The effect of pre-ozone oxidation on acute toxicity and inert soluble COD fractions of a textile finishing industry wastewater

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Abstract

The present work evaluates pre-ozonation for removal of acute toxicity, color and COD as well as reduction of inert soluble COD fractions in two wastewater samples (S1 and S2) taken from a textile finishing industry, located in Istanbul (Turkey). The wastewater samples were oxidized at original pH of 8.6–8.8 under 18.5–24 mg/L of applied ozone doses. Acute toxicity was monitored using *Daphnia magna*.

The results showed that pre-ozonation improved the biodegradability and reduced the acute toxicity. Acute toxicity in raw wastewaters was reduced by 80–90% using 129–200 mg/L transfered ozone (TrO_3) concentrations. At this point, 86–96% of color, 33–39% of soluble COD and 57–64% of total COD were removed from wastewaters. Both color and COD parameters were found related to the acute toxicity of the wastewater. Pre-ozonation decreased the inert soluble COD fraction (S_I) of raw wastewater while soluble product formation (S_P) increased slightly (5–10 mg/L). However, residual COD (the sum of S_I and S_P) remained below discharge limit.
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1. Introduction

The complex character of textile industry wastewater composed of dyestuff, surface-active materials and textile additives used in the processes needs to be handling carefully for both effluent toxicity and aesthetic problems. Textile wastewater treatment plant effluent [1–3] and many azo dyes [3–6] which cause the effluent color, have been found mutagenic/carcinogenic and toxic to aquatic life. Because the recalcitrants resist in biological treatment, many advanced oxidation processes (AOPs) such as photocatalytic oxidation [7], ultrasound [8], Fenton's oxidation (FO) [5,6,9] and photo-Fenton oxidation [10] and ozone oxidation have been attempted individually or combined with UV/H_2O_2 oxidants to decolorise, detoxify and enhance the biodegradability of textile wastewater and dyes [11–17]. Ozone oxidation being the most used

process, successfully enhanced the biodegradability of different recalcitrant/toxic pollutants [18,19].

O_3 can react with several classes of compounds through direct or indirect reactions (mainly, OH radical). Electrophilic attack by O_3 molecules may occur at atoms with a negative charge density (e.g. N, P, O or nucleophilic carbons) or to double/triple bonds like carbon–carbon, carbon–nitrogen, nitrogen–nitrogen [7]. Indirectly, O_3 can generate free hydroxyl radical ($OH^\bullet$) [20]. The hydroxyl radical is a powerful and non-selective oxidant that can react through three possible mechanisms: (i) hydrogen abstraction, (ii) electron transfer or (iii) radical addition after being generated according to following reactions.

$$O_3 \leftrightarrow O + O_2 \qquad (1)$$

$$O + H_2O \leftrightarrow 2OH^\bullet \qquad (2)$$

Both reactions occur simultaneously. The chromophore groups, absorbing visible light, are generally organic compounds with conjugated double bonds that can be broken by ozone (directly or indirectly) forming smaller molecules resulting in colorless effluent [7,11]. The wastewater characteristics (i.e., pH,

concentration of initiators, promoters and scavengers) play important role on the process efficiency, hence on the reaction kinetics.

Pre-ozonation was found to be effective to reduce inert COD fractions which provides information on biological treatability of textile industry wastewater because the type of the dyes and textile additives change continuously in the process [14,15]. Particularly, determination of soluble inert COD (S_I) of influent wastewater and soluble inert metabolic products (S_P) generated in the biological treatment gains importance to meet the stringent discharge limits and aquatic toxicity (>250 mg/L of COD and 3–4 dilution factor to fish defined in Turkey). A significant decrease in S_I was reported by increasing pre-ozonation times [15]. Pre-ozonation was found to be effective also on the other types of COD factions such as particulate inert COD (X_I), slowly biodegradable COD (S_H) and particulate slowly biodegradable (X_S) [15]. At a low ozone dose applied to textile industry wastewater, S_I removal remained limited and it was assumed that ozonation selectively favours the readily biodegradable COD compounds, as the ozone dose is increased, S_I removal is accomplished together with breakdown of the slowly biodegradable COD components [15].

The process efficiency of many different chemicals including textile industry wastewater and dyes by AOPs, mainly ozone which are expensive, has been optimized by different organisms such as *Vibrio fisheri* or Microtox [13,19], *Esherichia coli* [7] and *Daphnia magna* [5,6,9,21–23] which is as a standard [24] and reliable toxicity testing method while biodegradability depends heavily on the biomass selected and the results obtained are usually difficult for other researchers to reproduce [22].

This study investigates the effect of pre-ozonation on color removal, biodegradation and inert soluble COD fractions in a textile finishing industry wastewater at the conditions optimized by means of acute toxicity reduction which was measured using *D. magna*. A part it contributes to knowledge on this subject, it differs from the previous studies by its multi-disciplinar approach to explain the wastewater characteristics, biodegradation character and acute toxicity relations in textile industry wastewater. The results indicated the importance of toxicity-based optimization of pre-ozonation to prevent the aquatic environment for the case of discharge before submitted to biological treatment of wastewater, and to comply with the stringenthening discharge limits for this widespread and essential industrial sector.

2. Materials and methods

2.1. Characterization of the industry

In the industry, located in Istanbul (Turkey), cotton and polyester fabrics are dyed using reactive, dispersive dyes. The annual capacity of the industry is 2020 tonnes of cotton and polyester fabrics. One hundred and thirty employees work as three shifts a day, and 6 days a week. The wastewater resources are the bleaching and dyeing units for cotton processing and dyeing of synthetic fabric. Total process wastewater originated from the industry is around 500 m^3/day.

2.2. Sampling and conservation

Raw textile wastewater samples (S1 and S2) were taken from the process wastewater balancing tank. The samples were delivered to the laboratory cooled and kept at 4 °C during experimental study. Toxicity tests were done within 1 day while chemical analyses were realized in 3 days after collection.

2.3. Ozonation

Ozone was generated from air by ozone generator. A closed cylindrical pyrex glass reactor with a diameter of 40 mm and height of 1100 mm was used in the ozonation experiments (Fig. 1). A tubular cylindrical porous diffuser was placed at the bottom of the reactor to transfer input ozone gas into aqueous solution at the regular intervals. Teflon tubing line was used for the connection between ozone generator and the reactor. The appropriate ozone concentrations were adjusted by changing the electrical current on the ozone generator. All experiments were performed at room temperature (25 °C) and at original pH of wastewater using 1 L aqueous solution [25]. A foam preventer was added into the reactor to avoid from foam forming during oxidation. An 18.5–24 mg/L of ozone dose was applied for ozonation experiments with an air flow rate of 0.566 m^3/h.

After ozonation, the samples were aerated for 5 min to remove possible residual ozone because residual ozone could not be measured in short ozonation period due to color problem. The ozone concentration in input gas and in 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 [26] was performed to measure ozone concentration. Hence, the transferred ozone
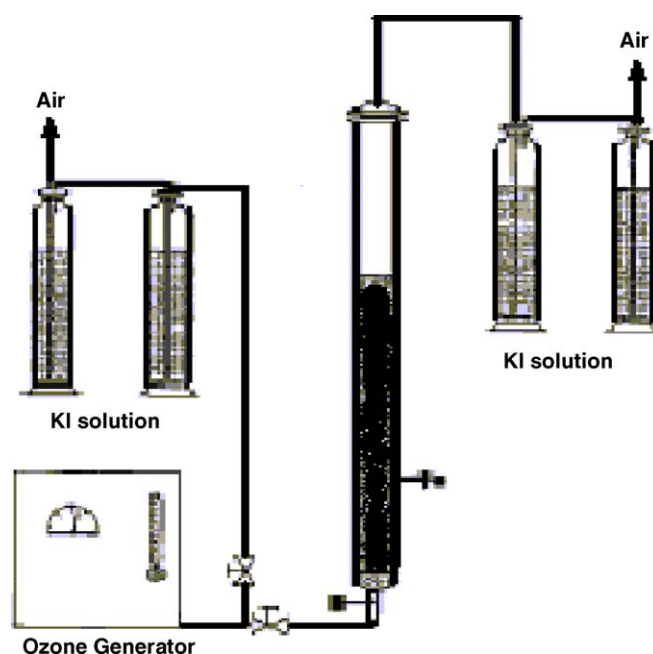

Fig. 1. Experimental set-up.

(TrO$_3$) was calculated as:

TrO$_3$ (mg/L) = input O$_3$ concentration

$$- \text{O}_3 \text{ concentration in off gas} \qquad (3)$$

To avoid dilution errors during kinetics experiments, ozonation experiment repeated a few times under same experimental conditions. The samples were withdrawn from the reactors at each time interval for COD, color, absorbance and toxicity measurement after filtered through 0.45 μm Millipore micro filter.

2.4. Determination of COD fractions

Four aerated cylindrical batch reactors, one fed with the unfiltered raw wastewater (R1, C_{TO}), second with raw wastewater (S_{TO}) filtered through 0.45 μm filter paper (R2), third fed with pre-ozonated total wastewater (R3) after 30 min oxidation, and the fourth fed with pre-ozonated filtered wastewater (R4), were used. The seed was obtained from a lab-scale fill-draw aerobic reactor operated under steady-state with the same wastewater. An initial biomass concentration of 50 mg VSS/L was sustained in all reactors. Aliquots were removed periodically from the mixed liquor and analyzed for total and soluble (filtered) COD. Data were collected until the COD profiles reached a plateau. Any water loss from the reactors by evaporation was replaced by adding distilled water before measuring COD. The experiment was concluded at a point where the threshold level was established as less than 3–5% variation between consecutive samples [27,28]. At this stage the supernatant samples were also taken from both reactors to conduct the toxicity tests [28,29].

2.5. Daphnia magna

The toxicity was measured using 24 h newborn D. magna at different dilution rates [6,24]. Raw and pre-ozonated samples were tested within 2 h. Daphnids were grown in the laboratory at 16 h day light and 8 h dark periods supplying a 3000 lux illumination. They were fed by Selenastrum capricornutum (300,000 cells/mL) and baker's yeast (Schizosaccharomyces cerevisiae, 200,000 cells/mL). All solutions were prepared in bidistilled water at pH 8.0. Room temperature was kept at 20 ± 1 °C and minimum 6 mg/L of dissolved oxygen was supplied by air filtered through activated carbon. Experiments were carried out quadruplicate and five daphnids were used in each test beaker with 50 mL of effective volume. Results were evaluated on the basis of immobilization percentage obtained by dividing the number of immobilized animals by total animals.

2.6. Analytic measurements

The samples were filtered through 0.45 μm membrane filter (Millipore) for measuring toxicity, COD, color in APHA platinum–cobalt (Pt–Co) unit and absorbances at 450, 500 and 550 nm wave lengths which is a color measuring range of textile industry wastewater [6,7,25]. COD was measured according to ISO6060 [30]. All other chemical parameters were measured according to Standard Methods [31]. Absorbance measurements were made using Pharmacia LKB-Novaspe II model spectrophotometer. HACH-Dr-B model spectrophotometer was used for color measurements. All chemicals used were of analytical grade. KI solution used for residual O$_3$ titration was prepared daily.

Removal efficiency of COD and color parameters were obtained according to formula given below.

$$\text{Removal}\,(\%) = \frac{C_0 - C}{C_0} \qquad (4)$$

where C_0 and C are the initial and final COD or color values of wastewater.

3. Results and discussion

3.1. General

The characteristics of the wastewater samples are given in Table 1. Color of S1 (3300 Pt–Co unit) was more intense than S2 (1000 Pt–Co). The high conductivity (9400 and 12,500 μS/cm for S1 and S2, respectively) of both samples was toxic to D. magna without dilution (effluent becomes toxic over 10,000 μS/cm [2]). Ammonia over 25 mg/L was found to immobilize more than 50% of D. magna [21]. Because both samples resulted in 100% toxic even when they were tested after 75% diluted at which the conductivity and ammonia parameters were below the toxic limits, therefore, the ozone oxidation was applied to oxidize the toxic organic content in the samples as well as for affecting the inert COD fractions of wastewater. The toxicity tests were performed at both 50 and 75% dilutions to evaluate the effectiveness of ozone oxidation for reduction of toxic component in detail in the wastewater.

Table 1
Raw wastewater characteristics of the textile industry

| Parameter	Sample 1 (S1)	Sample 2 (S2)
COD (mg/L)	1600	1560
Soluble COD (mg/L)	950	900
BOD$_5$ (mg/L)	150	170
TSS (mg/L)	750	250
VSS (mg/L)	330	190
TKN (mg/L)	70	16
NH$_3$–N (mg/L)	45	5
Total P (mg/L)	30	14
Conductivity (mS/cm)	9400	12500
Chloride (mg/L)	1650	1750
Sulphate (mg/L)	525	590
Alkalinity (mg/L)		470
Color (Pt–Co)	3300	1000
Absorbance at		
450 nm (cm^{-1})	0.91	0.28
500 nm (cm^{-1})	1.04	0.32
550 nm (cm^{-1})	0.71	0.27
pH	8.8	8.6
Immobilization at 75% dilution (%)	100	100
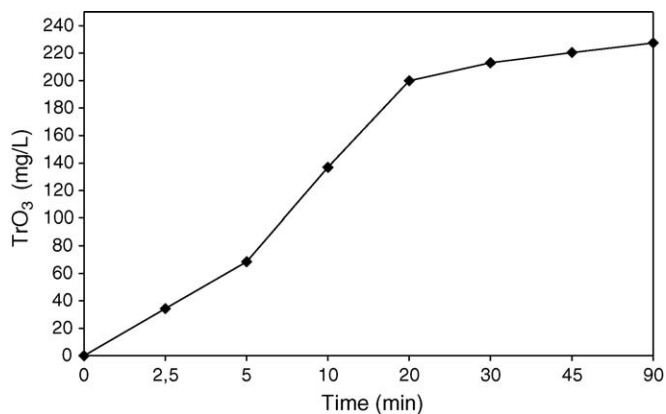
Fig. 2. Transferred ozone dose for S1 (initial ozone concentration = 24 mg/L-min).

3.2. O_3 oxidation and raw wastewater toxicity removal

Fig. 2 displays the usage of ozone in S1 under 24 mg/L applied ozone dose. TrO_3 dose increased linearly during first 20 min reaction period resulting in and 200 mg/L cumulative TrO_3 and 9.5 mg/L-min of ozone transfer rate. TrO_3 did not change much at the prolonged ozonation period and the cumulative TrO_3 concentration was found to be 227.52 mg/L up to 90 min. Absorbances at 450, 500 and 550 nm were reduced at a range of 85–90% during 5 min when 68.5 mg/L of ozone concentration was transferred. In this reaction time period, a first-order reaction kinetic rate expression was applied for the absorbance removal in raw wastewater. It was found that absorbance removals at 450, 500 and 550 nm obey first-order kinetic [23] which yielded 0.27 min^{-1} ($R^2 = 0.92$), 0.39 min^{-1} ($R^2 = 0.87$) and 0.50 min^{-1} ($R^2 = 0.88$) kinetic constants (k), respectively. Absorbance removals were over 95–97% at the end of 20 min of ozonation period (Fig. 3).

Fig. 4 illustrates the removal of soluble COD, color (Pt–Co) and toxicity tested at 50 and 75% dilutions of pre-ozonated wastewater (S1). This sample displayed 100% immobilization at both dilutions (Table 1). More than 95% of color was removed during 10 min by 140 mg/L of TrO_3 concentration. During first 2.5 min, soluble COD removal was insignificant and it remained
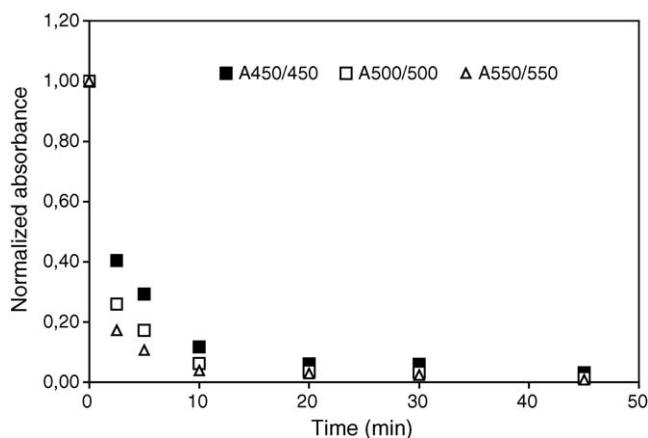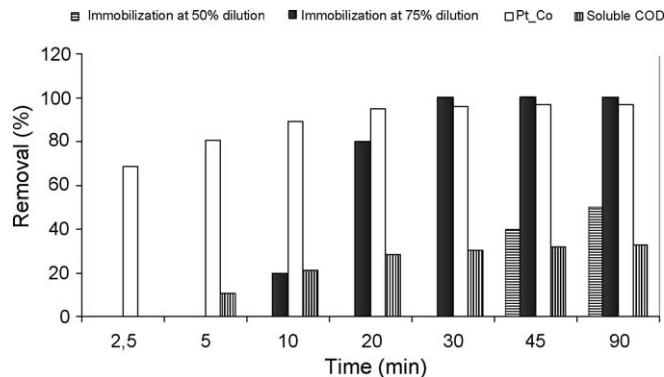

Fig. 4. Color (Pt–Co), soluble COD and toxicity (at 50 and 75% dilutions) removal for S1 by ozone.

constant (950 mg/L). It increased gradually up to 20 min of oxidation by increasing ozone dose and reached steady state condition at the end of 45 min with a 33% soluble COD removal. When the pre-ozonated S1 sample was tested at 50% dilution, its toxicity (immobilization) decreased 40 and 50% at the end of 45 and 90 min, respectively. However, an 80% of toxicity removal already obtained at the end of 20 min at 75% dilution that transfer of ozone was at the almost steady-state condition. Besides, at the end of 30 min of oxidation 75% diluted sampled did not display any toxicity (Fig. 4).

An 18.5 mg/L ozone dose was also applied for S2. As can be seen in Fig. 5, TrO_3 increased linearly in 30 min resulting in 4.3 mg/L-min of ozone transfer rate ($R^2 > 0.94$). The rate of TrO_3 continued to increase up after 30 min ozonation period. As can be seen from Fig. 6, not only the rate of TrO_3 rate but also absorbance removals at 450, 500 and 550 nm were very low according to these reported for S1. The kinetic constants of absorbances at 450, 500 and 550 nm were found to be 0.08 min^{-1} (R^2, correlation constant = 0.96) 0.10 min^{-1} ($R^2 = 0.77$) and 0.10 min^{-1} ($R^2 = 0.87$) in 20 min reaction time that they were 3–5 times lower than those were achieved for S1. The different TrO_3 doses for S1 and S2 can be explained by wastewater composition and the color intensity and also other varying ozone initiators, promoters and scavengers in textile industry wastewater. Consequently, 70–85% absorbance removals from S2 were

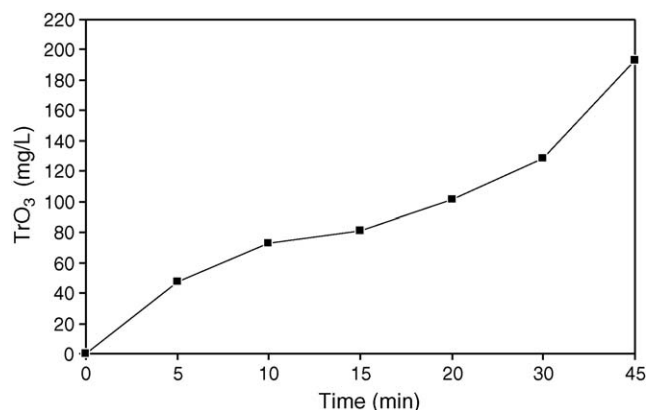Fig. 3. Normalized absorbances at 450, 500 and 550 nm for S1.

Fig. 5. Transferred ozone dose for S2 (initial ozone concentration = 18.5 mg/L-min).
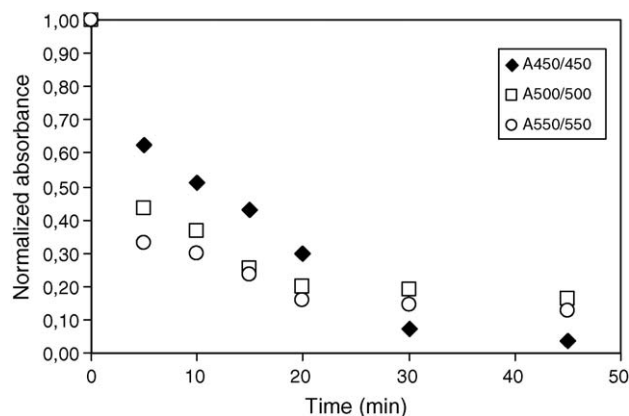
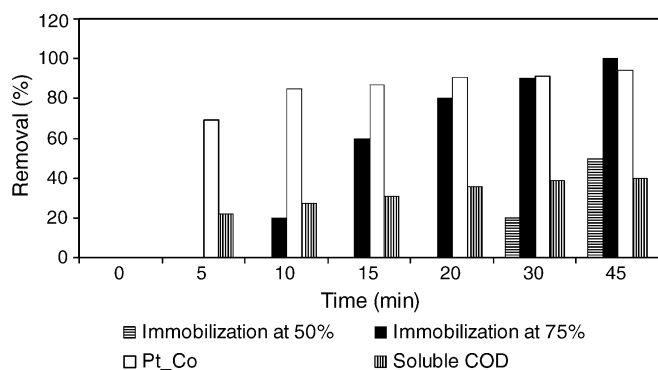Fig. 6. Normalized absorbances at 450, 500 and 550 nm for S2.

Fig. 7. Color (Pt–Co), soluble COD and toxicity (at 50% dilution) removal for S2 by ozone.

achieved in 20 min ozonation time while 85–90% absorbance removals were reported in 5 min for S1 under same experimental condition. Thirty minutes of ozone oxidation resulted in high absorbance removal (>90%) at 450 nm. As illustrated in Fig. 7, COD and color removals gradually increased. When TrO$_3$ dose reached 47.52 mg/L (5 min) a 70% of color removal was obtained. Maximum color removal (98%) was obtained at a 193 mg/L of ozone dose at the end of 45 min of oxidation. Soluble COD removal continued to improve by 15% between 5 and 30 min when a 39% COD removal was obtained; however, between 30 and 45 min, it remained constant. A 20% of

toxicity was removed after 10 min while at the end of 15 min a 60% of toxicity removal was obtained for 75% diluted sample. The toxicity of 75% diluted sample was removed completely after 45 min whereas a 50% of toxicity removal was recorded for 50% diluted sample (Fig. 7). The reason of starting of color and soluble removal before toxicity can be explained by the toxic colorless dye-ozonated by products formation [9,11] as well as wastewater characteristics (e.g. pH, concentration of initiators, promoters and scavengers) which may play important role in toxicity [32].

High toxicity removal (90%) obtained at higher dilution (75%) indicates that the composition of oxidized wastewater is affecting the toxicity test. However, testing samples at 75% dilution was indicative to evaluate the changes occurring in the wastewater composition. Thus, more than toxicity removal it was useful to define the ozonation condition for investigating the soluble inert COD fractions.

3.3. Effect of ozone on soluble inert COD fractions

The experimental conditions of inert COD fractions determination performed on S1 and S2 samples are shown in Tables 2 and 3 for raw and pre-ozonated wastewater, respectively. The calculation details of the inert COD fractions are given elsewhere [28,29]. The soluble inert fractions (S_I) of raw wastewater samples were found to be in the order of 15–16% of total COD. These values (280 and 255 mg/L, for S1 and S2, respectively) were in the range found in the previous studies [14,15]. The soluble microbial products (S_P) were found to be low as 10 mg/L for both samples (Fig. 8). In other words, the contribution of microbial products on residual COD ($S_R = S_I + S_P$) which varied in the range of 16–17% of the total COD, was not significant.

The values of S_I decreased by 33 and 32% for S1 and S2, respectively, due to pre-ozonation as shown in Fig. 8. On the other hand, pre-ozonation providing 85% color removal, but only 19% COD reduction at optimum contact time of 15 min for a textile industry raw wastewater, reduced S_I only at 7%, indicating selective preference of ozone for simpler compounds [14]. However, depending on wastewater characteristics, the ozone consumption and its effect on the removal of inert soluble COD fraction vary. In this study, at much lesser amount of consumed

Table 2
Reactor conditions for determination of inert COD fractions in raw wastewater

Sample no.	Raw total wastewater reactor (R1) (COD, mg/L)		Filtered raw wastewater reactor (R2) (COD, mg/L)	
	Total COD, C_T	Total soluble COD, S_T	C_T	S_T
S1				
Initial	1700	950	1020	945
End of experiment	450	290	325	285
Duration (h)	816	816	816	816
S2				
Initial	1685	1000	1070	995
End of experiment	360	265	305	260
Duration (h)	768	768	768	768

Table 3
Reactor conditions for determination of inert COD fractions in pre-ozonated wastewater after 30 min oxidation

Sample no.	Pre-ozonated total wastewater reactor (R3) (COD, mg/L)		Pre-ozonated filtered wastewater reactor (R4) (COD, mg/L)	
	Total COD, C_T	Total soluble COD, S_T	C_T	S_T
S1				
Initial	1100	850	920	850
End of experiment	330	210	250	205
Duration (h)	432	432	432	432
S2				
Initial	1000	795	835	790
End of experiment	255	190	200	187
Duration (saat)	504	504	504	504

Table 4
Comparison of COD removal and inert soluble COD fraction obtained by pre-ozone oxidation in textile industry wastewater

O_3 dose (mg/min)	Time (min)	TrO_3 (mg/L)	Initial total COD (C_{T1})	Total COD Rem. (%)	Soluble COD (mg/L)	Soluble COD Rem (%)	S_I/C_{T1} (%)	Reference
62	30	1385 (pH final = 8.08)	955	32	675	29	34	[15]
24	30	213	1600	35	950	10	17	This study (S1)
18.5	30	129	1560	39	900	11	18	This study (S2)

ozone with respect to previous study [15] as seen in Table 4. The same removal of total COD was obtained. However, because its S_I fraction was also too high (34% of total COD), higher ozone dose should be needed to reduce S_I effectively.

On the other hand, S_P increased slightly in both pre-ozonated samples (Fig. 8). It was explained that ozone prefentially attacks readily biodegradable COD, in other terms, pre-ozonation resulted in a significant decrease of readily biodegradable COD (S_S), generated a significant level of rapidly hydrolysable COD [14,15], thus, this causes increase in S_P also. However, this slight increase obtained in this study can be attributed to low soluble COD removal due to oxidation pattern of applying lower ozone dose than the literature [15]. Therefore, the decomposition of organic compounds to lower molecules took time and resulted in prolonged biosynthesis time, sequentially lesser microbial products are formed. This phenomenon can be assumed also an advantage of low ozone dose to meet the discharge limits.
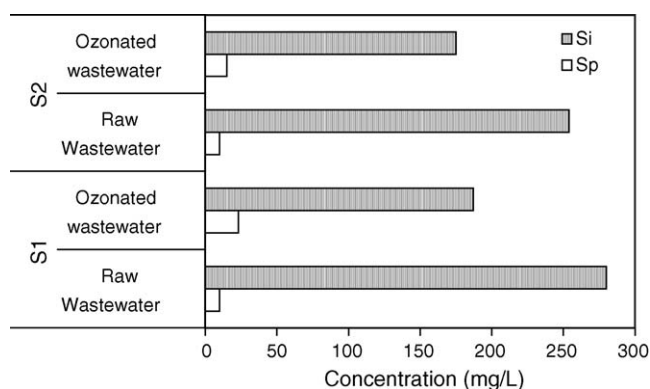
4. Conclusions

This study was designed to evaluate pre-ozonation for removal of acute toxicity as well as removal of color and COD in two textile industry raw wastewater samples (S1 and S2). The effect of pre-ozonation on inert soluble COD fractions which are important to meet to discharge limits, is also investigated. Acute toxicity was monitored using *Daphnia magna*.

Transferred ozone dose rates of 9.5 and 4.3 mg/L-min were achieved under the same applied ozone dose for S1 and S2 samples, respectively. A 30 min of ozone oxidation for both samples resulted in more than 80% toxicity removal at 75% dilution, >30% soluble COD, >85% color (Pt–Co) and >90% of absorbance removal. Pre-ozonation applied for 30 min decreased at the optimum doses decreased the inert soluble COD fraction (S_I) of raw wastewater while soluble product formation (S_P) for both samples increased slightly; however, residual COD (the sum of S_I and S_P) remained below discharge limit.

The results indicated that pre-ozonation effectively reduced acute toxicity which should be removed completely by a sequential biological treatment. The following studies performed in the same industry wastewater also for different sampling times, supported this point well (data not shown).

Fig. 8. Inert COD fractions variation in raw and ozonated samples.

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