Ozonation of Dyes and Textile Wastewater in a Rotating Packed Bed

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Ozonation of Dyes and Textile Wastewater in a Rotating Packed Bed

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This study investigates the ozonation of Reactive Red 120 and Acid Red 299 dyes in the synthesized solution and textile wastewater by using a rotating packed bed. The decomposition rate of Reactive Red 120 and Acid Red 299 dyes via ozonation can be described by the pseudo-first-order kinetics. Ozonation of Reactive Red 120 exhibited the higher mineralization rate compared with that of Acid Red 299. The biodegradability of the two dyes could be significantly promoted during the ozonation. The BOD5/TOC (5-day biological oxygen demand/total organic carbons) ratios of the ozonated Reactive Red 120 and Acid Red 299 solutions would increase and have the maximum values. Moreover, the oxidized textile wastewater revealed the fast decolorization and moderate COD (chemical oxidation demand) removal rates. The optimal ADMI (American Dye Manufactures Institute) and COD removal of the textile wastewater were 93% and 37% in 30 minutes ozonation time, respectively. The performance evaluation of ozonation in the rotating packed bed indicated that the higher water flow rate, gas ozone concentration and rotational rotating speed would increase the efficiency of mineralization.

Key Words: Ozonation; Rotating Packed Bed; Reactive Red 120; Acid Red 299.

INTRODUCTION

Textile production is one of the main industrial sectors in Taiwan. The wastewater discharges by the dye manufacturing and dyeing/finishing plants have caused a serious pollution in the environment. The organic dye or pigment
is considered as the potentially hazardous substance according to the study of the U.S. Environmental Protection Agency (EPA). Industrial wastewater generated from the textile dyeing processes generally contains amounts of chemical oxidation demand (COD) and color due to the used dyes. However, the removal of COD and color in the textile wastewater are limited while the dyes are resistant to the biological treatment process. Ozonation can be applied prior to the biological aerobic treatment because the chemicals are converted into smaller and biodegradable intermediates.[1–4]

Ozonation is an effective way to reduce the COD and total organic carbons (TOCs) by oxidizing the stream solutions with ozone. Ozone may attack on the pollutants via two different reaction pathways: (1) the direct ozonation by the ozone molecule, and (2) the radical ozonation by the highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in the aqueous solution. The radical ozonation is non-selective and vigorous. The ozonation process in the acid condition mainly takes place through the direct oxidation reaction, which is selective. Furthermore, the rate-limiting step in many ozonation processes is attributed to the gas-liquid mass transfer rate. Note that the ozonation performance can be enhanced by increasing the gas-liquid mass transfer rate of ozone. Rotating packed beds (RPBs) have been used as gas-liquid contactors for the applications of adsorption, distillation and stripping, etc.[5,6] RPBs are designed to generate high acceleration of liquid owing to the centrifugal force. The target solution contacted with gas flows through the packed material in the environment of high gravity. This novel technology is also named “Higee.” According to previous studies,[5–7] RPBs have the high gas-liquid mass transfer coefficients, which are important for accelerating the gas-liquid mass transfer rate. Recently, RPBs have been introduced as ozonation contactors by Lin and Liu[8] and Chen et al.[9–11]

This study aims at investigating the ozonation performance of two dyes in the aqueous solution on the decolorization, mineralization and biodegradability in the aqueous solution. Moreover, the ozonation of the real textile wastewater is carried out in a RPB to obtain the practicable results for the application of RPB in the textile industry. The different operating conditions of the RPB are evaluated for the efficiency of mineralization. Consequently, the present study can provide the useful information about the ozonation of dyes using a RPB.

MATERIALS AND METHODS

Figure 1 shows a schematic diagram of the ozonation apparatus. The ozone containing gas is introduced into a RPB, which is used as the gas-liquid contactor. A liquid-storage tank is equipped with a thermostat to maintain the constant temperature for the solution at 25°C in all experiments.
Ozonation of Red Dyes and Textile Wastewater

Table 1: Typical operating conditions of ozonation in the RPB.

<table>
<thead>
<tr>
<th>Gas phase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate, q</td>
<td>1.98 L/min</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 kg/cm²</td>
</tr>
<tr>
<td>Influent ozone concentration, ((O_3)_{in})</td>
<td>40 mg/L</td>
</tr>
<tr>
<td>Ozone dosage applied, (q \times (O_3)_{in})</td>
<td>79.2 mg/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid phase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of solution</td>
<td>4000 ml</td>
</tr>
<tr>
<td>Water flow</td>
<td>1.2 L/min</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>1500 rpm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specification of the RPB</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner radius of packed bed</td>
<td>0.0385 m</td>
</tr>
<tr>
<td>Outer radius of packed bed</td>
<td>0.0825 m</td>
</tr>
<tr>
<td>Axial height of packed bed</td>
<td>0.02 m</td>
</tr>
<tr>
<td>Weight of packing in packed bed</td>
<td>0.131 kg</td>
</tr>
<tr>
<td>Volume of packed bed</td>
<td>(3.35 \times 10^{-4} ) m³</td>
</tr>
<tr>
<td>Volume of housing case</td>
<td>(3.37 \times 10^{-3} ) m³</td>
</tr>
<tr>
<td>Specific area of packing per unit volume of packed bed</td>
<td>840 m²/m³</td>
</tr>
<tr>
<td>Total packing area</td>
<td>0.281 m²</td>
</tr>
<tr>
<td>Voidage</td>
<td>0.984 m³/m³</td>
</tr>
</tbody>
</table>

Ozone-containing gas is generated from the pure oxygen by the ozone generator. Before the ozone dissolution experiments were started, the ozone-containing gas was by-passed to be analyzed to ensure the stability and determine the ozone concentration. A portion of the gas stream at the preset flow rate was directed into the contactor when the set conditions are reached. All the components in this system are made from stainless steel and Teflon. The ozone generator used was manufactured by JEU TU CO., Japan (Series No, SG-01A-PSA4). The concentration of ozone gas was measured by the potassium iodide technique based on the Standard Methods (APHA, 1992). Table 1 lists the model operating conditions of ozonation in the RPB contactor. The ozonation performance of the RPB was evaluated to treat the local textile plant wastewater by changing the conditions of rotational speed, water flow and gas flow.

The specification of the RPB contactor is given in Table 1. The 304 stainless steel wire cut in the sharp of annular rings was stacked in the packed bed. The density and diameter of the wire were 8478 kg/m³ and \(2.2 \times 10^{-4} \) m, respectively. The rotator is connected to a rotor shaft on two bearings, which are, in turn, mounted on a steel structure. The shaft is connected to a motor, which is controlled by a speed regulator. The rotational speed can be operated properly at 1,500 rpm, which provides gravitational forces of 152 g based on the arithmetic mean radii of the RPB. Liquid entered the RPB through six holes in the liquid distributor. These six holes are arranged in a vertical group of three, and the groups are spaced 180° apart. The liquid was sprayed on the inside...

edge of RPB and thrown outward by centrifugal force. The gas was introduced from the outside and flows countercurrently to the liquid in the RPB.

The dye compounds used in this study were Reactive Red 120 (RR-120) and Acid Red 299 (AR-299). The chemical formulas of Reactive Red 120 and Acid Red 299 are C\textsubscript{44}H\textsubscript{24}Cl\textsubscript{2}N\textsubscript{14}Na\textsubscript{6}O\textsubscript{20}S\textsubscript{6} and C\textsubscript{26}H\textsubscript{24}N\textsubscript{5}NaO\textsubscript{5}S, respectively. The two dyes were used and provided by the local textile plant. The initial concentrations of the two dyes (C\textsubscript{0}) were set at about 100 mg/L in the synthesized solution. In addition, the ozonation of the textile wastewater discharged from the textile plant was also carried out for the information of the practical application. The properties of the synthesized dye solutions and textile wastewater used were shown in Table 2.

The absorbance of Reactive Red 120 and Acid Red 299 from 400 to 700 nm was scanned by a UV/VIS spectrophotometer (CINTRA 20, GBC, Dandenong, VIC, Australia) to find the maximum absorbance at 513 and 512 nm, respectively. The quantity at the wavelength of maximum absorbance called as the characteristic wavelength can be used to determine the concentration of dyes (C\textsubscript{t}) during ozonation. The color was measured by tristimulus filter method of the American Dye Manufactures Institute (ADMI).\textsuperscript{12}

The reaction solution was prepared with 4000 ml Milli-Q water in the experiments. A TOC analyzer (model 700, OI Corporation, TX, USA) was employed to measure the total carbon concentration (TOC) of the ozonated solutions. A portable conductivity meter (SUNTEX, SC-120) was used to measure the electrical conductivity of textile wastewater. Chemical Oxygen Demand (COD) and Suspended Solid (SS) were analyzed according to
Table 2: The properties of the synthesized dye solutions and textile wastewater used in this study.

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Synthesized RR-120 solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Synthesized AR-299 solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Textile wastewater&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye concentrations</td>
<td>mg/L</td>
<td>100.8</td>
<td>107.5</td>
<td>13.8 (as RR-120)&lt;sup&gt;b&lt;/sup&gt; or 8.2 (as AR-299)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>ADMI</td>
<td>unit</td>
<td>36,736</td>
<td>41,400</td>
<td>9,511</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>µs/cm</td>
<td>—</td>
<td>—</td>
<td>487</td>
</tr>
<tr>
<td>pH</td>
<td>—</td>
<td>6.58</td>
<td>6.77</td>
<td>10.6</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;5&lt;/sub&gt; or COD</td>
<td>mg/L</td>
<td>0.121&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.95&lt;sup&gt;c&lt;/sup&gt;</td>
<td>485.8&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>19.3</td>
<td>38.0</td>
<td>—</td>
</tr>
<tr>
<td>SS</td>
<td>mg/L</td>
<td>ND&lt;sup&gt;e&lt;/sup&gt;</td>
<td>ND&lt;sup&gt;e&lt;/sup&gt;</td>
<td>17.2</td>
</tr>
</tbody>
</table>

<sup>a</sup>Synthesized solution was dyes with pure water (Milli-Q).

<sup>b</sup>The wastewater was from location processes and the concentrations of RR-120 and AR-299 are determined by the absorbances of the characteristic wavelengths of 513 and 512 nm, respectively.

<sup>c</sup>BOD<sub>5</sub> value.

<sup>d</sup>COD value.

<sup>e</sup>ND: not detected, less than 0.01 mg/L.
Standard Methods.\[12\] A pH controller (model PC-310, SUNTEX, Taipei, Taiwan) was utilized to monitor the variation of the pH value.

The 5-day biological oxygen demand (BOD) test was analyzed according to the Standard Methods (APHA, 1992). The microbial seed used for BOD test was the activated sludge taken from a domestic wastewater treatment plant. The working sludge that did not go through the acclimation process was used within 6 hours after the sludge samples collected from the treatment plant.

RESULTS AND DISCUSSION

The dynamic variations of $C_t$, $TOC_t$, $BOD_5$, COD and ADMI (which is calculated from the absorbances at 438, 540 and 590 nm) in the course of ozonation using the RPB are simultaneously monitored for the investigation. In the first section, the ozonation of Reactive Red 120 and Acid Red 299 in the aqueous solution were performed. Furthermore, the kinetic model adopting schemes with pseudo-first-order kinetics was employed to obtain the reaction rate constant. In the second section, the performance of the textile plant wastewater via ozonation was evaluated under different conditions.

Ozonation of Reactive Red 120 and Acid Red 299

As shown in Figure 2, the decomposition rates of Reactive Red 120 and Acid Red 299 dyes by the ozone treatment followed the pseudo-first-order kinetics as: $-dC/dt = kC$, where $C$ and $k$ are the concentration of dyes (mg/L) and pseudo-first-order rate constant (1/min), respectively. The values of $k$ were determined by plotting the $\ln(C_t/C_0)$ values versus the reaction time.\[13,14\] Figure 2 illustrated that the experimental data were well fitted by a pseudo-first-order kinetics (the R square values were between 0.99 and 0.95). The values of $k$ are 1.87 and 2.21 min$^{-1}$ for Reactive Red 120 and Acid Red 299, respectively, according to the slopes of the linear lines. It showed that Acid Red 299 was more reactive with ozone than Reactive Red 120 with the comparison of the $k$ values. Nevertheless, the two dyes can be efficiently decomposed by ozonation within a short time.

The variations of total carbon concentration (TOC) and pH value during the ozonation of Reactive Red 120 and Acid Red 299 dyes were presented in Figure 3a. The result showed that mineralization rate of the Red 120 was apparently higher than that of Acid Red 299. The TOC removal for Reactive Red 120 and Acid Red 299 were 71% and 59% in 60 minutes under the experimental condition, respectively. Namely, the intermediate compounds of ozonated Reactive Red 120 was faster to be oxidized by the molecular ozone than Acid Red 299. In addition, the solutions would become acidic rapidly within 2 ozonation minutes from the neutral condition. Thus, the oxidation mechanism was considered to be processed by the molecular ozone
The decomposition rates of Reactive Red 120 and Acid Red 299 dyes by ozonation treatment.

Figure 2: The decomposition rates of Reactive Red 120 and Acid Red 299 dyes by ozonation treatment.

predominantly. The initial values of ADMI (ADMI₀) for Reactive Red 120 and Acid Red 299 were 36736 and 41400 units, respectively. As shown in Figure 3b, the decolorization rate of Acid Red 299 during the ozonation is greater than that of Reactive Red 120. However, both the reduction of ADMI increased with the ozonation time to reach 100% within 2 minutes. It was because that the first attack of ozone on the dyes went through the cleavage of the dye chromophores, resulting in the significant decrease of absorbance in the visible wavelengths.

To study the biodegradability of intermediates during the ozonation processes of the dyes, the BOD₅/TOC value was employed as an index to monitor the variation of biodegradability. Figure 4 compared the variation of the BOD₅/TOC values during the ozonation of Reactive Red 120 and Acid Red 299. The results implied that the biodegradability would significantly be promoted by the ozonation treatment. The BOD₅/TOC ratios of the ozonated Reactive Red 120 and Acid Red 299 had the highest values at the certain times, increasing from 0.006 to 5.47 in 20 minutes and from 0.175 to 1.96 in 10 minutes, respectively. Note that the BOD₅/TOC value of Reactive Red 120 was apparently greater than that of Acid Red 299. It showed that
there existed the certain ozonation time to obtain the maximum BOD₅/TOC
value during the ozonation of the two dyes. According to previous
studies,[14,16,17] the main final oxidation products of Reactive Red 120 and
Acid Red 299 during the ozonation would include sulfate, nitrate, formate,
and oxalate. The primary oxidized byproducts or the ozonation pathway of
these two commercial dyes were still required the further investigation. The
trends observed during the ozonation of the dyes in the aqueous solution can
be referable for the ozonation treatment of the textile wastewater.

**Ozonation of Textile Wastewater**

The ozonation of the textile wastewater containing Reactive Red 120
and Acid Red 299 was carried out to study the variations of COD/COD₀,
AMD/ADMI₀ and pH. The initial values of COD (COD₀) and ADMI (ADMI₀) in

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**Figure 3:** The variations of TOC, ADMI and pH values of Reactive Red 120 and Acid Red 299
dyes during ozonation.
The variations of BOD₅/TOC values of Reactive Red 120 and Acid Red 299 dyes during ozonation. The ADMI value of the wastewater is the lump of different dye sources. The apparent concentrations of dyes in the wastewater are determined by each characteristic wavelength. Accordingly, Reactive Red 120 and Acid Red 299 seem to contribute about 52.9% \((= 13.8/100.8 \times 36736/9511 \times 100\%)\) and 33.2% \((= 8.2/107.5 \times 41400/9511 \times 100\%)\) of the ADMI value of the wastewater, respectively. As shown in Figure 5, the textile wastewater via ozonation has the high reduction of ADMI of 93% in 30 minutes. On the contrary, the efficiency of the mineralization was found relatively slow where the COD removal was only 37% in 30 minutes ozonation time. The initial pH value in the alkaline condition of pH \(= 10.6\) decreased into the neutral situation of pH \(= 7.2\) in 30 minutes ozonation time. The increase of acidity (decrease of pH value) may be caused by the generation of the organic acids during ozonation. In the alkaline environment, the oxidation of the textile wastewater was mainly via the radical ozonation of OH radicals generated from the transformation of ozone molecules.\(^{[18]}\) The decrease of the pH value during the ozonation in the textile wastewater is smaller compared with that in the synthesized solution due to its higher buffer capacity of the ionic containment. The conductivity of the textile wastewater is about 9.25 ms/cm. With respect to ADMI, the removal efficiency of ADMI is relatively slower in the textile wastewater because of the competition of its other containing substances for the oxidants.

The ozonation performance of the textile wastewater using the rotating packed bed was evaluated with the different operating conditions including the rotational speed, water flow and applied ozone dosage. The model operation
Figure 5: The variations of COD/COD$_{0}$, AMDI/ADMI$_{0}$ and pH of textile wastewater during ozonation.

The condition is water flow of 1.2 L/min, rotational speed of 1500 rpm and applied ozone dosage of 79.2 mg/min. Figure 6 compared the COD removal in the different operating conditions. It showed that the decrease of the water flow rate, rotational speed and applied ozone dosage would decrease the efficiency of mineralization. The reason for this circumstance is due to the variation of the mass transfer rate of ozone.\[11\] The higher rotational speed and water flow would increase the gas-liquid mass transfer coefficient of ozone. In addition, the higher mass transfer rate of ozone would also be achieved by increasing the

Figure 6: Comparison of different operating conditions in rotating packed-bed reactor during ozonation of textile wastewater, where the model operating condition is gas flow of 1.98 L/min, ozone concentration of 40 mg/L (ozone dosage 79.2 mg/min), water flow of 1.2 L/min and rotational speed of 1500 rpm. The operating parameters in other cases not being noted are the same as those in the model operating condition.
applied ozone dosage, which is the product of the gas flow rate and inlet ozone concentration. The highest removal efficient of COD obtained at 30 minutes was 37% in the condition with the water flow rate of 1.2 L/min, rotational speed of 1,500 rpm and applied ozone dosage of 79.2 mg/min. Consequently, this study can provide useful information for the ozonation of the textile wastewater in a rotating packed bed.

CONCLUSIONS

This study investigates the oxidation of Reactive Red 120, Acid Red 299 dyes and a local textile wastewater by ozonation treatment. Ozonation is performed in a rotating packed bed. Experimental results indicate that the decomposition rates of Reactive Red 120 and Acid Red 299 dyes by ozone treatment followed pseudo-first-order kinetics with the reaction constant of 1.87 and 2.21 min$^{-1}$, respectively. The two dyes are oxidized rapidly by ozonation along with the remarkable efficiencies of decolorization in a short time. The mineralization efficiency of Reactive Red 120 via ozonation is found better than that of Acid Red 299. In addition, the ozonation shows the remarkable improvement of the biodegradability.

The BOD$_5$/TOC ratios of the ozonated Reactive Red 120 and Acid Red 299 would increase with ozonation time and have the maximum values at certain moments. The primary oxidized by-products or the ozonation pathway of these two commercial dyes require further investigation. As for the ozonation of the textile wastewater, it shows the high decolorization and moderate COD removal efficiencies. The removal percentages of ADMI and COD in the textile wastewater can be achieved 93% and 37% in 30 minutes’ ozonation time, respectively. Furthermore, the increase of the rotational speed, water flow and applied ozone dosage would increase the mineralization efficiency of the textile wastewater in a rotating packed bed.

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