Decolorization and Mineralization of Reactive Dyes, by the H$_2$O$_2$/UV Process With Electrochemically Produced H$_2$O$_2$

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Abstract

Decolorization of Reactive Red 238, Reactive Orange 16, Reactive Black 5 and Reactive Blue 4 was studied in the UV/H$_2$O$_2$ process with H$_2$O$_2$ being produced electrochemically. The experimental results show that decolorization increased considerably when switching on the electrochemical production of H$_2$O$_2$. Complete decolorization (>99%) was achieved for all dyes under the applied experimental conditions, partial mineralization (49–85%) was obtained, which depends on the type of dye.

Reactive Red 238 was used to investigate operational parameters and it was found that decolorization was influenced by the applied electrical current of the electrochemical cell and flow rate. Decolorization and mineralization of Reactive Red 238 can be described by pseudo-first order kinetics. It was found that the initial concentration of Reactive Red 238 has a negative influence on the pseudo-first order reaction constant.

Keywords: Decolorization, hydrogen peroxide, reactive dyes, in-situ H$_2$O$_2$, AOP, Reactive Red 238

1. Introduction

The main pollution in waste water from the textile finishing industry originates from the dyeing and finishing processes. These processes require the input of a wide-range of chemicals and synthetic dyes, which are generally organic compounds of complex structures. Synthetic dyes, present in textile waste water, introduce intensive color and toxicity to the aquatic system. Among textile dyes, azo dyes constitute the largest and most important class of commercial dyes. Anthraquinone dyes constitute the second most important class after azo dyes and are characterized by their good fastness, which is caused by their very stable anthraquinone structures. This work is therefore focused on the removal of reactive azo and anthraquinone dyes from waste water streams.

Dyes in dye-baths are present in a wide concentration range, namely from 10 to 10,000 mg/l. Under typical reactive dyeing conditions, 30–50% of the initial dye remains in the spent dye-bath and is diluted by 20–40% upon rinsing. This residue is in hydrolyzed form and has no affinity for the fabric, thus resulting in colored effluent.

Most dyes are resistant to biodegradation due to the complex chemical structure. Physical techniques such as adsorption on activated carbon, ultrafiltration, nanofiltration, reverse osmosis, coagulation, and electro-coagulation can be used for the removal of these pollutants. The negative effect of these methods is however the formation of sludge, which is caused by the non-destructive nature of these techniques. Attractive alternatives to these physical water-treatment processes are the advanced oxidation processes (AOPs), which are able to decolorize and mineralize organic water contaminants.

Over recent years, various advanced oxidation processes such as O$_3$/UV, O$_3$/H$_2$O$_2$, H$_2$O$_2$/UV and Fenton’s reagent (H$_2$O$_2$/Fe(II)) have been investigated as wastewater treatment for the decolorization of colored waste waters. Chemical oxidation using UV in the presence of
H₂O₂ is proved to be a powerful AOP method for the oxidation of dyes. In H₂O₂/UV processes the photolysis of hydrogen peroxide effectively generates hydroxyl radical (OH•) species:

\[ \text{H}_2\text{O}_2 + \nu \rightarrow 2\text{OH}^\cdot \] (1)

This hydroxyl radical is a strong oxidation agent, which can degrade organic pollutants present in wastewater. In addition, the H₂O₂/UV process has several advantages over other AOPs:

1. no sludge formation during treatment,
2. it can be carried out under ambient conditions,
3. the oxygen formed in this process is useful for aerobic biological processes.

The oxidation products are usually oxygenated compounds of low molecular weight that are easily biodegradable or, in some instances, the simple organic compound is fully oxidized to carbon dioxide and water.

Hydrogen peroxide is a strong oxidation agent and can be purchased in high concentrations (normally ~35 wt%). These high hydrogen peroxide concentrations present an increased risk with respect to storage, handling and shipment and will result in subsequent safety precautions. In-situ production of hydrogen peroxide, by electrochemical reduction of dissolved oxygen, minimizes these risks.

The production of hydrogen peroxide by electrochemical reduction of dissolved oxygen in neutral and acid solutions is described by equation 2. The production of the peroxide anion by electrochemical reduction of oxygen in alkaline solutions is described by equation 3. Equation 4 describes the equilibrium between hydrogen peroxide and the peroxide anion.

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \] (2)

\[ \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \] (3)

\[ \text{HO}_2^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2 \] (4)

Carbon-based electrodes are used during the electro-synthesis of hydrogen peroxide; gas-diffusion electrodes (GDEs) are commonly preferred over other carbon materials where, due to the low solubility of the oxygen in an aqueous solution, devices with high specific surface area are needed to supply commercially-reasonable current densities for the practical implementation of the process. The produced hydrogen peroxide can be used for the oxidation of organic pollutants.

The objective of this work was to develop a process for the decolorization of textile dyes based on the electrochemical production of hydrogen peroxide and UV irradiation. Four different commercial important reactive dyes with azo and anthraquinone chromophores were selected for this purpose.

### 2. Experimental

#### 2.1. Chemicals

Reactive Orange 16 (RO 16), Reactive Black 5 (RB 5) and Reactive Blue 4 (RB 4) were purchased from Sigma-Aldrich, the Netherlands. Reactive Red 238 (RR 238) was supplied by Svilanit, Slovenia. The chemical structure of that dye was confidential and not available. All reactive dyes were used without further purification. The characteristics of the reactive dyes were given by the supplier except for the characteristics of RR 238, these were obtained from literature. The characteristics of each dye are listed in Table 1.

The other chemicals used in this study were NaOH and K₂SO₄, both analytical grades and supplied by Sigma-Aldrich, the Netherlands. Oxygen, >99.5%, was supplied by Air Liquide, the Netherlands.

#### 2.2. Analytical Methods

The hydrogen peroxide concentration was measured by photometric analysis using a Lovibond PC Checkit photometer.

Total organic carbon (TOC) was determined by spectrophotometric analysis using a Hach-Lange DR5000 spectrophotometer and LCK 385 test supplied by Hach Lange, the Netherlands.

The dye concentration in the solution was measured by photometric analysis at the characteristic wavelength (λ_max). All dye solutions followed Beer-Lambert law in the concentration range of interest.

#### 2.3. Equipment

A batch-recycle laboratory setup was used to investigate the oxidation of reactive dyes. An aqueous solution of 0.1 M K₂SO₄ was used for the anolyte and catholyte, whereas the catholyte also contained hydrolyzed reactive dye. The volume of the anolyte was 5 liters and the volume of the catholyte was 5 liters. The anolyte was circulated through the electrochemical cell by a centrifugal pump and fed back to the reservoir. The catholyte was fed to the electrochemical reactor, then to the UV-reactor (medium pressure UV lamp: Heraeus TQ150 supplied by UV-Consulting Peschl, Germany) and then back to the reservoir. Oxygen was supplied at 0.5 l/min to the gas chamber of the electrochemical cell; a wash bottle maintained a slight overpressure in the gas chamber.

Hydrogen peroxide was produced at the cathode in a plate-and-frame electrochemical cell and consisted of three compartments (anolyte, catholyte and gas compartment). The anolyte and catholyte solutions were separated by a cation exchange membrane (CEM) and the catholyte...
compartment was separated from the gas compartment by a gas diffusion electrode (GDE). The anode and cathode were placed face-to-face and had a geometrical surface area of 100 cm². The anode was made of iridium oxide coated on a titanium plate and supplied by Magneto Special Anodes, the Netherlands. The GDE consisted of a mixture of furnace-black, graphite and PTFE pressed onto a woven nickel mesh. Hydrogen peroxide was produced under galvanostatic conditions using a power supply (Delta Elektronika SM120-25D, the Netherlands). Figure 1 shows the scheme of the used setup.

3. Results and Discussion

3.1. Influence of Flow Velocity and Electrical Current

RR 238 with an initial concentration of 50 mg/l is used to assess the effect of flow and electrical current on the decolorization and mineralization of RR 238. The obtained results for decolorization and hydrogen peroxide concentration are presented in Figures 2 and 3, the results for TOC reduction (mineralization) in Table 2.

Figure 2 shows that, with UV irradiation alone, only an average of 17% decolorization is achieved after 60 mi-

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**Table 1. Main characteristics of the reactive dyes used**

<table>
<thead>
<tr>
<th>Textile dye</th>
<th>RR 238</th>
<th>RO 16</th>
<th>RB 5</th>
<th>RB 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trade name</td>
<td>Cibacron Red FN-R</td>
<td>Remazol Brilliant Orange 3R</td>
<td>Remazol Black B</td>
<td>Procion Blue MX-R</td>
</tr>
<tr>
<td>CAS no.</td>
<td>–</td>
<td>12225-83-1</td>
<td>17095-24-8</td>
<td>13324-20-4</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₂₀H₁₅ClFN₇O₁₃S₄Na₄</td>
<td>C₂₀H₁₇N₃O₁₊S₃Na₂</td>
<td>C₂₂H₂₉N₆O₁₉S₆Na₄</td>
<td>C₂₂H₂₇Cl₂N₆O₆S₂Na₂</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>944.2</td>
<td>617.5</td>
<td>991.8</td>
<td>681.4</td>
</tr>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>543</td>
<td>481</td>
<td>991.8</td>
<td>598</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>Not known</td>
<td>~50</td>
<td>~55</td>
<td>~35</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>Not available</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Azo group</th>
<th>Azo group</th>
<th>Azo group</th>
<th>Anthraquinone group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive group</td>
<td>Vinylsulphone, chlorofluorotriazine</td>
<td>Vinylsulphone</td>
<td>Vinylsulphone</td>
<td>Dichlorotriazine</td>
</tr>
<tr>
<td>Type of dye</td>
<td>Reactive azo</td>
<td>Reactive azo</td>
<td>Reactive azo</td>
<td>Reactive anthraquinone</td>
</tr>
</tbody>
</table>

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Figure 2. Decolorization of RR 238 at different flow velocities and electrical currents, hydrogen peroxide production switched on at t = 60 min.
nutes of treatment. For this reason a powerful oxidation agent is needed such as the hydroxyl radical. In fact the rate of decolorization, seen as the slope of the curve in Figure 2, increased considerably when the electrochemical cell was switched on.

The electrochemical cell produces hydrogen peroxide, which under UV irradiation forms hydroxyl radicals (OH•) (Eq. 1). Hydroxyl radicals can oxidize organic compounds such as dyes; the oxidation products (P) can also be further oxidized. A simplified reaction scheme, which describes the complete oxidation (i.e. mineralization) of dyes during UV/H₂O₂ oxidation, is as follows²,12:

\[
dye + hν \rightarrow \text{products (P)} \quad (5)
\]

\[
\text{OH}• + \text{dye} \rightarrow \text{products (P)} \quad (6)
\]

\[
P + \text{OH}• \rightarrow \text{final products (CO₂, H₂O, NO₃–, SO₄²–)} \quad (7)
\]

It is clear from Figure 2 that an increasing electrical current results in reduced decolorization; at 180 min. 98%, 95% and 90% decolorization was obtained at 1 A, 2.5 A and 5 A respectively. Higher electrical currents resulted in increased hydrogen peroxide concentrations; at t = 180 min. 54 ppm, 204 ppm and 516 ppm hydrogen peroxide are obtained at 1 A, 2.5 A and 5 A respectively (Figure 3).

At higher concentrations of hydrogen peroxide scavenging of OH• radicals increases and can subsequently result in the suppression of the oxidation of dyes and therefore lower decolorization rates.²

The flow velocity also seems to have an influence on the decolorization rate; at t = 180 min. and a current of 2.5 A 93%, 95% and 96% decolorization was obtained at 50 l/h, 100 l/h and 150 l/h respectively. The influence of the flow velocity can also be related to the scavenging mechanism. The hydrogen peroxide concentration in the output of the electrochemical cell is influenced by the flow velocity; lower flow velocities result in higher concentrations of hydrogen peroxide. The decreased decolorization rate at lower flow velocities is therefore attributed to the increased hydrogen peroxide concentration, i.e. scavenging of hydroxyl radicals by hydrogen peroxide. A decreasing mineralization rate was also observed at lower flow velocities for RR 238. Mineralization of RR 238 is expressed in terms of TOC reduction and shown in Table 2. This decrease in mineralization at lower flow velocities can also be explained by increased scavenging of hydroxyl radicals due to increased hydrogen peroxide concentrations at the output of the electrochemical cell.

![Figure 3. Production of hydrogen peroxide during the decolorization of RR 238 at different flow velocities and electrical currents, hydrogen peroxide production switched on at t = 60 min.](image)

**Figure 3.** Production of hydrogen peroxide during the decolorization of RR 238 at different flow velocities and electrical currents, hydrogen peroxide production switched on at t = 60 min.

It seems that an increasing hydrogen peroxide concentration negatively influences the decolorization; this can be explained by the scavenging mechanism of the hydroxyl radical by hydrogen peroxide.²,12

\[
\text{H}_2\text{O}_2 + \text{OH}• \rightarrow \text{HO}_2• + \text{H}_2\text{O} \quad (8)
\]

\[
\text{HO}_2• + \text{OH}• \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (9)
\]

\[
2\text{HO}_2• \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (10)
\]

**Table 2. Mineralization of reactive azo dye RR 238 under different conditions during hydrogen peroxide production.**

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>TOC reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 l/h</td>
</tr>
<tr>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>2.5</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>36</td>
</tr>
</tbody>
</table>

The initial solutions contained 15.1 ± 1.3 mg/l TOC, UV irradiation (photolysis) resulted in a neglectable TOC reduction, but after switching on the hydrogen peroxide production; TOC reductions increased considerably. TOC values reduced with 41%, 54% and 56% on average at 1 A, 2.5 A and 5 A respectively. There seems to be a positive effect of the applied electrical current on TOC reduction, which can be explained by two mechanisms:

1. electrochemical reduction of RR 238 and/or its oxidation products
2. oxidation of RR 238 oxidation products by hydrogen peroxide due to increased hydrogen peroxide concentrations

**3.2. Influence of the Initial RR 238 Concentration**

Next the influence of the initial concentration on the decolorization and mineralization of RR 238 was investigated. These experiments were conducted at a flow rate of 150 l/h and an electrical current of 1 A as these conditions exhibited the fastest decolorization.
An increased RR 238 concentration results in an increased operating time in order to obtain similar decolorization (Figure 4). These results can be quantified by assuming pseudo-first order kinetics with respect to the RR 238 concentration (Eq. 11).

\[
\frac{dC}{dt} = k \cdot C \tag{11}
\]

where \(k\) is the pseudo-first order reaction constant, \(t\) the time and \(C\) the dye concentration at \(t\). Integration of (Eq. 11) using an initial dye concentration \(C_0\) at \(t = 0\) gives

\[-\ln \left( \frac{C}{C_0} \right) = k \cdot t \tag{12}\]

The results are presented in Figure 4. In all cases linear behavior was observed at \(t > 40\) min. The pseudo-first order reaction constants, shown in Figure 4, were obtained by linear regression (\(R^2 > 0.99\)) at \(t > 40\) min.

Initially the hydrogen peroxide concentration is low (Figure 4), which can explain the slight deviation from linear behavior at \(t < 40\) min. Decolorization at increased hydrogen peroxide concentrations (\(t > 40\) min.) resulted in pseudo-first order reaction kinetics in RR 238, which corresponds with the results obtained for other azo dyes\(^2\),\(^4\),\(^1\),\(^\text{11,12}\). The decrease of the pseudo-first order constant at increasing concentrations of dye was also observed by Mitrović et al\(^\text{16}\) using Reactive Orange 16 and Mohey El-Dein et al\(^\text{17}\) using Reactive Black 5. This effect of the dye concentration was attributed to the absorption of UV light by the dye resulting in a reduced photolysis rate of hydrogen peroxide (eq. 1) at increasing dye concentrations.

Pseudo-first order kinetics was also found for the mineralization of RR 238, which is shown in Figure 5. The pseudo-first reaction order constant for mineralization of RR 238 decreases at increasing concentration of RR 238, which is similar to the decolorization results. The pseudo-first order reaction constants, shown in Figure 5, were obtained by linear regression (\(R^2 > 0.92\)) at \(t > 40\) min. Remarkably, the hydrogen peroxide concentration, which is not constant and differs for each RR 238 concentration (Figure 6), has obviously a negligible influence on the pseudo-first reaction order constant.

Initially the hydrogen peroxide concentration increases linearly (Figure 6). This increase corresponds with approx. 60% of the electrochemical hydrogen peroxide production, which means that max. 40% of the produced hydrogen peroxide was converted into hydroxyl radicals. The differences in the obtained hydrogen peroxide concentrations are attributed to reduce scavenging of hydroxyl radicals by hydrogen peroxide at increasing RR 238 concentrations. The first order decolorization and mineralization of RR 238 results in an increased reaction rate of the corresponding reactions (eq. 6 and eq. 7) at increased RR 238 concentrations. Less hydroxyl radicals are therefore available for the scavenging reaction with hydrogen peroxide (eq. 8), which results in...
increased hydrogen peroxide concentrations at increased dye concentrations. As time progresses decolorization and mineralization rates decreases due to reduced residual concentrations. The scavenging reaction increases and as a result the hydrogen peroxide concentration decreases from a certain point, resulting into a maximum hydrogen peroxide concentration. If all reactive oxidation products of RR 238 are oxidized then the hydrogen peroxide concentration is assumed to decrease to 18 mg/l as found in the experiment without RR 238 (0 mg/l RR 238).

3. 3. Influence of Type of Reactive Dye

In order to demonstrate the general applicability of this approach decolorization experiments were conducted using three other commercial reactive dyes at a concentration of 50 mg/l: Reactive Orange 16, Reactive Blue 4 and Reactive Black 5. The obtained decolorization results are similar and are shown in Figure 7.

![Figure 7. Decolorization of 50 mg/l RR 238, RO 16, RB 4 and RB 5 at 1 A and 150 l/h.](image)

For all four reactive dyes the rate of decolorization, seen as the slope of the curve in Figure 7, increased considerably when the electrochemical cell was switched on. There are, however, differences in decolorization rates which can be related to the structure of the specific reactive dye (Table 1). It seems that azo dyes with the vinylsulphone reactive group (RB 5, RO 16) decolorize faster (k = 0.060 min⁻¹ and 0.061 min⁻¹ respectively) than the azo dye with the chlorofluorotriazine group (RR 238) and the anthraquinone dye with the chlorotriazine reactive group (RB 4) (k = 0.040 min⁻¹). This finding corresponds with the conclusions of Colonna et al.: anthraquinone dyes seem to be, in general, a little more resistant to the treatment than azo dyes. Mineralization of these reactive dyes shows the same behavior, i.e. 85%, 62%, 58% and 49% mineralization at t = 240 min. for RO 16, RB 5, RR 238 and RB 4 respectively.

The obtained pseudo-first order constant for the decolorization of RO 16 is lower than obtained by Mitrovic et al. They found a maximum pseudo-first order constant of 0.329 min⁻¹ at 0.7–1.4 g/l H₂O₂ while using 50 mg/l RO 16, a volume of 100 ml and a 28 W UV lamp (low pressure). The lowest pseudo-first order constant, which is 0.142 min⁻¹, was obtained at 340 mg/l H₂O₂ (which is still one order of magnitude higher than the average H₂O₂ concentration during our experiments). The obtained pseudo-first order constant for the decolorization of RB 5 is lower than obtained by Mohey El-Dein et al. who obtained a pseudo-first order constant of 0.134 min⁻¹. Their results were obtained using 87 mg/l RB 5, an initial concentration of 4.8 g/l H₂O₂, a total volume of 3.8 liters and the same type of lamp as used within this research. Lucas & Peres obtained a lower pseudo-first order constant (k = 0.0186 min⁻¹) with 100 mg/l RB 5, while using 25 mg/l H₂O₂, 500 ml and a 15 W UV lamp (low pressure). The differences of the obtained pseudo-first constants compared to literature are ascribed to the different experimental conditions (such as volume, dye concentration, H₂O₂ concentration, UV power and type of lamp). The results of this research show that decolorization of reactive dyes, using electrochemically produced H₂O₂, can be performed at a similar rate as with classical AOP using H₂O₂/UV.

4. Conclusions

Decolorization of RR 238 by the UV/H₂O₂ process with electrochemically produced H₂O₂ has been investigated. The experimental results show that decolorization of RR 238 is influenced by the applied electrical current of the electrochemical cell. The decolorization rate of RR 238 exhibit pseudo-first order kinetics with respect to the RR 238 concentration.

It was found that pseudo-first order reaction constants for decolorization and mineralization were negatively influenced by an increasing initial dye concentration. Four different dyes (RR 238, RO 16, RB 4 and RB 5) were completely (>99%) decolorized by the UV/H₂O₂ process with electrochemically produced hydrogen peroxide. Under the applied experimental conditions up to 49%–85% mineralization could be obtained depending on the type of dye.

5. Acknowledgements

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and Technology of the Republic of Slovenia I am very grateful for the given opportunity to do this scientific research.

6. References


Povzetek

Z uporabo UV/H$_2$O$_2$ postopka, kjer smo H$_2$O$_2$ proizvedli elektrokemijsko, smo preučevali razbarvanje reaktivnih barvil Reactive Red 238, Reactive Orange 16, Reactive Black 5 in Reactive Blue 4. Iz eksperimentalnih rezultatov je razvidno, da se razbarvanje znatno poveča, ko vključimo elektrokemijsko proizvodnjo H$_2$O$_2$. Popolno razbarvanje vseh barvil (>99 %) smo dosegli pod uporabljenimi eksperimentalnimi pogoji, delna razgradnja (49–85 %) pa je bila odvisna od vrste barvila.