The application of photocatalysis on TiO₂ for degrading COD in paper mill wastewaters

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ABSTRACT: Photocatalysis is a feasible wastewater treatment under limited conditions. The treatment degraded COD by 90% or more when the initial COD concentration was 500 mg/L or less. Microtox analyses revealed that the acute toxicity in these wastewaters was also degraded significantly. When the initial concentration was greater than 1000 mg/L, however, photocatalysis degraded COD by less than 50%. The processes from which the wastewaters were generated also had an impact on the effectiveness of photocatalysis. The degradation of COD and toxicity was lower in wastewater samples from kraft and semi-chemical pulping mills than in the samples from the other mills.

Application: Photocatalysis on TiO₂ is a feasible treatment method to degrade COD and toxicity in wastewaters when the initial COD is less than 500 mg/L.

In general, pulp and paper mills discharge from 5000 gal to more than 30,000 gal of wastewater per ton of paper produced. This wastewater often contains wood extractives, including resin acids and fatty acids [1–6]. In addition to the wood extractives, pulping and bleaching chemical by-products may also be present, including chloroform, organic sulfur compounds, and chlorinated phenols [1]. If present in sufficient concentrations, many of the compounds in pulp and paper mill wastewaters would be toxic to wildlife if they leave the mill untreated [1–6].

These chemicals may be significantly degraded in biological treatment systems—even greater than 90% in some secondary treatment systems. However, there are situations in which biological treatment methods may not be adequate for site-specific water quality requirements. For example, a mill may be built in a location where the water body is inadequate for discharging mill effluents. Such a mill must be designed for zero discharge. McKinley Paper in Santa Fe is a zero-discharge mill that relies on post secondary treatment (ultrafiltration, reverse osmosis, and crystallization) before water is recycled back into the process [7]. New treatments that can degrade low levels of organic compounds in wastewater are needed for tightened environmental regulations in the future and possible mill closures.

In this study, our goal was to assess the feasibility of using TiO₂ as a photocatalyst for degrading the chemical oxygen demand (COD) and toxicity in wastewaters, after primary treatment, from various types of pulp and paper mills. The mills we included in our study are kraft pulp, semi-chemical pulp, and thermomechanical pulp (TMP) mills; a paper mill that purchases pulp; and a paper mill that processes and uses TMP and kraft pulp and recycled fiber. Additional goals were to assess the sensitivity of photocatalysis to the initial COD concentration and to the type of processes from which the wastewater came.

PHOTOCATALYSIS

Photocatalysis is an ambient-temperature process in which organic compounds in wastewater can be oxidized on a photocatalyst, such as titanium dioxide (TiO₂) [8–12]. Energy from light (hν) is utilized in photocatalysis to oxidize organic pollutants. The primary processes in photocatalysis have been extensively researched [8–12]. Equations 1–5 elucidate a general mechanism for the photocatalytic oxidation of organic compounds (denoted as RH) on TiO₂:

\[ \text{TiO}_2 + h\nu \rightarrow h^+ + e^- \]  \hspace{1cm} (1)

\[ h^+ + e^- \rightarrow \text{heat} \]  \hspace{1cm} (2)

\[ e^- + O_{2,\text{ads}} \rightarrow O_{2,\text{ads}}^- \]  \hspace{1cm} (3)

\[ h^+ + \text{H}_2\text{O}_{\text{surface}} \rightarrow \cdot\text{OH}_{\text{surface}} + H^+ \]  \hspace{1cm} (4)

\[ h^+ + \text{OH}_{\text{surface}} \rightarrow \cdot\text{OH}_{\text{surface}} \]  \hspace{1cm} (5)

Briefly, upon illumination of TiO₂ with near-ultraviolet light (\( \lambda < 380 \text{ nm} \)), electron-hole pairs are formed within TiO₂ particles (Eq. 1). The electrons (e⁻) and holes (h⁺) migrate to the surface, become trapped in defects in the crystal structure of TiO₂, and participate in oxidation and reduction reactions, or they recombine (Eq. 2). Surface hydroxyl groups react with the trapped hole on illuminated TiO₂, leading to the formation of hydroxyl radicals (·OH) and the liberation of a hydrogen ion (Eq. 4).

The hydroxyl radicals oxidize adsorbed organic species on the surface of the TiO₂ particles (Eq. 5). Crystal structure [13, 17, 18], particle size [14, 15], surface area, and morphology [16] greatly influence the photocatalytic efficiency of TiO₂. Concentrations of dissolved oxygen, TiO₂, and organics, and the light intensity profile within the reaction slurry significantly affect the photocatalytic efficiency [19, 20].

Applications of photocatalysis for the pulp and paper industry have been explored, primarily in the treatment of bleach plant effluents [21–26]. Yeber et al. observed approximately 50% degradation of both COD and toxicity with supported TiO₂ in a wastewater from bleaching kraft pulp [21–23]. Balcioglu et al. observed that wastewaters treated by photocatalysis enhanced the biodegradability of remaining pollutants in bleach plant effluent, that the effectiveness of photocatalysis was strongly affected by the initial COD and chloride ion concentrations, and that photocatalysis is significantly more effective on pretreated waters than on raw or untreated wastewaters [24, 25]. Using total organic carbon (TOC) as a measure of the effectiveness of photocatalysis, Perez et al. found that the TOC in the laboratory-made wastewaters from bleaching pulp with...
chlorine dioxide (ClO₂) decreased from approximately 300 mg/L to less than 50 mg/L after 20 h in the photocatalytic reactor [26].

**MATERIALS AND METHODS**

**Sources of effluents**

Table 1 describes the wastewaters. Each mill wastewater was collected after primary clarification. The samples were filtered to remove suspended wood fibers and were placed in a refrigerator until used. In addition, we prepared a synthetic wastewater in our lab by solubilizing abietic acid in methanol and diluting the solution with deionized water. Abietic acid is commonly found in pulp and paper mill wastewaters [3, 27].

**Materials**

We tested three different brands of TiO₂ before settling on one that was composed of 80% anatase and 20% rutile. The size of its anatase crystals is approximately 30 nm, with a surface area of 50 m²/g. The gaseous effluent consisted of excess oxygen, carbon dioxide, water vapor, and other gaseous by-products. This effluent exited the reactor through an outlet line and was bubbled through a barium hydroxide solution. CO₂ was captured as barium carbonate, which precipitated out of the solution. The presence of barium carbonate precipitate was evidence that CO₂ was being generated in the reaction, but we were not able to quantify the precipitate reliably.

**Analytical methods**

The COD was the main parameter used to evaluate the performance of the photocatalytic process. We analyzed COD by standard methods for closed reflux colorimetry. BOD₅ analyses were also performed before and after treatment according to standard methods [28]. In addition, we measured pH using an electronic pH probe and Microtox analyses (Microtox 500 Analyzer, Microbics Corp.), which gives a rough estimation of acute toxicity.

Various metals in the wastewater were measured with inductively coupled plasma (ICP). An effort was made to identify the organic species in each wastewater sample by using gas chromatography and mass spectrometry (GC/MS). However, no organics were identified with the methods used, which suggests that any organic compounds in the wastewater were below the detection limits or that any such compounds did not elute from the GC column.

**Experimental procedure**

With the cooling water circulating to prevent the temperature of the exiting water from rising above 50°C, 500 mL of the slurry was introduced into the reaction vessel. Oxygen flow was initiated through the slurry under continuous stirring. A 10 mL sample was withdrawn, and the light was turned on. Subsequent samples were withdrawn every hour for test periods of 4 h or 8 h.

Each trial was repeated. The reaction time was 4 h in the first trial and 8 h in the second trial. In the second trial, the gaseous effluent line was bubbled through a barium hydroxide solution to collect the carbon dioxide as barium carbonate, which precipitates from solution.
RESULTS AND DISCUSSION

Controls

Controls were run on a selected wastewater to assess the extent of volatilization, photolysis, and the adsorption of organics species in the wastewater during the photocatalytic oxidation tests. All of the controls were performed on wastewater from a paper mill that purchases its pulp (Wastewater 5 in Table I). COD was used to evaluate the extent of photolysis, adsorption, and volatilization. Table II describes the controls and summarizes the results.

The results of the control tests indicate that neither volatilization (Run 1) nor photolysis (Run 4) is a significant mechanism for COD degradation in the wastewaters. Up to 12% COD reduction could be attributed to the adsorption of the organics on the TiO₂ particles (Runs 2 and 3).

Sensitivity to laboratory operating conditions

We varied four operating parameters to assess the sensitivity of COD degradation to each:

1. The source of TiO₂ photocatalyst
2. The concentration of TiO₂
3. The concentration of oxygen used in the purge gas
4. The flow rate of the purge gas.

Each test was run for 4 h, and the effectiveness of photocatalysis was measured as the COD degradation observed in the wastewater. The wastewater used for the control tests was Wastewater 5 in Table I.

Source of TiO₂ photocatalyst

Of three TiO₂ samples, the one composed of 80% anatase and 20% rutile demonstrated the highest photoactivity and was the one we used exclusively in subsequent experimental tests. The difference in photoactivity between the brands is a function of their chemical and physical properties, including crystal structure, crystal size, crystallinity, surface properties, and surface area [13–18]. The enhanced photoactivity of the one we chose has been attributed to the interaction of the anatase and rutile phases, which tends to stabilize the charge separation [17] and minimize charge recombination (Eq. 2). Studies on the effects of catalyst properties on the photoactivity of TiO₂ can be found in the relevant literature [8–18].

TiO₂ concentration

The concentration of TiO₂ was varied from 0 g/L to 1 g/L. Each test was run for 4 h with pure oxygen purge gas at a flow rate of 0.5 L/min. The degradation rate of COD at each TiO₂ concentration is shown in Fig. 2. The COD degradation in the wastewater increased with increasing TiO₂ concentration up to 1 g/L and then decreased slightly at concentrations above 1 g/L.

We expected to find such an optimum TiO₂ concentration because of two opposing effects. As TiO₂ concentration increases from 0 g/L to 1 g/L, the concentration of active surface sites in the wastewater increases, as does the apparent COD degradation. However, light penetration into the reaction slurry decreases as the TiO₂ concentration increases. At some TiO₂ concentration, the penetration of light into the reaction slurry begins to fall off, with fewer and fewer TiO₂ particles exposed to light. In our test system, the concentration of 1 g/L had a greatest COD degradation, at 98%, and this concentration was used for all subsequent tests.

Oxygen concentration

The oxygen in the purge gas was varied from 0% (pure nitrogen) to 100% (pure oxygen) at a constant flow rate. Figure 3 presents the results as the rate of COD degradation plotted against the percent of oxygen. The need for dissolved oxygen is apparent since very little reduction in COD was observed in the absence of oxygen.

The photocatalytic oxidation of organic compounds in water has been successfully modeled using Langmuir–Hinshelwood kinetics for both organic species and oxygen concentrations (C_H₂O and C_O₂, respectively) [19, 20, 26, 29–31]. We obtained the trendline in Fig. 3 by using the Langmuir–Hinshelwood kinetic model (Eq. 6) and setting the model parameters, K′ and K′′, to values that best fit the data.

\[
\frac{d[C_H]}{dt} = \frac{k'K'C_O}{1 + K'C_O}
\]  

(6)

In this equation, the parameter K′ is a function of the type and concentration of TiO₂, the geometry of the test system, the illumination spectrum and light intensity profile in the reactor, the extent of mixing in the reactor, the operating temperature and pressure, the presence of other chemicals in the wastewater, and the intrinsic rate constants for the photocatalytic processes. The parameter K′′ is a function of the adsorption characteristics of the organics and oxygen on TiO₂. At low oxygen concentrations, Eq. 6 approximates a first-order expression, meaning that the reaction rate increases as a function of oxygen concentration. At high oxygen concentrations, Eq. 6 approximates a zero-order reaction, meaning the reaction rate is constant.


<table>
<thead>
<tr>
<th>TiO₂ CONCENTRATION, g/L</th>
<th>TiO₂ CONCENTRATION, g/L</th>
<th>OXYGEN IN PURGE STREAM, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>12</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>0.0</td>
<td>0.5</td>
<td>3</td>
</tr>
</tbody>
</table>

Table II describes the controls and summarizes the results.
III. Characteristics of various wastewaters before and after photocatalysis.

<table>
<thead>
<tr>
<th>Mill</th>
<th>Time, h</th>
<th>COD</th>
<th>BOD</th>
<th>BOD/COD</th>
<th>Conductivity</th>
<th>pH</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>0</td>
<td>1397</td>
<td>361</td>
<td>0.26</td>
<td>2.11</td>
<td>7.74</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1165</td>
<td>289</td>
<td>0.25</td>
<td>2.15</td>
<td>6.5</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>833</td>
<td>256</td>
<td>0.31</td>
<td>2.24</td>
<td>7.53</td>
<td>0.47</td>
</tr>
<tr>
<td>TMP</td>
<td>0</td>
<td>1556*</td>
<td>339</td>
<td>0.22</td>
<td>0.62</td>
<td>7.23</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>804</td>
<td>225</td>
<td>0.28</td>
<td>0.74</td>
<td>6.29</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>719</td>
<td>253</td>
<td>0.35</td>
<td>0.79</td>
<td>6.82</td>
<td>0.26</td>
</tr>
<tr>
<td>TMP/Kraft</td>
<td>0</td>
<td>497</td>
<td>168</td>
<td>0.34</td>
<td>0.89</td>
<td>8.29</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>63</td>
<td>31</td>
<td>0.49</td>
<td>0.87</td>
<td>7.53</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>34</td>
<td>20</td>
<td>0.59</td>
<td>0.78</td>
<td>8.43</td>
<td>n.a.</td>
</tr>
<tr>
<td>Paper mill</td>
<td>0</td>
<td>259</td>
<td>111</td>
<td>0.43</td>
<td>0.82</td>
<td>7.94</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20</td>
<td>12</td>
<td>0.6</td>
<td>0.84</td>
<td>8.44</td>
<td>0.0</td>
</tr>
<tr>
<td>Semi-chem.</td>
<td>0</td>
<td>2107*</td>
<td>2214*</td>
<td>n.a.</td>
<td>1.95</td>
<td>8.5</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2064*</td>
<td>1791*</td>
<td>n.a.</td>
<td>1.97</td>
<td>8.8</td>
<td>0.38</td>
</tr>
</tbody>
</table>

*Outside of calibrated range and above the limit of 1500 mg/L. n.a. = data not available

IV. Characteristics of semi-chemical wastewater before and after photocatalysis.

<table>
<thead>
<tr>
<th>Strength</th>
<th>Time, h</th>
<th>COD</th>
<th>BOD</th>
<th>BOD/COD</th>
<th>Conductivity</th>
<th>pH</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>0</td>
<td>2107</td>
<td>2214</td>
<td>n.a.</td>
<td>1.95</td>
<td>8.5</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2064</td>
<td>1791</td>
<td>n.a.</td>
<td>1.97</td>
<td>8.8</td>
<td>0.38</td>
</tr>
<tr>
<td>50%</td>
<td>0</td>
<td>1913</td>
<td>n.a.</td>
<td>n.a.</td>
<td>1.5</td>
<td>10.0</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1659</td>
<td>n.a.</td>
<td>n.a.</td>
<td>1.1</td>
<td>8.1</td>
<td>n.a.</td>
</tr>
<tr>
<td>25%</td>
<td>0</td>
<td>904</td>
<td>326</td>
<td>0.36</td>
<td>0.66</td>
<td>8.3</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>357</td>
<td>118</td>
<td>0.33</td>
<td>0.53</td>
<td>7.3</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*Outside of calibrated range and above the limit of 1500 mg/L. n.a. = data not available

4. Relative COD concentration in various wastewaters as a function of time.

Figure 3 shows that using a purge gas containing 20% oxygen (similar to air) resulted in a COD degradation rate that is 75% of that obtained using pure oxygen. However, as the organic concentration increases, the difference increases between the rate obtained with pure oxygen and that obtained with air. Therefore, only the data obtained with pure oxygen are reported subsequently.

Oxygen flow rate

Finally, we evaluated the effect of oxygen flow rate by measuring the COD degradation at purge gas flow rates of 0.25 L/min, 0.5 L/min, and 0.75 L/min. A slightly lower COD degradation rate was observed at purge gas flow rates of 0.25 L/min and 0.75 L/min than at 0.5 L/min. A possible explanation is that as the flow rate increases, the oxygen replacement rate in the reaction slurry increases up to 0.5 L/min. However, as the flow rate increases further, there are more gas bubbles, and they are larger. These gas bubbles scatter the incident light more effectively, thus reducing the amount of light absorbed by the TiO₂ particles in the reaction slurry. All subsequent experiments were run with a purge gas flow rate of 0.5 L/min.

Wastewater samples

To compare water quality, we tested each sample prior to and following the photocatalysis reaction tests for COD, biochemical oxygen demand (BOD), conductivity, pH, and toxicity. Since the final wastewater samples contained TiO₂, the samples were allowed to settle overnight, and only the decanted water was used for all measurements.

Tables III and IV summarize the results obtained for each water sample. In these tables, toxicity is expressed as 100/EC₅₀ at 15 min. The COD measurement for the semi-chemical pulp mill wastewater was well over the calibrated range and above the standard reagent limit (1500 mg/L) for COD analyses. Therefore, this sample was diluted with deionized water to 50% and 25% of its original strength, and photocatalytic tests were conducted on those samples as well. The results for the semi-chemical wastewater, as received and after dilution, are shown in Table IV.

As Tables III and IV show, the ratio of BOD to COD generally increases after treatment with photocatalysis. This result supports the conclusions of Yeber et al. that treatment with TiO₂ photocatalysis enhances the biodegradability of the organic compounds in wastewaters [23].

The tables also show that the pH of the reaction slurry does not change significantly with photocatalysis treatment. The pH generally decreases in the reaction slurry during photocatalytic oxidation, since hydrogen ions are typically released during the hydration or hydroxylation of the TiO₂ surface upon illumination (Eq. 4). The general lack of change in pH may be explained by the presence of several other metal ions in the wastewaters, which would buffer the reaction slurry.

As also reflected in Tables III and IV, the toxicity generally decreases with photocatalysis.

The graphs in Figs. 4 and 5 show the degradation of COD in each type of wastewater and the rate at which COD is degraded. The trendline in the second graph was generated by assuming Langmuir–Hinshelwood kinetics (Eq. 7) and by setting the model parameters, k and K, to values that best fit the data. In this equation, the oxygen concentration is assumed to be constant. Moreover, the
equation has been used successfully to model the photocatalytic degradation of organics in water at constant oxygen concentrations [19, 20, 26, 29-31].

\[
\frac{d[C_{OH}]}{dt} = \frac{kK[C_{OH}]}{1 + K[C_{OH}]} \tag{7}
\]

As Figs. 4 and 5 show, both the initial COD concentration and the source of the wastewater are key factors in the performance of photocatalysis as a treatment for pulp and paper mill wastewaters. From Eq. 7, we see that the rates of COD removal from the wastewaters should follow first-order kinetics at low initial COD concentrations (increasing with increasing COD concentrations) and then become zero-order kinetics at higher COD concentrations (a constant rate of degradation).

This is, in fact, what we observe in Fig. 5. However, there are two outliers in this graph: the data points for the synthetic and the Kraft wastewaters. For the synthetic wastewater, the COD degradation rate is much higher than observed in actual pulp and paper mill wastewaters. For the Kraft wastewater, the COD degradation rate falls far below the rates observed in the other types of pulp and paper mill wastewaters.

Photoactivity can be degraded by the presence of metal and chloride ions in the wastewaters [32-34]. Therefore, the highest rate of organic removal should be observed in the wastewater containing the lowest concentrations of inorganic contaminants. The highest rate of COD degradation was observed in the synthetic wastewater, since it contained no contaminants other than acetic acid and methanol. The Kraft wastewater, for which photocatalysis was least effective, contained metal ions and most likely chloride ions and sulfur-containing contaminants, all of which would inhibit the effectiveness of photocatalysis [32-35].

Table V lists the metal ions in the various wastewaters from the mills.

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Metal Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>Sodium, magnesium, calcium</td>
</tr>
<tr>
<td>TMP</td>
<td>Sodium, magnesium</td>
</tr>
<tr>
<td>TMP/Kraft</td>
<td>Iron, calcium, magnesium</td>
</tr>
<tr>
<td>Paper mill</td>
<td>Calcium, potassium, Magnesium, calcium, sodium</td>
</tr>
</tbody>
</table>

V. Metals present in various wastewaters.

COD, BOD, and toxicity

COD, BOD, and toxicity degradation by photocatalysis in each of the wastewaters, showing results (a) after 4 h and (b) after 8 h.

COD, BOD, and toxicity

Figure 6 summarizes the results of COD, BOD, and toxicity degradations for each type of wastewater after 4 h and 8 h in the photocatalytic reactor. The results for each type require some comments.

Kraft mill wastewater. Photocatalysis was not able to effectively degrade the COD or BOD in the Kraft mill wastewater. The COD and BOD were reduced by 17% and 20%, respectively, after 4 h, and by 40% and 29%, respectively, after 8 h. The toxicity decreased by 30% after 4 h and decreased further after 8 h. The wastewater was initially a dark brown color. After 4 h in the reactor, the wastewater retained a slight brown color. However, after 8 h, the wastewater was water-white.

The relatively low rate of organic contaminant removal by photocatalysis in Kraft wastewaters is not attributable only to the high concentrations of organics. It is also caused by metal ions, chloride ions, and sulfur-containing compounds, all of which tend to decrease the efficiency of photocatalysis [32-35]. In addition, the initial brown color may have impaired the penetration of light into the reaction slurry, thus decreasing the apparent degradation of COD in the wastewater.

TMP mill wastewater. Photocatalysis was more effective in reducing the COD and toxicity in the TMP wastewater than in the Kraft wastewater, even though the initial COD concentrations in TMP and Kraft were similar (about 1500 mg/L). This finding indicates that the types of both organic and inorganic species in the wastewater affect the effectiveness of photocatalysis. The Kraft wastewater likely contained sulfur- and chloride-containing compounds from the pulping and bleaching operations at a bleached Kraft mill, which reduces the effectiveness of photocatalysis [32-35]. The TMP wastewater did not contain these compounds, since the TMP process does not utilize sulfur- or chloride-containing chemicals.

The TMP wastewater was dark brown initially, but after 4 h, it was water-white. However, the toxicity increased slightly after 4 h and then decreased over the next 4 h in the photocatalytic reactor. This result indicates that the potentially harmful compounds in the TMP wastewater were initially oxidized to more highly toxic compounds but were subsequently degraded as the reaction continued.

TMP, Kraft, and recycled fiber wastewater. Photocatalysis reduced the COD significantly in the wastewater obtained from the pulp mill processing TMP, Kraft, and recycled fiber. The initial COD concentration was approximately 500 mg/L. This wastewater was initially light brown, but it was water-white after 4 h in the photocatalytic system. The COD and BOD were reduced by 87% and 81%, respectively, and the toxicity was not detectable after 4 h. This outcome shows that photocatalysis has the ability to effectively treat this type of wastewater.

Semi-chemical wastewater. We were unable to assess the effectiveness of photocatalysis for the treatment of semi-chemical wastewater as received. The COD concentration in the sample was well above the calibrated range of our analytical method and well above the recommended range of COD concentrations in our vial of standard reagent for COD analyses. However, we observed reductions of 19% for BOD and 29% for toxicity in this wastewater as received.
As already discussed, this wastewater was diluted with deionized water to 50% and 25% of its original strength (Table IV). Because of equipment problems, the BOD and toxicity for wastewater diluted to 50% were not accurately obtained and are not reported. The reductions in COD and toxicity were 60% and 11%, respectively, after the wastewater was diluted with deionized water to 25% of its original strength. The rate of COD degradation observed for the wastewater at 25% strength was higher than that observed in kraft mill wastewater and only slightly lower than observed in other pulp and paper mill wastewaters.

**Paper mill wastewater.** This wastewater was used for the control experiments and sensitivity assessment, as described previously. It also had the lowest initial COD concentration, at 220 mg/L, of all the wastewaters. The photocatalytic treatment of this wastewater effectively degraded over 90% of the initial COD and BOD, and the toxicity was not detectable after 8 h in the photocatalytic reactor.

**Synthetic wastewater.** Synthetic wastewater was also tested for the sake of making comparisons. The synthetic wastewater contained no contaminants other than abietic acid and methanol. Without other reactions or other contaminants competing for adsorption sites on the TiO₂ particles, the COD was more extensively degraded than it was in actual pulp and paper mill wastewater. This result demonstrates the need to use actual field samples of wastewater in feasibility assessments of new technologies.

**CONCLUSIONS**
Photocatalysis with TiO₂ is a feasible method for degrading both COD and toxicity in various types of pulp and paper mill wastewaters. However, the use of photocatalysis has limitations. The effectiveness of photocatalysis depends on the initial concentration of toxic organic materials and on the types of other potentially harmful materials in the wastewater.

Photocatalysis can be applied to effectively treat wastewater streams with initial COD concentrations of 500 mg/L or less. Although the data obtained in this study cannot identify specific organic and inorganic contaminants that acted to inhibit photocatalysis, the data do show that photocatalysis is effective mostly for the treatment of wastewaters that are generated in processes with relatively low chemical usage.

This technology should be investigated further for possible use in pulp and paper mills. Photocatalysis could help reduce the environmental impact of effluents. Alternatively it could make it more feasible to increase water recycling and possibly close the system. To apply photocatalysis to large-scale systems will require new reactor designs, catalyst immobilization, and high contact between catalyst, light, oxygen, and compounds that contribute to COD.

**LITERATURE CITED**

This paper is also published on TAPPI’s web site <www.tappi.org> and summarized in the September Solutions! for People, Processes and Paper magazine (Vol. 87 No. 9).

**INSIGHTS FROM THE AUTHORS**

This research complements earlier research by expanding the technology to the pulp and paper industry. It is different from previous research in that actual wastewaters from various mills were used, and the COD, BOD, and toxicity were the measures of effectiveness rather than the degradation of a single compound in otherwise clean water.

The effectiveness of photocatalysis differs with different wastewaters, but photocatalysis could serve as a tertiary treatment of wastewaters. To implement photocatalysis in a large-scale system would require a way to remove and recover the photocatalyst (titanium dioxide) from water. It would also require an effective method for illuminating the photocatalyst. One possibility is to use a falling film reactor with titanium dioxide immobilized onto a wall over which the falling film flows. Consequently, the next step in this research is to assess the effectiveness of using a falling film reactor with photocatalysis.

A mill might benefit from photocatalysis if it needed to recycle more water, such as in a mill closure or partial closure. Photocatalysis might also help reduce the environmental impact of mill discharges.

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