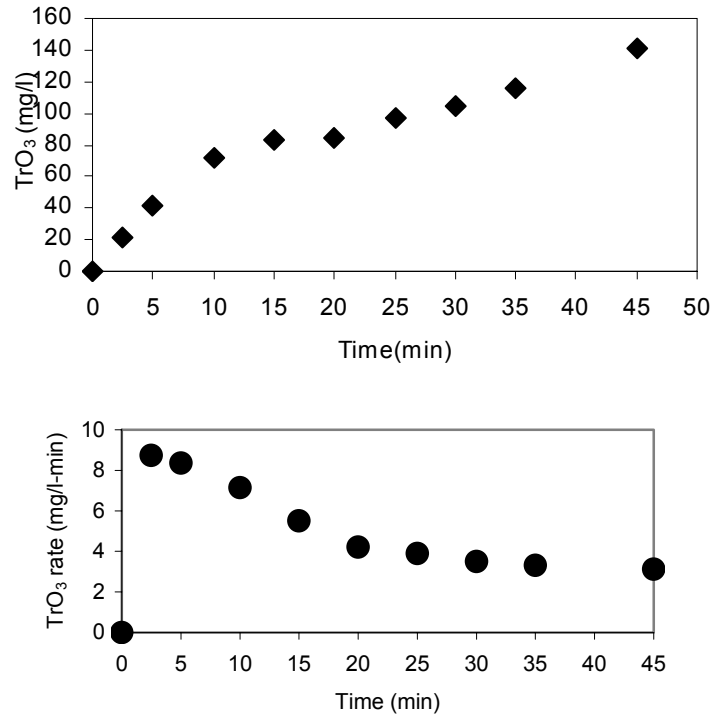
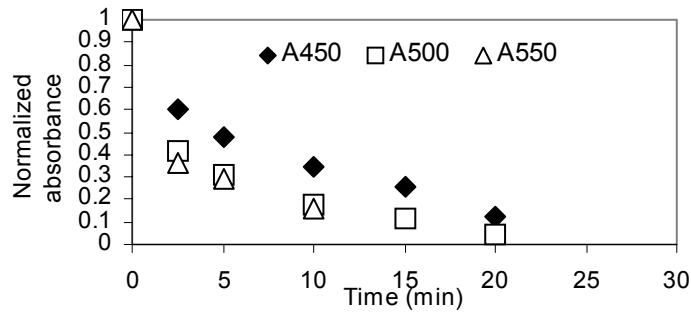*Figure 1.* Transfered ozone dose (a) and transfered ozone rate (b).
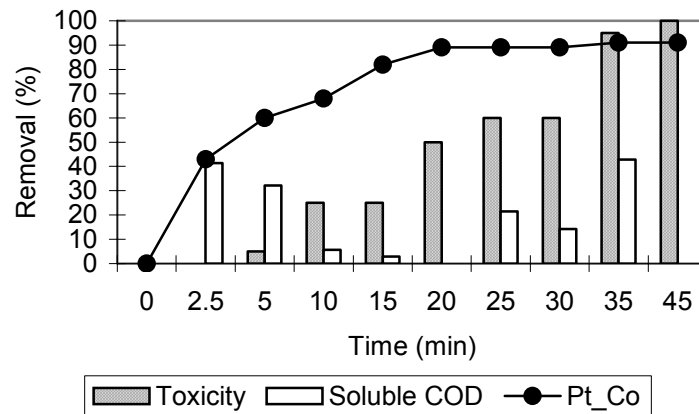

Figure 2. Normalized absorbance curves

Figure 3. Colour, soluble COD and toxicity reduction during O_3 oxidation

According to equations 5-7, the addition of H_2O_2 was expected to increase the removal of toxicity, COD and colour. However, toxicity removal did not improve during 20 min of ozonation at original pH of wastewater. On the other hand, there was a slight (from 6% to 7.1%) and significant (from 0 to 10%) COD removal improvement at the end of 10 and 20 min respectively. A higher colour removal was recorded starting from 5 min (66%) and it reached 89% at the end of 15 min where toxicity was also removed higher than that of O_3 oxidation alone. This result evidenced the relation between colour and toxicity removal [8] which seemed slightly related to COD [18]. Meanwhile, according to O_3 oxidation alone, there was significant improvement in absorbance removals (Figure 4). First order absorbance degradation kinetic constants at 450, 500 and 550 nm are shown in Table 3.

OH radical is the most powerful oxidant and its formation in the O_3/H_2O_2 system is much more faster than O_3 treatment. However, the pH affects the decomposition of H_2O_2 in the solution. Therefore, the optimization of the pH and the ratio of O_3:H_2O_2 dose should be detailed further. Besides, the applied O_3 dose as well as the oxidation time should be optimized to evaluate its contribution to toxicity removal, instead causing any toxicity increase in the effluent [5,12].
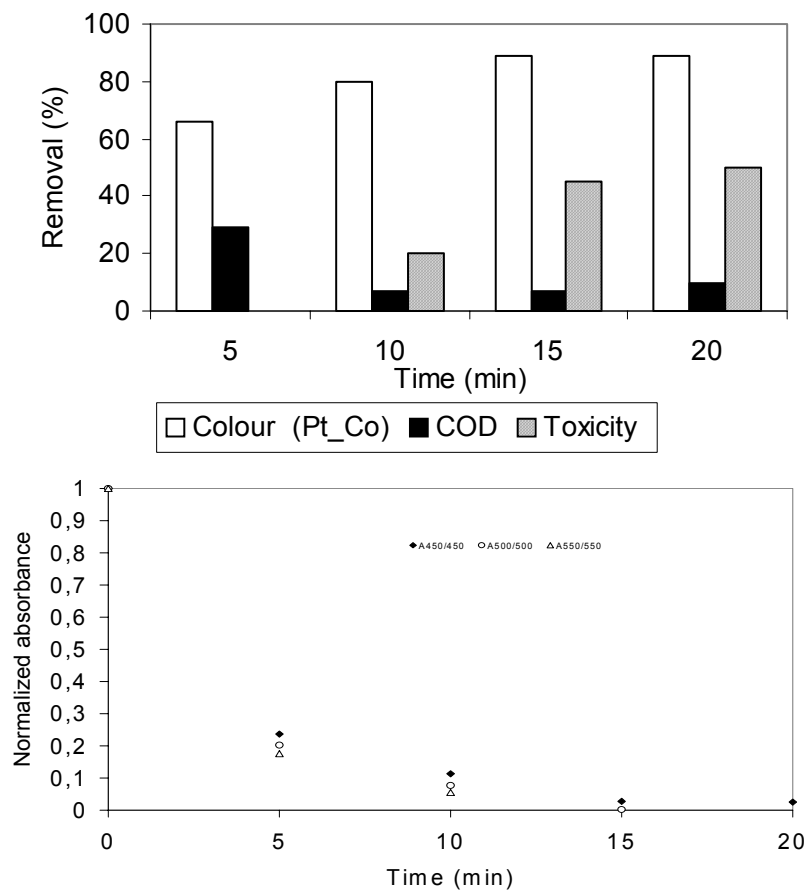

Figure 4. The effect of H_2O_2 addition on ozone oxidation at original wastewater pH
(a-removal of colour, soluble COD and toxicity, b-absorbance)

Table 3. Absorbance kinetics for O_3/H_2O_2 oxidation for 20 min

	450 nm	500 nm	550 nm
k (min^{-1})	0.206	0.3598	0.301
R^2	0.94	0.92	0.98

10 min ozonation at 5, 9 and 11.0 pH values did not improve the toxicity removal (0% at all pH values) as shown in Figure 5. The soluble COD removal was improved at 3% and 6% at 9.0 and 11.0 pH values, respectively with respect to O_3 oxidation alone. Because O_3 decomposes readily to OH• radicals at high pH (11.0-12.0) which are much more powerful than molecular

O_3, thus it favours higher TOC removal due to ozonation time [13]. However, no significant increase in this study can be attributed to the presence of Na_2CO_3, a considerable amount of $OH^\bullet$ radicals will be scavenged by CO_3^{2-} thus wasting $OH^\bullet$ oxidant [13]On the other hand, lesser colour removal was obtained at 5.0 and 9.0 pH values (48% and 60% respectively) while the colour removal was the same at 11.0 pH.
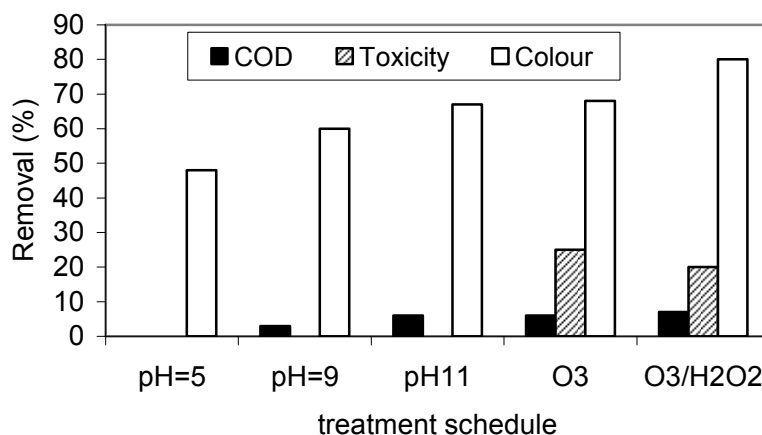

Figure 5. Comparison of colour, soluble COD and toxicity removal versus treatment

4. CONCLUSIONS
This study aimed to evaluate pre-ozonation at a low ozone dose for removal of acute toxicity as well as colour and COD in a textile industry wastewater. The effect of pH varying from 5 to 11 and the H_2O_2 dose of 600 mg l^{-1} on ozone oxidation were also investigated. Acute toxicity of raw and treated samples was monitored using 24 h new born *Daphnia magna* according to standard procedure.

- By applying 9.5 mg min^{-1} ozone dose rate for 20 min 60% toxicity removal was obtained at 50% dilution when >85% colour (Pt-Co) and >90% of absorbance removals were also achieved.
- To obtain 50% toxicity removal corresponding 50% removal when the sample will not diluted the sample had to be ozonated for 35 min when also >30% soluble COD was recorded.
- The fluctuation in COD removal was related to the rapid oxidation of suspended solids resulting in increased soluble COD.
- The composition of wastewater which is also related to the intensity of the colour, was related to the acute toxicity of the wastewater.
- Varying pH form 5 to 11 did not improve the toxicity neither colour removal.
- Addition of H_2O_2 increased the colour as well as absorbance removal.

The results obtained this study are expected to contribute to control the textile industry wastewater pollution and to protect aquatic environment. However, there is still need some further studies to optimize O_3 dose, and ratio of O_3/H_2O_2. Besides, these kind of studies are recommended to be supported by chronic toxicity experiments to improve the discharge standards.

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