The effect of pre-ozonation on the $\text{H}_2\text{O}_2/\text{UV-C}$ treatment of raw and biologically pre-treated textile industry wastewater

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Abstract Advanced chemical oxidation of raw and biologically pretreated wastewater by ozonation, $\text{H}_2\text{O}_2/\text{UV-C}$ treatment and the successive combination of ozonation and $\text{H}_2\text{O}_2/\text{UV-C}$ oxidation was investigated. For the raw textile wastewater, the application of successive $\text{O}_3 + \text{H}_2\text{O}_2/\text{UV-C}$ oxidation enhanced the COD and TOC removal efficiency of the $\text{H}_2\text{O}_2 (50 \text{mM})/\text{UV-C}$ process by a factor of 13 and 4, respectively. In case of the biotreated textile wastewater, the preliminary ozonation step increased COD removal of the $\text{H}_2\text{O}_2 (10 \text{mM})/\text{UV-C}$ treatment system from 15% to 62%, and TOC removal from 0% to 34%, but did not appear to be more effective than applying a single ozonation process in terms of TOC abatement rates. Enhancement of the biodegradability was more pronounced for the biologically pre-treated wastewater with a two fold average increase in the $\text{BOD}_5/\text{COD}$ ratio for the studied chemical oxidation systems.

Keywords Advanced oxidation processes; EE/M; EE/O; $\text{H}_2\text{O}_2/\text{UV-C}$; ozonation; textile industry wastewater

Introduction Considering both the volume and chemical composition of the discharged effluent, the textile industry is one of the major polluters among all industrial sectors. Effluents from the textile dyeing, washing and rinsing stages contain high concentrations of dissolved solids and are strongly colored due to the intense of refractory and polyaromatic dyestuffs (Easton, 1995). These properties make the decolourization and effective oxidation of dye-house effluents via conventional treatment methods such as biological oxidation, coagulation, and adsorption quite inappropriate (Reife and Freeman, 1996). Moreover, applying these physicochemical treatment technologies results in a phase transfer of pollutants thus creating another source of waste. Consequently, appropriate “destructive” chemical technologies should be preferred for the fast and effective treatment of pollutants present in textile industry wastewater.

So far, the application of Advanced Oxidation Processes (AOPs) to a variety of organic and inorganic model pollutants has been investigated in detail (Legrini et al., 1993; Glaze et al., 1987; Masten and Davies, 1993; Beltran et al., 1997a and b). However, relatively fewer works dealt with the application of AOPs to actual textile wastewater or dye-bath effluent mainly because of their inability to cope with complex background matrices and high pollution loads normally encountered in real industry wastewater (Akmehmet Balcıoğlu and Arslan, 1997; Akmehmet Balcıoğlu and Arslan, 1998; Arslan et al., 1999; Akmehmet Balcıoğlu and Arslan, 2001). Appreciably higher oxidant concentrations, UV doses and treatment times are required that economically make the real scale stand-alone application of AOPs unfeasible (Scott and Ollis, 1995; Marco et al., 1997). Hence their sequential application, where ozone first reacts with the high UV-absorbing components present in the
wastewater and their oxidation products or any pollutants being resistant to ozonation are concomitantly destroyed via UV-C catalyzed H₂O₂ oxidation, seems practically more attractive. Thus, the present study aimed to investigate the advanced oxidation of raw and biologically pretreated textile wastewater by ozonation, H₂O₂/UV-C oxidation, and their sequential application in the form of ozonation followed by H₂O₂/UV-C. Relative changes in the biodegradability (expressed as the BOD₅/COD ratio) of raw and biotreated textile wastewater during advanced oxidation was also examined.

Materials and methods

Textile wastewater

Raw and biologically pre-treated textile wastewater was collected weekly from a local dye-house mill in Istanbul processing both cotton and polyester fibers. The wastewater samples were stored at 4°C in a cold room in 10 L plastic carboys prior to their use. Table 1 summarizes the average values of the selected process parameters for the raw and biologically pretreated textile effluents.

The ozone reactor

Ozonation experiments were performed for 1 h in a 1,500 mL capacity ozone bubble column (Arslan and Akmehmet Balcioglu, 2000) with counter current recirculation of the liquid to the gas flow. Ozone was produced from dry and pure oxygen by a Fischer OZ 500 Model ozone generator and the ozone input rate was determined iodometrically (IOA, 1998) as 3.51 g/h. The ozone-oxygen mixture was introduced from the reactor bottom through a sintered glass plate diffuser at a rate of 2340 mg/(L × h) at a rate of 100 L/h as monitored by rotameter incorporated into the generator.

The photochemical reactor

H₂O₂/UV-C oxidation of textile effluents was conducted for 1 h in a 2,500 mL capacity annular batch photoreactor. The UV-C reactor was a 304 SS tube (L = 500 mm; d = 85 mm) equipped with a 25 W low-pressure mercury vapor UV-C lamp (L = 450 mm; d = 25 mm) that was placed into a quartz envelope (L = 460 mm; d = 31 mm). Both UV-C lamp and quartz lamp housing were centred in the reactor tube. The incident light flux and effective path length of the UV-C lamp were determined by hydrogen peroxide actinometry (Nicole et al., 1990) as \( I_0 = 2.0 \times 10^{-5} \) Einstein/(L × s) and 1.72 cm, respectively. Mixing was provided by circulating the reaction solution with a peristaltic pump (Cole Parmer) at a rate of 250 mL/min.

Analytical procedure

Treated samples were analyzed for total organic carbon (TOC), chemical oxygen demand (COD), BOD₅, absorbance at 254 nm (UV₂₅₄) representing the aromatic content of waste-

Table 1 Characterization of the raw and biotreated textile wastewater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw</th>
<th>Biotreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>336</td>
<td>58</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1,476</td>
<td>325</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>491</td>
<td>30</td>
</tr>
<tr>
<td>Alkalinity (mg/L CaCO₃)</td>
<td>557</td>
<td>115</td>
</tr>
<tr>
<td>pH (units)</td>
<td>10.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Colour (1/m)*</td>
<td>27</td>
<td>18</td>
</tr>
<tr>
<td>UV₂₅₄ (1/m)</td>
<td>254</td>
<td>146</td>
</tr>
</tbody>
</table>

* Absorbance recorded at 566 and 531 nm wavelength for raw and biotreated textile wastewater, respectively
water and absorbance at 566 nm and 531 nm \( (A_{566}, A_{531}) \) wavelengths representing color of the raw and biotreated wastewater, respectively. TOC of the samples was determined by a Carlo Erba TCM 480 model TOC-analyzer (Fisions Instruments). BOD\(_5\) and COD measurements were conducted in accordance with Standard Methods (APHA-AWWA-WPCF, 1989). Spectrophotometric measurements were performed by a Shimadzu UV-120 model single-beam spectrophotometer.

**Calculation of electrical energy requirements**

Operating costs are directly affected by the power input and treatment performances of the applied AOPs. To ease up comparison of overall treatment efficiencies, the empirical figure-of-merit developed for AOPs, EE/O (the electrical energy required to remove a pollutant by one order of magnitude in 1 m\(^3\) of water or wastewater) and EE/M (the electrical energy required per unit of mass removed), have been calculated by the following formulae for substrate removal rates via ozonation and H\(_2\)O\(_2\)/UV-C treatment (Bolton and Cater, 1994):

\[
EE/O = \frac{38.4xP(kW)}{k_d(1/\text{min})xV(L)}
\]

(1)

and on the basis of TOC removal for batch systems and zero-order removal rates;

\[
EE/M = \frac{P(kW)xrt(h)}{V(m^3)x\Delta\text{TOC}(g/m^3)}
\]

(2)

where \( P \) is the power input of the UV-lamp or the ozone generator, \( k_d \) is the first-order decolourization rate constant, \( t \) is oxidation time, \( V \) is the volume of the treated textile effluent and \( \Delta\text{TOC} \) the amount of TOC removed during the oxidation period which was chosen as 1 h.

**Results and discussion**

**H\(_2\)O\(_2\)/UV-C oxidation of raw and biotreated textile wastewater**

To investigate the influence of UV-C light on the removal rate efficiencies, separate control experiments were conducted with UV-C light only. During direct UV-C photolysis, no changes in the investigated process parameters was observed for raw textile wastewater (not shown data). For the H\(_2\)O\(_2\)/UV-C oxidation of raw textile wastewater, 50 mM H\(_2\)O\(_2\) was required for sufficient OH\(^*\) production that was necessary to observe a significant colour and COD reduction. Even at this H\(_2\)O\(_2\) concentration, raw textile wastewater did not suffer any significant oxidation (Figure 1a,b). Overall COD removal after H\(_2\)O\(_2\)/UV-C treatment was negligible for the raw textile effluent.

![Figure 1](https://iwaponline.com/wst/article-pdf/45/12/297/424873/297.pdf)

**Figure 1** Changes in \( A_{566} \) and \( UV_{254} \) (a), and COD and TOC (mg/L) parameters during H\(_2\)O\(_2\) (50 mM)/UV-C oxidation of raw textile wastewater as a function of treatment time
The biologically pre-treated textile was treated analogously by a UV-C control experiment and the H₂O₂/UV-C processes in the presence of 10 mM and 50 mM H₂O₂. According to the obtained results (Figure 2a–d), increasing the initial H₂O₂ dose from 10 mM to 50 mM exerted an appreciable effect on removal efficiency in terms of all followed process parameters. The addition of H₂O₂ had a dramatic effect on decolourization rates and overall colour removal efficiency of the biotreated effluent increased from only 4% by applying mere UV-C to 34% and 88% after H₂O₂/UV-C oxidation in the presence of 10 mM H₂O₂ and 50 mM H₂O₂, respectively. Elevating the H₂O₂ concentration from 10 mM to 50 mM also improved overall UV₂₅₄ and COD removal efficiencies significantly. This observation is a logical consequence of the higher UV-C absorbance of the introduced H₂O₂ changing from 19 1/m to 95 1/m at λ = 254 nm and the doses of 10 mM and 50 mM H₂O₂, respectively. From the obtained data it can be simply inferred that H₂O₂/UV-C oxidation did not appear to be feasible as a stand-alone oxidation method because of the requirement of at least 1,700 kg H₂O₂ per metric ton of wastewater for effective treatment.

**Ozonation of raw textile wastewater**

As is obvious from Figure 3a and b, compared to the H₂O₂/UV-C treatment system, O₃ much more quickly reduces in particular UV-VIS absorbances of the raw textile effluent. Significant changes in the followed process parameters occurred within the first 10 min of ozonation and remained almost constant thereafter. After 1 h ozonation (applied specific ozone dose = 2 mg O₃/mg CODᵢ), 99% colour and 18% COD removals were achieved. As in the case of raw wastewater, the treatment performance of ozonation for COD and colour removal rates by far exceeded that of the H₂O₂/UV-C oxidation process regardless of the H₂O₂ dose. Biotreated textile wastewater could be decolourized in only 10 min, whereas overall UV₂₅₄ and COD removal efficiencies were 74% and 54%, respectively (Figure 3b). In fact, for the biologically pretreated textile wastewater quite similar overall UV₂₅₄ and COD removal efficiencies were obtained for ozonation or H₂O₂/UV-C oxidation. It can be
concluded that ozonation can be effectively applied to both raw as well as pre-treated wastewater, while H$_2$O$_2$/UV-C oxidation should be used only for polishing purposes after secondary treatment and high doses.

**Sequential ozonation + H$_2$O$_2$/UV-C oxidation of raw and biotreated textile wastewater**

For sequential oxidation of the raw textile effluent, the H$_2$O$_2$ (50 mM)/UV-C treatment period was reduced to 55 min and a preceding 5 min (ozone dose = 195 mg/L) ozonation stage was introduced instead, so that the total treatment duration of 1 hour was not extended. The biologically pre-treated textile wastewater was treated analogously, except that this time the ozonation period was extended to 20 min (ozone dose = 780 mg/L), while for the following H$_2$O$_2$/UV-C reaction the treatment period was consequently reduced to 40 min. H$_2$O$_2$/UV-C oxidation of the raw textile wastewater could be considerably stimulated by a pre-ozonation step (Figure 4a).

Overall COD removal efficiency increased from 2% (H$_2$O$_2$/UV-C) and 18% (O$_3$) to 27%, whereas overall TOC removal rate was accelerated from 14% (H$_2$O$_2$/UV-C) and 17% (O$_3$) to 50% by successive treatment of the raw textile effluent. Enhancement of the H$_2$O$_2$/UV-C process resulted from the positive effect of 5 min pre-ozonation removing almost 60% UV$_{254}$ of the raw textile wastewater.

Sequential treatment of the biologically pretreated textile wastewater by applying ozonation followed by H$_2$O$_2$/UV-C is presented in Figure 4b. As is obvious from Figure 4b, by introducing an initial ozonation step, not only the concentration of H$_2$O$_2$ could be
reduced from 50 mM to 10 mM so as to obtain the same removal rates compared with
the stand-alone chemical oxidation, but also the total COD removal (62%) exceeded those
of mere ozonation (54%) and 50 mM H₂O₂/UV-C oxidation (41%).

The effect of H₂O₂/UV-C treatment on the biodegradability of raw and biotreated textile wastewater
The potential of ozone and AOPs in improving biodegradability has been addressed fre-
quently in the past (Gilbert, 1987; Jochimsen and Jekel, 1997; Alvares et al., 2001). In the
present study, changes in the biodegradability during advanced chemical oxidation of
raw and biotreated textile effluents have been expressed in terms of BOD₅/COD ratios
(Table 2).

According to Table 2, BOD₅/COD increased for photochemical oxidation, decreased in
the case of ozonation and slightly decreased for direct UV-C-photolysis, indicating that the
variations in the BOD₅/COD ratio are closely related to the extent, speed and pathway of
the oxidation process in question. Ozone reduced both BOD₅ and COD of the untreated tex-
tile effluent samples simultaneously, in other words, the intermediate products formed
throughout the course of the experiment were not much more amenable to biological acti-
vated sludge treatment. The H₂O₂/UV-C process, though noticeably slow as compared to
the ozonation, appeared to be capable of forming more biodegradable species than
ozonation.

For the biotreated textile wastewater, a considerably different trend in the variation of
biodegradability was observed (Table 2). During oxidative treatment, ozonation and the
H₂O₂(50 mM)/UV-C process were almost equal in terms of biological degradability alter-
nation, increasing the biodegradability by a factor of 1.5–2.0 ultimately. Using H₂O₂ at an
initial dose of 10 mM during H₂O₂/UV-C treatment was not sufficient to cause a consider-
able conversion of the parent compounds and hence did not significantly differ from direct
UV-C photolysis. The fact that the enhancement in biodegradability was more pronounced
for the biotreated wastewater is once again a logical consequence of the inability of AOPs
in degrading highly polluted wastewater effectively. Table 3 summarizes obtained k₄ values,
final absolute UV₂₅₄, COD and TOC removal rates together with the calculated EE/O and EE/M values for O₃ (overall dose = 2340 mg/L) and H₂O₂(50 mM)/UV-C treatment of
raw and biologically pretreated textile wastewater at their natural pH for 1 h.

According to Table 3, although the ozonation process outperformed the treatment
efficiency of the H₂O₂/UV-C process in terms of all examined process parameters and for

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Changes in the BOD₅/COD ratios during the treatment of raw and biotreated textile wastewater via ozonation, H₂O₂/UV-C and their sequential application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>UV-C</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.31</td>
</tr>
<tr>
<td>5</td>
<td>0.30</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
</tr>
<tr>
<td>20</td>
<td>0.29</td>
</tr>
<tr>
<td>40</td>
<td>0.30</td>
</tr>
<tr>
<td>60</td>
<td>0.28</td>
</tr>
<tr>
<td>Biotreated</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.27</td>
</tr>
<tr>
<td>10</td>
<td>0.27</td>
</tr>
<tr>
<td>20</td>
<td>0.26</td>
</tr>
<tr>
<td>40</td>
<td>0.22</td>
</tr>
<tr>
<td>60</td>
<td>0.23</td>
</tr>
</tbody>
</table>
both effluent types, considering the obtained EE/O and EE/M values, decolourization and mineralization of the raw textile wastewater via ozonation appeared to be more energy consuming than the H$_2$O$_2$/UV-C processes because of the higher power input of the ozone generator and the lower reactor volume of the ozone reactor.

### Conclusions

Among the examined chemical oxidation processes (O$_3$, H$_2$O$_2$/UV-C and O$_3$ + H$_2$O$_2$/UV-C):

1. Ozonation of biotreated textile wastewater and H$_2$O$_2$/UV-C oxidation of raw and biotreated textile wastewater are economically feasible.
2. Destruction of aromaticity (UV$_{254}$ removal) and colour removal proceeded rapidly, whereas TOC and COD removals were seriously delayed.
3. A subsequent biological treatment is most effective after the successive O$_3$ + H$_2$O$_2$/UV-C combination.
4. Extended chemical treatment diminishes or at least levels off chemical oxidation efficiency.

### References


