Treatment of wastewater from a cotton dyeing process with UV/H$_2$O$_2$ using a photoreactor covered with reflective material

Claudinei Fernandes de Melo, Flavio T. da Silva and Teresa C. B. de Paiva

ABSTRACT

Wastewater containing several dyes, including sulfur black from the dyeing process in a textile mill, was treated using a UV/H$_2$O$_2$ process. The wastewater was characterized by a low BOD/COD ratio, intense color and high acute toxicity to the algae species *Pseudokirchneriella subcapitata*. The influence of the pH and H$_2$O$_2$ concentration on the treatment process was evaluated by a full factorial design $2^3$ with three replicates of the central experiment. The removal of aromatic compounds and color was improved by an increase in the H$_2$O$_2$ concentration and a decrease in pH. The best results were obtained at pH 5.0 and 6 g L$^{-1}$ H$_2$O$_2$. With these conditions and 120 min of UV irradiation, the removal of the color, aromatic compounds and COD were 74.1, 55.1 and 44.8%, respectively. Under the same conditions, but using a photoreactor covered with aluminum foil, the removal of the color, aromatic compounds and COD were 92.0, 77.6 and 59.4%, respectively. Moreover, the use of aluminum foil reduced the cost of the treatment by 40.8%. These results suggest the potential application of reflective materials as a photoreactor accessory to reduce electric energy consumption during the UV/H$_2$O$_2$ process.

Key words | acute toxicity, degradation rate, first-order kinetics, photolysis, reflective material, UV irradiation

INTRODUCTION

Textile mills utilize large volumes of water during dyeing and finishing processes. It is estimated that the average water consumption of a textile mill is 117 L kg$^{-1}$ of fiber (Feitkenhauer & Meyer 2001). Consequently, very large volumes of colored wastewaters are generated because the dyes do not bind to the fibers. In addition to their strong coloration, these wastewaters present large amounts of surfactants and inorganic ions (carbonate, chlorite and sodium), high pH values, variable temperatures, wetting agents, sequestering agents, low BOD/COD ratio, and sometimes heavy metals (Cu, Cr, Ni) (Arslan et al. 1999; Alaton et al. 2002; Lopez Cisneros et al. 2002). The major environmental impact of strongly colored wastewaters is attributed to light absorption, which interferes with the photosynthesis of aquatic plants and algae (Nilsson et al. 2006). Furthermore, some studies have shown that azodyes are metabolized by anaerobic microorganisms yielding carcinogenic and mutagenic aromatic amines (Pinheiro et al. 2004).

Conventionally, textile wastewaters are treated using a coagulation/flocculation process followed by an activated sludge treatment (Choy et al. 1999; Kunz et al. 2002). In Brazil, approximately one-third of textile mills treat these effluents using conventional methods (CPRH 2001). However, coagulation/flocculation processes are not destructive and only transfer dyes to another phase, producing wastes that require subsequent treatment (Modirshahla & Behnajady 2006). In addition, activated sludge treatment is not able to degrade the dyes completely because most of them are designed to resist sweat, soap, water, light and microbiological oxidation (Banat et al. 1996; Shu & Chang 2005). Therefore, it is necessary to employ a treatment processes that is capable of destroying dye molecules.

Several advanced processes have been evaluated for the treatment of textile wastewaters. Chemical degradation by oxidation agents such as chlorine and ozone are effective for the reduction of color and organic matter from textile...
wastewaters. However, these processes have serious disadvantages: (i) the organochlorine compounds generated by oxidation with chlorine can be more toxic than the parent compounds; and (ii) the cost of the ozonation process is high because the continuous generation of ozone is required due to its short half-life (Robinson et al. 2001).

Advanced oxidation processes (AOP) can convert recalcitrant pollutants into innocuous chemicals at fast reaction rates (Alaton et al. 2002). AOP are oxidative processes that generate enough hydroxyl radicals to act as principal oxidant agents (Glaze et al. 1987). These radicals are non-selective and highly reactive with the majority of organic molecules \( (E^0 = 2.8 \text{ V}) \) (Lopez Cisneros et al. 2002). Azbar et al. (2004) compared several AOP \( (\text{O}_3, \text{O}_3/\text{UV}, \text{H}_2\text{O}_2/\text{UV}, \text{O}_3/\text{H}_2\text{O}_2/\text{UV} \) and \( \text{Fe}^{2+}/\text{H}_2\text{O}_2) \) and conventional chemical treatment (coagulation using \( \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}, \text{FeCl}_3 \) and \( \text{FeSO}_4) \) for the removal of COD and color from polyester and acetate fiber dyeing wastewater. These authors found that AOP had levels of COD and color removal that were much higher than those obtained by coagulation.

Among several AOP, oxidative degradation by homogeneous UV radiation in the presence of hydrogen peroxide (the \( \text{UV/H}_2\text{O}_2 \) process) appears to be one of the more appropriate processes for wastewater treatment. The advantages of \( \text{H}_2\text{O}_2 \) are related to its high thermal stability at the concentrations used for wastewater treatment, its commercial availability and complete water miscibility. Moreover, the formation process of hydroxyl radicals by the \( \text{UV/H}_2\text{O}_2 \) process has high quantum efficiency and can be performed at room temperatures. The \( \text{UV/H}_2\text{O}_2 \) process, in comparison with other AOP, does not generate sludge and has high rates of organic matter removal (Vandevivere et al. 1998; Aleboyeh et al. 2005; Daneshvar et al. 2005).

Hydroxyl radical formation is caused by the homolytic cleavage of \( \text{H}_2\text{O}_2 \) molecule under UV radiation (Equation (1)), which yields two hydroxyl radicals per molecule (Georgiou et al. 2002; Tang 2004).

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\text{HO}^* \tag{1}
\]

The degradation rates in this process, as well as other AOP, are directly related to the amount of hydroxyl radicals formed during the treatment. The amount of hydroxyl radicals, in turn, depends on the intensity of the UV radiation, \( \text{H}_2\text{O}_2 \) concentration, pH, the presence of hydroxyl scavengers and other factors (Daneshvar et al. 2005). However, a high concentration of \( \text{H}_2\text{O}_2 \) may reduce degradation rates due to reaction of \( \text{HO}^* \) radicals with \( \text{H}_2\text{O}_2 \), yielding peroxy radicals (\( \text{HO}_2 \)) which have a lower oxidation potential than the \( \text{HO}^* \) radical (Daneshvar et al. 2005) (Equation (2)):}

\[
2\text{HO}^* + \text{H}_2\text{O}_2 \rightarrow 2\text{HO}_2^* \tag{2}
\]

Because the \( \text{UV/H}_2\text{O}_2 \) process is relatively expensive (mainly due to the consumption of electric energy), it should only be applied for the treatment of wastewaters containing biologically recalcitrant compounds.

In this work, the results of the characterization of a wastewater from the dyeing process of a textile mill are shown and the kinetics of color removal from wastewater by the \( \text{H}_2\text{O}_2/\text{UV} \) process and the effects of \( \text{H}_2\text{O}_2 \) concentration, pH and the use of reflective material over the photoreactor on the removal of color, COD and aromatic compounds are discussed.

## EXPERIMENTAL

### Materials

The textile wastewater used in this work was collected from a cotton dyeing process in a textile mill located in the city of Barbacena-MG, Brazil. The wastewater contained the dyes Remazol Turquoise Blue G, Levafix Blue CA gran and Sulfur Black.

Considering that different dyes are used during each season and consequently the composition of wastewater undergoes frequent alterations, it was collected a single sample of 50 L. This sample was homogenized and divided into 500 mL aliquots, which were stored at \(-18 \text{ C}\), as recommended by the Brazilian technical standards NBR 9897 (ABNT 1997a) and NBR 9898 (ABNT 1997b).

### The photoreactor

The \( \text{UV/H}_2\text{O}_2 \) reactions were performed in a water-jacketed glass reactor with 0.5 L capacity (Figure 1), designed as described by Azbar et al. (2004) with modifications. Thermostatic bath water (TE 184, Tecnal, Brazil) at 25 \( \text{C} \) was used to supply the circulation system of the glass jacket. The radiation source was a mercury-vapor UV lamp emitting at 254 nm (125 W, UV-C, manufactured by Philips, Brazil) enveloped in a quartz tube. Both the lamp and the quartz tube were axially centered into the reactor. The wastewater...
was mixed by magnetic stirring using Teflon-coated bars.

**Experimental procedure**

A mercury-vapor lamp was turned on at least 20 min before experiments. The samples of wastewater (0.5 L) were transferred to the photoreactor and the H$_2$O$_2$ was added. Doses of 5 mL were withdrawn at defined time intervals and transferred to a glass bottle containing a sufficient amount of the enzyme catalase to convert the residual H$_2$O$_2$. The samples were subsequently analyzed to determine color, COD and aromatic compounds. Temperature was maintained at 25 °C by means of cooling water flowing through the jacket. The reactions were performed with the photoreactor being either covered or uncovered with aluminum foil. The incident light flux was determined by hydrogen peroxide actinometry (Nicole et al. 1990) as 5.6 × 10$^{-5}$ Einstein L$^{-1}$ s$^{-1}$.

**Experimental design**

The experiments were performed using the photoreactor without a reflective surface, and the irradiation time was 45 min. All of the experiments were performed using the same UV dose. The influence of the independent variables, the concentration of H$_2$O$_2$ ($X_1$) and the pH ($X_2$) on decolorization ($Y_1$) and the reduction of aromatics ($Y_2$), were investigated by a full factorial design $2^2$ with three replicates of the central experiment. The responses were fit to the linear model of Equation (3).

$$\hat{Y} = b_0 + b_1 x_1 + b_2 x_2 + b_{1,2} x_1 x_2$$

(3)

where $\hat{Y}$ is the response predicted by the model, $b_0$, $b_1$, $b_2$ and $b_{1,2}$ are the model coefficients calculated from experimental data and $x_1$ and $x_2$ are the dimensionless values of the independent variables $X_1$ and $X_2$.

An estimation of the model coefficients and their respective standard errors and ANOVA of the models were determined according to the algorithms described by (Barros Neto et al. 2007) using Microsoft Excel 2007 software. Line contour graphs were plotted by OriginPro 8.0 software. The conditions, expressed in both coded and uncoded variables, of the experimental design are shown in Table 1.

**Removal kinetics of COD, color and aromatic compounds using the photoreactor with and without an aluminum surface**

As a consequence of the results obtained in the experimental design (item 2.4), the removal kinetics of COD, color and aromatic compounds was evaluated by the treatment of wastewater (0.5 L) using 6.0 g L$^{-1}$ of H$_2$O$_2$ and pH 5.0 in the photoreactor with and without an aluminum surface. Doses of 5 mL were withdrawn at defined time intervals.
and transferred to a glass bottle containing an sufficient amount of catalase to convert the residual H$_2$O$_2$ before they were analyzed.

**Analytical methods**

The samples were previously centrifuged for 20 min at 3,500 rpm. The UV–VIS spectrum was recorded in the range of 200–800 nm by a UV/VIS GBC CINTRA20 spectrophotometer. Color reduction was monitored by the area of the visible spectrum. Aromatics content was evaluated by the absorbance at 254 nm (Ravikumar & Gurol 2002). Chemical oxygen demand (COD) was measured using a standard method (APHA/AWWA/WEF 1998). Residual H$_2$O$_2$ was determined using a spectrophotometric method based on the reaction with ammonium metavanadate (Nogueira et al. 2005). Five-day biochemical oxygen demand (BOD5) was estimated following the procedures described by the Brazilian technical standard NBR 12614/1992 (ABNT 1992). Acute toxicity to the algae *P. subscaptata* was determined using the protocol described by CETESB (1991).

**RESULTS AND DISCUSSION**

**Characterization of textile dyeing wastewater**

The results of dyeing textile wastewater characterization are shown in the Table 2.

The high pH value (11.8) can be explained by the use of sodium hydroxide in the dye baths. The COD value (1127 ± 15 mgO$_2$ L$^{-1}$) was attributed to the dyes and detergents present in the wastewater. The value was lower than the COD determined by Perkowski & Kos (2002) for polyacrylamide fibers dyeing wastewater (1290 mgO$_2$ L$^{-1}$). The COD determined by Azbar et al. (2004) for the wastewater from polyester and acetate fibers dyeing was 950 mgO$_2$ L$^{-1}$. The BOD/COD ratio was 0.020 ± 0.005, which indicates the very low biodegradability of the wastewater. The result is according to the BOD/COD range for textile wastewater (<0.1) suggested by Pagga et al. (Pagga & Brown 1986). The assay used to evaluate the acute toxicity to the algae *P. subscaptata* showed that the dilution of the wastewater causing 50% inhibition relative to a negative control (without wastewater) after 96 h of testing was only 2.5 (% v/v). This result indicates that the acute toxicity of the wastewater was high. Villegas-Navarro et al. (2001) also demonstrated that textile dyeing wastewater has acute toxicity. These authors used the crustacean *Daphnia magna* to evaluate similar wastewaters from several textile mills, and the 48 h-LC50 ranged from 0.7 to 22% v/v. The acute toxicity of textile dyeing wastewaters can be attributed to the presence of dyes and detergents, including the dye sulfur black, which has been decreasingly used because it reacts with sodium sulfide and disulfide (to solubilize the dye) producing hydrogen sulfide which has an unpleasant odor and high toxic potential (Alcântara & Daltin 1996; Esteves 1992).

**The treatment of textile dyeing wastewater by the UV/H$_2$O$_2$ process**

The results of the experimental design are presented in the Table 3.

It was observed that the reduction of the color and the aromatic compounds ranged from 4.3 to 74.5% and 6.0 to 60.2%, respectively. A higher reduction of color and

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**Table 1** Conditions of experimental design 2 expressed in both coded and uncoded levels

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>H$_2$O$_2$ (g L$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>6.0</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>-1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>1.0</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>3.5</td>
<td>8.5</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>3.5</td>
<td>8.5</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>3.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The duration of the reaction was 45 min in the photoreactor without a reflective surface.

**Table 2** Main physicochemical and ecotoxicological characteristics of the textile dyeing wastewater

<table>
<thead>
<tr>
<th>Parameter (unity)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.8 ± 0.1</td>
</tr>
<tr>
<td>Area of the visible spectrum (dilution 1:4)</td>
<td>224</td>
</tr>
<tr>
<td>Absorbance at 254 nm (dilution 1:9)</td>
<td>0.919</td>
</tr>
<tr>
<td>COD (mgO$_2$ L$^{-1}$)</td>
<td>1127 ± 15</td>
</tr>
<tr>
<td>BOD (mgO$_2$ L$^{-1}$)</td>
<td>22 ± 5</td>
</tr>
<tr>
<td>Total solids (mg L$^{-1}$)</td>
<td>5158 ± 16</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.020 ± 0.005</td>
</tr>
<tr>
<td>Acute toxicity expressed as 96 h LC50% (v/v)</td>
<td>2.5 ± 0.2</td>
</tr>
</tbody>
</table>

The analyses were performed with three replicates ($n=3$).
Table 3 | Results of the full factorial design $2^3$ with three replicates of the central experiment

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\text{H}_2\text{O}_2$ (g L$^{-1}$)</th>
<th>pH</th>
<th>Removal (%)</th>
<th>Color</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>12</td>
<td>21.8</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>5</td>
<td>74.5</td>
<td>60.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>12</td>
<td>4.3</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>5</td>
<td>21.8</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>8.5</td>
<td>25.9</td>
<td>28.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>8.5</td>
<td>37.0</td>
<td>36.9</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.5</td>
<td>8.5</td>
<td>30.4</td>
<td>33.6</td>
<td></td>
</tr>
</tbody>
</table>

The independent variables studied were the concentration of $\text{H}_2\text{O}_2$ ($X_1$) and pH ($X_2$), and the responses were the removal of color ($Y_1$) and the removal of aromatics ($Y_2$).

Aromatic compounds was obtained at pH 5.0 and 6.0 g L$^{-1}$ of $\text{H}_2\text{O}_2$ (experiment #2).

The results fitted the model of Equation (3), and the analyses of the statistical significance of parameters are shown in the Table 4.

The term $b_{1,2}$ for color and aromatic removal were considered insignificant at a 95% confidence level because the $p$-values were very close to 0.05. Therefore, the models obtained for color and aromatic compounds reductions are described in terms of actual variables by Equations (4) and (5), respectively.

$$Y_1 = 48.9 + 7.0X_1 - 5.0X_2$$ (4)

$$Y_2 = 29.6 + 6.8X_1 - 2.9X_2$$ (5)

Table 4 | Estimation of the coefficients of the linear models for the decolorization and reduction of aromatics responses with the respective standard errors and t-values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model coefficient</th>
<th>Standard error</th>
<th>t-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_1$ color removal</td>
<td>$B_0$</td>
<td>30.8</td>
<td>2.1</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>17.6</td>
<td>2.8</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>$B_2$</td>
<td>-17.6</td>
<td>2.8</td>
<td>-6.3</td>
</tr>
<tr>
<td></td>
<td>$B_{1,2}$</td>
<td>-8.8</td>
<td>2.8</td>
<td>-3.1</td>
</tr>
<tr>
<td>$Y_2$ reduction of aromatic compounds</td>
<td>$B_0$</td>
<td>29.3</td>
<td>2.4</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>17.1</td>
<td>4.3</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>$B_2$</td>
<td>-10</td>
<td>4.3</td>
<td>-4.9</td>
</tr>
<tr>
<td></td>
<td>$B_{1,2}$</td>
<td>-6.7</td>
<td>4.3</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

The percentage of variance explained by the model for color reduction ($Y_1$, Equation (4)) was not very high (86.9%, Table 5). However, the model represented the experimental data appropriately and was statistically significant ($p$-value = 0.017 < significance level = 0.05). The lack of fit was insignificant ($p$-value = 0.167 > significance level). Similar results were obtained for the removal of the aromatic compounds ($Y_2$, Equation (5)). The percentage of the explained variance was 84.4% (Table 4). The model was significant ($p$-value = 0.024), and the lack of fit was insignificant ($p$-value = 0.118).

The models proposed in Equations (4) and (5), which are plotted as line contour graphs (Figure 2), show the estimates for the removal of color and aromatic compounds.

The removal of color and aromatic compounds were improved by decreasing the pH. At alkaline conditions, $\text{H}_2\text{O}_2$ undergoes decomposition producing oxygen and water in spite of the presence of hydroxyl radicals (Equation (6)). Furthermore, the deactivation of hydroxyl radicals increases at higher pH values. Its reaction with $\text{HO}_2^-$ (Equation (7)) is 100 times faster than with $\text{H}_2\text{O}_2$ (Equation (8)) (Galindo & Kalt 1998). The reactivity of the species $\text{HO}_2^-$ and $\text{O}_2^-$ is much lower than that of $\text{HO}^*$ radicals; hence, their presence reduced the rates of degradation.

$$\text{HO}_2^+ + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HO}^* (k = 3 \text{ M}^{-1}\text{s}^{-1})$$ (6)

Table 5 | ANOVA results of the linear models for the decolorization and aromatics reduction responses

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>$F_{\text{value}}$</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color removal</td>
<td>Model</td>
<td>2</td>
<td>2,464.02</td>
<td>1,252.01</td>
<td>13.22</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>4</td>
<td>372.80</td>
<td>93.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lack of fit</td>
<td>2</td>
<td>310.21</td>
<td>155.11</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
<td>2</td>
<td>62.59</td>
<td>31.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>6</td>
<td>2,836.82</td>
<td>2,557.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Percentage of explained variance</td>
<td>= 86.9</td>
<td>Maximum explained variance = 97.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduction of aromatic compounds</td>
<td>Model</td>
<td>2</td>
<td>1,569.6</td>
<td>784.8</td>
<td>10.84</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>4</td>
<td>289.8</td>
<td>72.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lack of fit</td>
<td>2</td>
<td>255.8</td>
<td>127.9</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
<td>2</td>
<td>34.1</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>6</td>
<td>1,859.4</td>
<td>857.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Percentage of explained variance</td>
<td>= 84.4</td>
<td>Maximum explained variance = 98.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The removal of aromatic compounds and color was improved by increasing the H$_2$O$_2$ concentration. When the H$_2$O$_2$ concentration was higher, more hydroxyl radicals were generated, which increased the degradation rates without reaching the inhibitory level.

Evaluation of the effect of aluminum foil on degradation rates

Nicole et al. (1990) evaluated the use of reflective materials on the surface of photoreactors and demonstrated that the photolysis rate of H$_2$O$_2$ can increase up to 4.8 times when the photoreactor is covered with aluminum foil. This evidence was applied to treat the dyeing wastewater using a photoreactor covered with aluminum foil, and a H$_2$O$_2$ concentration of 6.0 g L$^{-1}$ at pH 5.0.

The kinetics of the removal of COD, color and aromatic compounds are shown in Figure 3 for the experiments performed in presence or absence of the aluminum surface.

The experimental data were fit to the first-order model described in Equation (9). The coefficients of determination ($R^2$) ranged from 0.976 to 0.996, showing that the model was appropriate.

$$\frac{X}{X_0}(\%) = 100 \times e^{-kt}$$

where $X/X_0$ (%) is the residual color, aromatics content or COD in percentage, $k$ is the first-order kinetics constant and $t$ is time in minutes.

The use of the reflective surface increased the rates of color, aromatic compounds and COD removal to 71.0, 78.0 and 57.0%, respectively. This result can be explained by the higher amount of incident photons into reactor when the aluminum was used. This increased the photolysis of H$_2$O$_2$ and consequently the amount of hydroxyl radicals available to degrade organic matter. This was confirmed by the increase of 42.0% of H$_2$O$_2$ consumption at 120 min of UV irradiation.

Evaluation of the acute toxicity after the treatment

Although the UV/H$_2$O$_2$ process has proven to be efficient for removing color and COD, there are serious concerns about the formation of toxic by-products during the oxidation via the HO$^\cdot$ radical (Bizani et al. 2006; Osugi et al. 2006). Moreover, the presence residual H$_2$O$_2$ can increase the toxicity of the wastewater after the treatment (Watts et al. 2005). Therefore, the evaluation of the toxicity of the treated wastewater is an important step in this work. The 96 h EC50 value was reduced from 2.5% v/v (non-treated wastewater) to 0.05% v/v after UV/H$_2$O$_2$ treatment (reaction conditions: reactor covered with aluminum foil, 120 min of irradiation, 6 g L$^{-1}$ of H$_2$O$_2$ and pH 5.0). Therefore, the toxicity of the wastewater treated by H$_2$O$_2$/UV was significantly higher than the toxicity of the untreated wastewater. This increase in toxicity can be attributed to the residual H$_2$O$_2$ (3.0 g L$^{-1}$) and the presence of Cu$^{2+}$ ions formed during the degradation of the dye Remazol Turquoise Blue G in the wastewater as previously reported by Osugi et al. (2006). A significant fraction of this toxicity can be readily removed by conversion of the residues of
H₂O₂ to water and oxygen using MnO₂ or the enzyme catalase. The toxicity of the treated wastewater can be reduced further by increasing the pH of the wastewater and consequently precipitating Cu²⁺.

Cost evaluation

A comprehensive cost evaluation of the treatment using UV/H₂O₂ only considered the costs of H₂O₂ (50%) (0.54 $/kg) and electric energy (0.2675 $/kWh). A cost evaluation of the photochemical processes was estimated according to Equation (10) (Bolton et al. 1995).

\[
EE/O = \frac{P \times t \times 10^3}{V \times 60 \times \log(C_{initial}/C_{final})} \quad (10)
\]

where EE/O is the electric energy per order, P is the rated-power of the mercury-vapor lamp (kW), V is the volume (in liters) of wastewater treated, t is the irradiation time, \( C_{initial} \) and \( C_{final} \) are the COD before and the COD after the treatment, respectively.

To compare the cost of the treatment by H₂O₂/UV process when the photoreactor was covered with aluminum foil to when it was not covered, the time required to reach a COD removal of 40% in both conditions was estimated using the model described by Equation (9) fit to the kinetics of the COD removal (Figure 3(c)). The values of irradiation time required to reach 40% COD removal for the reactor with and without aluminum foil were 58.9 and 99.5 min, respectively. An evaluation of the cost of the treatment (with and without aluminum foil) is shown in Table 6.

The cost of the treatment using the photoreactor covered with aluminum foil was 40.8% lower than the cost of the treatment using the photoreactor without aluminum foil.
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**CONCLUSIONS**

No previous reports have been found on the application of a UV/H2O2 process to treat textile dyeing wastewater containing sulfur dye. Color, aromatic compounds and COD were efficiently removed from the wastewater. The time dependence of the removal of color, aromatic compounds and COD followed first-order kinetics. The use of aluminum foil as a reflective surface covering the photoreactor is a simple way to increase the incident irradiation into wastewater, which reduces the consumption of electricity and reagents. The cost of the treatment using the photoreactor covered with aluminum foil was 41.6% lower than the cost of the treatment without aluminum foil. The use of the UV/H2O2 process to treat effluents from the textile dyeing process is especially promising because this process uses a relatively inexpensive reagent, and it converts the dyes and detergents into low molecular weight by-products without the formation of sludge.

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