Oxidative treatment characteristics of biotreated textile-dyeing wastewater and chemical agents used in a textile-dyeing process by advanced oxidation process


*Water Environment Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea (E-mail: limbr@kist.re.kr)
**ESPC, Department of Environmental Science and Engineering, Tsinghua University, Beijing, 100084 China (E-mail: hyhu@tsinghua.edu.cn)
***Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580 Japan (E-mail: fujie@eco.tut.ac.jp)

Abstract The oxidative treatment characteristics of biotreated textile-dyeing wastewater and typical chemicals such as desizing, scouring, dispersing and swelling agents used in the textile-dyeing process by advanced oxidation process were experimentally studied. The refractory organic matters remained in the effluent of biological treatment process without degradation may be suitable for the improvement of biodegradability and mineralized to CO2 by combined ozonation with and without hydrogen peroxide. On the other hand, the refractory chemicals contained in the scouring agent A and swelling agent may not be mineralized and their biodegradability may not be improved by ozonation. However, the BOD/DOC ratio of scouring agent B increased from 0.3 to 0.45 after ozonation. Based on the results described above, advanced treatment process involving the ozonation without and with the addition of hydrogen peroxide, followed by biological treatment was proposed for the treatment of refractory wastewater discharged from the textile-dyeing process.

Keywords Advanced oxidation processes; biodegradability; refractory chemicals; textile-dyeing wastewater; treatment characteristics

Introduction

Textile industry wastewater is characterized by strong colour, large amount of suspended solids (SS), broadly fluctuating pH, high temperature, and high levels of chemical oxygen demand (COD). Especially, this process discharges wastewater containing textile effluent consisting of textile dye and other chemicals such as polyvinyl alcohol (PVA), formaldehyde urea, kerosene, phenolic compounds, etc. Aesthetic, environmental and health problems may be incurred from discharging of this wastewater to the environment (Nemerow, 1978; Venceslau et al., 1994; Banat et al., 1996).

The conventional activated sludge process cannot easily be used to treat textile wastewater because most commercial dyes and chemical agents are toxic to the organisms used in the process and result in sludge bulking (Grau, 1991; Cooper, 1993; Ganjidoust et al., 1999; Hsu and Chiang, 1997). Therefore, a post-treatment process such as coagulating sedimentation and/or pressure flotation is usually employed (Nicolaou and Hadjivassilis, 1992). Membrane separation has found increasing usage in the past two decades (Chen et al., 1997) in treating this type of refractory wastewater. Wet-air oxidation has proven to be an efficient method for COD removal in textile wastewaters (Lei et al., 1998, 2000). However, the high temperature and high pressure being applied to this process are not attractive to the bleaching and dyeing industries. More recently, chemical oxidation using ozone or advanced oxidation processes based on the generation of hydroxyl radicals (i.e. from the combination of ozone and hydrogen peroxide or UV radiation) and
Electrochemical methods have been applied to the removal of textile dyes from wastewaters (Gahr et al., 1994; Lin and Peng, 1996). Ruppert et al. (1994) used ozonation to treat dyehouse wastewater, and found that the colour removal was more efficient at high pH. Ozonation can achieve high colour removal, reduce the level of organic compounds, improve biodegradability, destroy phenols and ensure disinfection (Beszedits, 1980; Tzitzi et al., 1994).

The purpose of this study was to investigate the possibility of a combined chemical oxidation and biological process as an effective technique for the treatment of textile-dyeing wastewater. In addition, the oxidative treatment characteristics of chemical agents used in a textile-dyeing process by ozone and advanced oxidation were also investigated.

**Methods**

**Textile-dyeing wastewater and chemical agents used in this study**

**Textile-dyeing wastewater.** The textile-dyeing wastewater used in this study was taken from the effluent of a small-scale activated sludge process treating textile-dyeing wastewater from a textile industry located in Gamagori City, Aichi, Japan. The wastewater plant consisted of a preliminary treatment (screening, equalization and cooling) and activated sludge and flocculation system. Two aeration reactors, aeration tank A and B, composed the biological unit in this process. The volumes of the aeration tanks (A and B) of this treatment process were 402 and 730 m³, respectively. The average flow rate of the wastewater was 2,000 m³/d, with hydraulic retention time (HRT) of 48 h.

**Chemical agents.** Five typical chemical agents used in desizing, scouring, dispersing and swelling processes were collected from a textile industry in Japan. Desizing process removes the substance applied to the yarn in the sizing operation by swelling/solubilising, hydrolysing, or oxidizing method. The desizing wastewater discharged from the desizing process for natural fiber mainly contains starch, polyvinyl alcohol, and carboxymethyl cellulose. Scouring can be applied to both natural and synthetic materials to remove applied or natural substances. Due to their non-biodegradability or toxicity, many impurities in scouring effluent, such as antistatic agents (synthetic fibres), pesticides, cotton waxes and wool grease or wax can pose problems in the operation of biological treatment systems. The dispersing and swelling agents contain anionic surfactants and chlorobenzene, respectively.

**Ozonation experiment**

Ozonation experiment was performed in a batch operation apparatus consisting of a glass column (65 mm in diameter and 220 mm in height) as the main part of the reactor. Ozone gas from an ozonizer (PO-10, Fuji Denki Co., Japan) was diluted with dry air to adjust the concentration of ozone around 6-7 mg/L and was continuously fed into the reactor through a sintered glass filter at the flow rate of 1.0 L/min. The effective volume of the reactor was 250 mL. The pH value was not adjusted during all tests. Ozone concentration in the exhaust gas of the reactor was monitored spectrophotometrically at 254 nm, $A_{254}$, with the relationship between ozone concentration $C_{O_3} = 3.09 A_{254}$ for 50 mm cell. The molar ratio of $H_2O_2$ fed to DOC was 1:1. The reactions were started by the addition of hydrogen peroxide.

**Analytical methods**

Sampling was carried out, and the samples were analyzed for pH. Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined using a TOC analyzer (Model TOC-500, Shimadzu, Japan). DOC was determined using the filtrated sample through membrane filter with pore size of 0.45 µm. BOD was determined using a BOD
COD$_{Cr}$ was determined by a Hach DR/3000 (Loveland, Colorado) direct reading spectrophotometer using a Hach COD reactor. Biodegradability is defined as the ratio of BOD to DOC. The molecular size distribution of wastewater was determined by a gel chromatography (Shim-pack Diol-150, 7.9 mm I.D. × 500 mm, Shimadzu, Japan). Pure water was used as the mobile phase, i.e. eluent, at a flow rate of 1.0 mL/min.

**Results and discussion**

### Characteristics of textile-dyeing wastewater and chemical agents used

The characteristics of raw, biotreated textile-dyeing wastewater and its final effluent are summarized in Table 1. The average influent BOD concentration of the activated sludge process was around 220 mg/L and that of biological effluent was around 13 mg/L. The final effluent of the activated sludge process followed by the flocculation system was about 1 mg/L. The chemical coagulation unit could remove only a small part of total COD. The average removal efficiencies of DOC, BOD and COD$_{Cr}$ were 84.8, 99.5 and 85%, respectively. The values of BOD/COD$_{Cr}$ and BOD/DOC ratio in biologically treated effluent were 0.08 and 0.16, respectively. This fact indicated that some less biodegradable, i.e. refractory organic matters remained in the effluent of biological treatment process without degradation (Grau, 1991; Cooper, 1993; Correia *et al.*, 1994).

Also, the characteristics of five typical chemical agents investigated in this study in terms of COD, BOD and DOC are summarized in Table 1. The pH of swelling agent (about 11) is higher than that of the other chemical agents (4.5–6.7). The values of BOD/DOC ratio, reflecting the biodegradability, of dispersing and desizing agents were 0.80 and 1.77, respectively. Those of scouring agents A, B and swelling agent were 0.33, 0.30 and 0.16, respectively. This fact indicates that agents of scouring A, B and swelling have low biodegradability and contain refractory chemicals.

Molecular size distribution of the constituents in the raw wastewater, the effluent of biological treatment process and final effluent is shown in Figure 1. Raw textile-dyeing wastewater consists of three peaks with molecular sizes of approximately 100,000, 60,000 and 200 from the gel chromatogram. Peak areas at 7, 10 and 23 min decreased with decreasing DOC concentration, then gradually disappeared. The area at 12 min, however, did not change with biological treatment. This result indicates that the textile-dyeing wastewater cannot be effectively treated by the conventional process consisting of flocculation followed by activated sludge process.

### Biodegradability changes by ozone and O$_3$/H$_2$O$_2$

Biotreated textile-dyeing wastewater. Effluent of the biological treatment process was ozonated to characterize the chemical oxidation of the pollutants. Changes in BOD, DOC

**Table 1** Characteristics of influent, biotreated wastewater and chemical agents used in textile-dyeing process

<table>
<thead>
<tr>
<th>Items</th>
<th>Textile-dyeing wastewater</th>
<th>Chemical agents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent</td>
<td>Biotreated</td>
</tr>
<tr>
<td>pH (−)</td>
<td>6.7</td>
<td>8.2</td>
</tr>
<tr>
<td>BOD (g/L)</td>
<td>220</td>
<td>13</td>
</tr>
<tr>
<td>COD$_{Cr}$ (g/L)</td>
<td>780</td>
<td>145</td>
</tr>
<tr>
<td>DOC (g/L)</td>
<td>277</td>
<td>73</td>
</tr>
<tr>
<td>BOD/DOC (−)</td>
<td>0.79</td>
<td>0.18</td>
</tr>
<tr>
<td>BOD/COD$_{Cr}$ (−)</td>
<td>0.28</td>
<td>0.09</td>
</tr>
<tr>
<td>COD$_{Cr}$/DOC (−)</td>
<td>2.82</td>
<td>1.98</td>
</tr>
</tbody>
</table>
and COD of biologically treated effluent by advanced oxidation processes are shown in Figure 2. A remarkable increase in BOD was observed along with increasing ozone treatment time. The reduction in COD by ozonation was only around 30%. On the other hand, the effluent of the biological treatment process was efficiently oxidized by combined ozonation with hydrogen peroxide (O$_3$/H$_2$O$_2$, hereafter). The BOD of the wastewater after ozonation with H$_2$O$_2$ was abruptly increased, while that of the biologically treated effluent after 5 min was almost completely removed. The DOC and COD in the effluent of activated sludge process were decreased by 50% of the initial DOC and COD. COD reduction by O$_3$/H$_2$O$_2$ was higher than that from single ozonation.

The changes in biodegradability of the biotreated textile wastewater during ozonation and advanced oxidation were monitored by the BOD/DOC ratio. The BOD/DOC ratio of the biologically treated effluent increased from 0.16 to about 0.7 after ozonation. The experimental results show that the ozonation may be suitable for the improvement of biodegradability of non-biodegradable organic pollutants contained in the effluent of the activated sludge process. On the other hand, the BOD/DOC ratio of the biologically treated effluent increased from 0.16 to about 0.45 by combined ozonation with hydrogen peroxide at 5 min. These results demonstrate that the residual refractory organic matters in the effluent of biological treatment by O$_3$/H$_2$O$_2$ could be ultimately mineralized to CO$_2$ at the ratio of H$_2$O$_2$ to DOC of 1, while the improvement of biodegradability cannot be expected after 5 min.

The changes in molecular-size distribution of the biologically treated effluent by advanced oxidation processes are shown in Figure 3. The changes in molecular-size distribution of the pollutants during the oxidation demonstrate that the biodegradable matters with low molecular size were degraded by the oxidation. The peak area at 12 min

![Figure 3](image-url)
was divided to two peaks by ozonation and combined ozonation with hydrogen peroxide at 60 min. This indicates that the high molecular matters degraded to low molecular size with biodegradability by the oxidation.

Chemical agents. The pH of scouring agent A during ozonation decreased slightly from about 6.7 to 4.1. In the ozonation of the swelling agent, a decrease in pH from 5.3 to 3.8 was also observed. Especially, the pH of scouring agent B decreased abruptly from about 11 to 7. This indicates a possible formation of carboxylic acids during ozonation.

Changes in COD, DOC and COD/DOC ratio of scouring agents A, B and swelling agent during ozonation are shown in Figure 4. DOC and COD concentrations of scouring agent A and swelling agent decreased during the first 10 min, but increased from 10 to 40 min. The decrease in DOC and COD during the first 10 min may be due to the loss of carbon in solution to foam generated by aeration. The decrease in COD of scouring agent A after 40 min of oxidation was an indication that portions of biodegradable COD may be degraded easily before the degradation of non-biodegradable COD. Since both DOC and the COD/DOC ratio did not change with time, ozonation is not suitable for mineralizing organic substances in scouring agent A and the swelling agent. On the other hand, COD concentrations of scouring agent B did not change before 40 min, but decreased abruptly there after 40 min. The final COD removal after 60 min of oxidation was 18%. COD/DOC ratio did not change with time. This indicates that high molecular chemicals were degraded to low molecular ones, and finally mineralized after 40 min. The changes in biodegradability of the chemical agents during ozonation were monitored by the BOD/DOC ratio. The refractory organic matters contained in the swelling agent may not be mineralized and their biodegradability may not be improved by ozonation. However, after 60 min of ozonation, the BOD/DOC ratio of scouring agent B increased from the initial value of 0.3 to a value of 0.45. Increase in the BOD was an indication that portions of non-biodegradable COD have been converted to biodegradable matter.
Molecular size change of scouring agent B before and after ozonation is shown in Figure 5. Constituents of the scouring agent B were classified into two groups based on their molecular sizes. Further oxidation did not lead to any significant changes in the molecular weight distribution. Peak area of 11 min reduced with increased ozonation time. The change in molecular size distribution of the pollutants during oxidation demonstrated that high molecular chemicals were degraded to low molecular ones. Based on the results described above, it is confirmed that some of the refractory chemicals contained in scouring agent B can be mineralized and their biodegradability can be improved by ozonation.

Conclusions

The purpose of this study was to clarify the possibility of a combined chemical oxidation and biological process as an effective technique for the treatment of textile-dyeing wastewater. It was clarified that the organic substances contained in the textile-dyeing wastewater were not removed effectively by the conventional treatment process which consists of coagulation and biological treatment. It was shown from the experimental results that the biodegradability and removability of refractory organic matter in biotreated wastewater could be remarkably improved by advanced ozonation with the addition of hydrogen peroxide. In addition, the oxidative treatment characteristics of typical chemical agents (desizing, scouring, dispersing and swelling agents) used in textile-dyeing process by ozone were experimentally studied. The refractory chemicals contained in the scouring A and swelling agents may not be mineralized and their biodegradability may not be improved by ozonation. However, the scouring agent B can be mineralized and its biodegradability can be improved by ozonation. Our experimental results are useful for selection of effective treatment process for textile-dyeing wastewater.

References


