Solar Light Induced Photocatalytic Degradation of Textile Disperse Dye Coralene Dark Red 2B in Effluents

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Abstract: Degradation of textile de coralene dark red 2B was carried out using advanced oxidation method. The whole experiment was performed under solar light irradiation intensity in range of 400-500 Lux. Results show that degradation is affected by various parameters like intensity of solar light, concentration of dye, concentration of H₂O₂, amount of TiO₂, effect of pH exposure time. Considering all affection parameters, a protocol for degradation of coralene Dark red 2B was developed. Degraded samples were subjected to HPTLC to find out end degraded products. Results show that there is complete degradation of dye and no visible spot are obtained in the TLC plotter when scanned. This method was applied to treatment of effluent samples taken from dye industry of Ankleshwar city and promising results were obtained.

Keywords: Coralene Dark red 2B, Solar light, HPTLC, Degradation

1. Introduction

The textile dyes are a voluminous resource of coloured organic compounds that present an increasing environmental crisis [1]. The textile industry uses approximately 21-377 m³ of water per ton of textile produced and thus generates large quantities of wastewater from different steps of dyeing and finishing process [2]. They pose serious environmental problems because of their colour, low biochemical oxygen demand and high chemical oxygen demand. Various chemical and physical processes, such as chemical precipitation and separation, electro coagulation and elimination by adsorption on activated carbon, etc., are currently used for treating textile wastewater [3].

Disperse dyes are synthetic dyes. Disperse dye is one kind of organic substance which is free of ionizing Group. Disperse dyes are less soluble in water and used for dyeing synthetic textile materials. Disperse dyes is mainly used for dyeing polyester yarn of fabric [4].

Advanced oxidation processes (AOPs) are the group of water and wastewater treatments in which the main oxidative agent is the hydroxyl radical (HO·). This oxidant is characterized by one of the highest oxidative potentials in nature and therefore many organic compounds may be decomposed by AOPs [5].

Degradation of the dye with photocatalytic system and the effects of different parameters such as concentration of solar light coating of catalyst with cement binder and role of different commercial catalysts on the degradation efficiencies is already studied [6]. Investigations have been reported on variation of the parameters such as catalyst dosage, varying dye concentration and pH of the dye solution, H₂O₂ concentration [7].

Improving the knowledge concerning the degradation pathways may be there for helpful to optimize the process by identification of the byproducts and hence help in the determination of the metabolic degradation pathways.

HPTLC is a powerful analytical technique because of its reliability, simplicity, reproducibility and rapid measurement. Sample clean up, and its main advantage is that a large number of samples can be simultaneously analyzed. Choosing the appropriate mobile and stationary phases is the sole difficulty of the method. For a qualitative determination of a mixture of dyes, the TLC method is the best solution [8].

Here, in this paper solar assisted photo catalytic advanced oxidation method is used to degrade textile disperse dye coralene dark red 2B in effluents. Effluents were collected from shree Balaji, Pvt.LTD Ankleshwar GIDC Gujarat.

These effluents are added by local industries of the area to water sources is big issue in that area.

HPTLC Method was developed to check the complete degradation and end products obtained after degradation.

2. Experimental

2.1 Chemicals

The commercially available water soluble azo dye Coralene dark red 2B (λ max-502nm) was obtained from Shree Balaji processor G.I.D.C, Ankleshwar Gujarat. The chemicals like TiO₂, H₂O₂ were obtained from Chitichem, vadodara and Sanir tech-chem Pvt. LTD. Vadodara, respectively.

Toluene, methanol and acetone were of analytical grade. As stationary phase Aluminum backed silica gel plate (20x10 cm) 60F254 were supplied by e Merck, USA.

2.2 Instruments

Optical density measurements of solution were studied on thermo scientific, Evolution-201 (Sr.no.-5A30253001, MA
2.3 Methods

2.3.1 Method Development
The $\lambda_{\text{max}}$ value of Coralene dark red 2B was found to be 502 nm. All experiments were carried out using the samples exposed to direct sunlight during April 2017 to June 2017. The known concentration of dye solutions were prepared by dissolving 50 mg of coralene dark 2B in 1000 ml of double distilled water and investigated for its decolorization in the presence of TiO$_2$ nano particle at different catalyst dosages and pH level. Initially 100 ml of 50 mg/L dye sample were tested with different catalyst dosage (from 50 mg to 150 mg) in the presence of direct sunlight. Absorbance was recorded by thermo scientific instrument. The experiments were repeated at different pH levels (from 2 to 10) for the 100 ml of same standard dye solutions with the optimum catalyst dose.

After 120 minutes exposure to light, the samples were subjected to spectro photometric analysis and to HPTLC method to identity end degradation product.

2.3.2 Analysis of degraded End product
HPTLC method developed by using mobile phase consisting of Toluene: Methanol: Acetone (20:2:1). 5.0 µl of each sample was sprayed on the 20x10 cm plate. After drying the starting zone for 1 min, the silica gel plate was developed with each solvent according to the CAMAG method, in order to find the best eluent. Development was performed in the twin through chamber up to migration distance of measured from the lower plate edge. After drying for 10 min, the point at which the spectra recorded for various parameter, and wavelength 502 nm corresponding to the maximum absorbance, with TLC Scanner (CAMAG); evaluation was performed via peak height.

2.4 Calculations

The percentage of degradation was determined by using the following equation,

\[
\% \text{ Discoloration} = \left( \frac{(A_0 - A_t)}{A_0} \right) \times 100
\]  

Where, $A_0$ is the initial absorbance of dye solution & $A_t$ is absorbance at time interval ‘t’ (30, 60, 90, 120 min).

3. Results and Discussion

3.1 Chemical structure

Figure 1: Chemical structure of coralene dark red 2B  
[Molecular formula C$_{23}$H$_{26}$ClN$_2$O$_7$, Molecular weight 519.93 (g/mol)]

3.2 Typical Run

Figure 2: A typical run curve of Coralene dark Red 2B at wave length of 502nm  
[Dye = 50mg/L, H$_2$O$_2$ = 2250mg/L, pH= 3.5, TiO$_2$ = 100mg, Light intensity = 501×100 Lux]

The photocatalytic degradation of Coralene Dark 2B was observed at $\lambda_{\text{max}}$ = 502 nm. The results of typical run are graphically represented in fig.2. The plot of O.D v/s exposure time was found to be a straight line. The optical density of the reaction mixture decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure.

3.3 Effect of Dye concentration

Figure 3: Effect of dye concentration of dye on the degradation of coralene dark Red 2B  
[Dye = 30mg/L to 70mg/L H$_2$O$_2$, 2250mg/L pH; 3.5; TiO$_2$ 100mg; Intensity; 501×100 Lux]
Effect of variation of dye concentration was also studied by taking different concentrations of dyes, the initial concentrations of the dye from 30 to 70 mg/L in order to assess the appropriate amount of catalyst dose. This may be attributed to the fact that as the concentration of dyes was increased, more dyes molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dyes further. In this case of dye 100 mg/L, 95% decolorization occurred in 120 min.

We have applied this method also for another 120 min but there is no more change in degradation rate. It was observed that increase in concentration decreased the rate of the reaction.

3.4 Effect of pH

![Figure 4: pH effect on degradation of Coralene dark Red 2B](Image)

Figure 4: pH effect on degradation of Coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H₂O₂; 2250mg/L TiO₂ 100mg; pH; 2 to 10 Intensity 501×100 Lux]

To investigate the effect of pH on the decolorization efficiency of Coralene Dark Red 2B experiments were carried out at various pH values, ranging from 2.0 to 10, at a constant dye concentration of 100 mg/L. The pH was maintained with help of 0.1 N (HCL) and 0.1 N (NaOH) solutions.

The decolorization efficiency of dye at different pH values was shown in fig.4. The decolorization efficiencies were 93.65% and 80.67% after 120 min of irradiation for pH 2.0 and 10.0 respectively. The pH influences the adsorption of dye molecules on the TiO₂ become surface, which is an important step in photo degradation remains positively charged in acidic medium (pH<6.8) and negatively charged in alkaline medium (pH>6.8), as shown in the following equations

\[
\text{Ti} - \text{OH} + \text{H}^+ = \text{TiOH}_2^+ \quad (2)
\]

\[
\text{Ti} - \text{OH} + \text{OH}^- = \text{TiO}^+ + \text{H}_2\text{O} \quad (3)
\]

The pH changes can thus influence the adsorption of dye molecules onto the TiO₂ surface, an important step for the photo oxidation to occur. The acidic solution favors the adsorption of the dye onto photo catalyst surface; thus, the photo degradation efficiency increases.

3.5 Effect of Amount of Semiconductor

![Figure 5: Effect of Amount of Semiconductor](Image)

Figure 5: Effect of Amount of semiconductor of dye on the degradation of coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H₂O₂; 2250mg/L pH; 4.5 TiO₂ 50mg to 125 mg; Intensity; 501×100 Lux]

The effect of TiO₂ loading on the photo degradation rate has been examined by varying its amount from 50 mg to 125 mg/100mL in the reaction solution. Rate constant values increased with the increased in catalyst loading. In Fig.5. The Discoloration value 95 % has been shown to be maximal at 100 mg/100 mL of catalyst loading.

Photo catalytic degradation efficiency increased with an increase in catalysts mass. This behavior might be due to an increase in the amount of active site on surface of TiO₂ particles. After the optimum amount of TiO₂, the activity of photocatalytic decolorization decreased with increase of catalyst concentration. Because higher loading of catalyst also causes increase in turbidity of the solution which reduced the light penetration in photoactive volume. Hence photoactive volume shrinks and aggregations of TiO₂ particle causing decrease in the number of surface active sites.

3.6 Effect of Variation in H₂O₂ concentration

![Figure 6: Effect of Hydrogen Peroxide on Degradation](Image)

Figure 6: Effect of hydrogen peroxide on degradation of Coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H₂O₂; 750 mg/L pH; 3.5 TiO₂ 100 mg; Intensity; 501×100 Lux]

The experiment of varying concentration of H₂O₂ values was conducted to study the effect of H₂O₂ concentration on degradation dye. The percentage degradation efficiency by variation in hydrogen peroxide concentration is shown in
Fig. 6. The range of H$_2$O$_2$ concentration was studied in a range of from observed 750 mg/L to 3750 mg/L. The higher percentage of degradation was at 3750 mg/L, which is 98.61% as the lowest percentage was 750 mg/L. As expected, the higher the value of concentration H$_2$O$_2$, the higher percentage of degradation occur because the higher concentration of H$_2$O$_2$, the more hydroxyl radicals produce which degrade more dye molecule. The results indicate that the rate of the reaction increasing with the increasing in the oxidant concentration.

It is known that the addition of H$_2$O$_2$ was to increase the rate of dye to degrade by the formation of hydroxyl radical that react with the dye molecule compound. H$_2$O$_2$ play an important role in degradation process as the hydroxyl radical OH. Because the radical will attacked the positive ions and the decolorization of dye occur. As the more hydroxyl will attack the positive ions, the degradation process becomes better and faster.

3.7 HPTLC Spectra of Coralene Dark red 2B

<table>
<thead>
<tr>
<th>Component</th>
<th>Dye λ$_{max}$</th>
<th>Effluent O.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-1</td>
<td>502.24 nm</td>
<td>0.298</td>
</tr>
<tr>
<td>Sample-2</td>
<td>470.97 nm</td>
<td>0.332</td>
</tr>
<tr>
<td>Sample-3</td>
<td>428.12 nm</td>
<td>0.387</td>
</tr>
<tr>
<td>Sample-4</td>
<td>541.65 nm</td>
<td>0.223</td>
</tr>
<tr>
<td>Sample-5</td>
<td>530.80 nm</td>
<td>0.538</td>
</tr>
<tr>
<td>Sample-6</td>
<td>504.92 nm</td>
<td>0.512</td>
</tr>
</tbody>
</table>

HPTLC Analysis of degraded Coralene Dark red 2B

Fig.9 and Fig.10 shows the chromatogram of undegraded dye effluents at pH-6 and pH-8 respectively. These spectra show the heighted peaks, it indicates that it does not give total degradation of dye.

HPTLC Analysis of degraded Coralene Dark red 2B

Figure 7: HPTLC chromatogram for standard undegraded dye
[Coralene dark Red 2B; 50mg/L H$_2$O$_2$; 2250mg/L TiO$_2$ 100mg; pH; 2 to 10 Intensity 501×100 Lux]

Figure 8: HPTLC chromatogram for degraded typical run
[HPTLC chromatogram of undegraded and degraded dye are given in fig.7 and fig. 8. Using 50mg/L concentration of dye solution, TiO$_2$ as catalyst and H$_2$O$_2$. In fig.7 peak 2 is for undegraded dye at Rf value 0.71.]

Figure 9: HPTLC chromatogram for undegraded at pH-6
[Coralene dark Red 2B; 50mg/L H$_2$O$_2$; 2250mg/L TiO$_2$ 100mg; pH; 2 to 10 Intensity 501×100 Lux]

Figure 10: HPTLC chromatogram for undegraded at pH-8
[Coralene dark Red 2B; 50mg/L H$_2$O$_2$; 2250mg/L TiO$_2$ 100mg; pH; 2 to 10 Intensity 501×100 Lux]
The photocatalytic degradation of a typical run coralene dark red 2B was examined using TiO$_2$ catalyst under direct solar light. The results show that the maximum of 95% (50 mg/L) and 98% (3750 mg/L) degradation efficiency was achieved in 120 min. Further it was also noticed that the extent of degradation was found to depend on concentration of the TiO$_2$, pH of the dye solutions, H$_2$O$_2$ concentration and the dye concentration.

A new HPTLC method has been developed for the identification and quantification of coralene dark red 2B degradation products. Low cost, faster speed, and satisfactory precision and accuracy are the main features of this method. In HPTLC Analysis of degraded Coralene Dark red 2B spectra of all dye parameters were maximum 95 % decolorization achieved in 120 min. pH-6 and pH-8 dye solution were difficult to degradation direct sun light.

Since the degradation was achieved in presence of direct sun light, the present protocol can be adapted to the large scale industrial decoloration processes and may reduce the water pollution to a certain extent.

The results indicated that during the photocatalytic degradation coralene dark red 2B and textile wastewater, the decolorization rate was faster than the degradation rate.

### References


