Homogeneous photodegradation of dye aqueous solution with H$_2$O$_2$/UV process: The effects of inorganic anions and temperature

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ABSTRACT

Photodegradation of aqueous solution of Mordant red17 (MR17) azo dye in UV/H$_2$O$_2$, advanced oxidation process was investigated in this study. Results show that MR17 dye decolorization rate was mainly effected by different parameters such as solution pH, H$_2$O$_2$ concentration, initial dye concentrations and presence of different inorganic anions such as NO$_3^-$, Cl$^-$, CO$_3^{2-}$ ions. The degradation percent of the dye decreased by the presence of inorganic anions in the order of CO$_3^{2-}$ > Cl$^-$ > NO$_3^-$ ions. While increase the temperature of the solution medium from 283 to 318K led to increase the decolorization rate of MR17 dye from 0.048 to 0.164 min$^{-1}$. The low value of the apparent activation energy E$_a$ (24.91 kJ mol$^{-1}$) indicates that decolorization process of MR17 dye is achieved easily using H$_2$O$_2$/UV process. This results further proved by presence of 100% decolorization of MR17 dye in about 50 min and about 85.57% mineralization in a 3.0 h photoperiod.

INTRODUCTION

Dyes are used in different fields such as textile, tannery, paper and pulp, in addition to food, pharmaceutical, and cosmetic industries[1]. The wide use of dyes has resulted in an increase in the volume and complexity of the wastewater discharged to the environment. It was reported that there is a big amount of dyes are lost in the effluent during the dyeing process[2]. The greatest environmental concern with colored substances such as dyes in the surface water is their absorption and reflection of sunlight entering the water. Thus causing interferes with the growth of bacteria and plants and disturbance the ecology of the receiving water[3]. Also, most dyes have low biodegradability and toxic nature such as azo dyes can originate toxic by-products in the environment[4]. Mordant dyes are one class of azo-dyes characterized by the presence of a hydroxyl group ortho to the azo-group and are colored aromatic compounds which require the presence of a metal (mordant) such as chromium to properly set their color on fabrics by forming an insoluble compound. Synthetic mordant dyes (chrome dyes), representing about 30% of dyes used for wool, are especially useful for black and navy shades.
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However, mordant dyes are very hazardous to health since improper application of dichromate or incomplete reduction could lead to release of the toxic chromium (VI) salt into the environment\(^5\).

In the same time, less attention was given to the photodegradation of mordant dyes. Thus it is important to treat wastewater containing Mordant red 17 as one class of azo-dyes before discharge\(^6\). Effluents containing azo dyes are commonly treated by the combination of biological oxidation and physical-chemical treatment methods\(^7\). However, these traditional methods mainly provide a phase transfer of the contaminants from wastewater to solid waste (sludge)\(^8\). On the other hand, the decolorization and mineralization of a wide range of dyes to stable inorganic compounds, has been carried out by different advanced Oxidation Processes (AOPs)\(^9\) such as homogeneous\(^10,11\) and heterogeneous photocatalysis\(^12,13\).

AOPs refer to a set of different methods leading to the generation of highly oxidative species such as hydroxyl radicals (‘OH) which are capable of oxidizing the pollutants to such an extent that the treated wastewater may be reintroduced into receiving streams\(^14,15\). The strategies for generating the reactive ‘OH radicals for these oxidation methods include UV photolysis of ozone or hydrogen peroxide\(^16\), Fenton or photo-Fenton type reactions, and TiO\(_2\) photocatalysis\(^17\).

This study aimed to investigate UV/\( \text{H}_2\text{O}_2 \) process for the photodegradation of the Mordant red 17 azo dye. Also, to examine the effect of several parameters such as the initial concentrations of both the dye and \( \text{H}_2\text{O}_2 \) and the presence of inorganic anions on the degradation kinetics of the dye. The effect of temperature of the solution medium on the decolorization rate was investigated. In addition the effect of Mineralization of the dye was studied as indicator of the decrease in the chemical oxygen demand (COD).

**EXPERIMENTAL**

**Chemicals**

\( \text{H}_2\text{O}_2 \) (30% w/w), ferrous ammonium sulphate ferrion indicator, mercury (II) sulphate, \( \text{HNO}_3 \), \( \text{NaOH} \), and potassium dichromate were purchased from BDH Limited, Poole, England and used without further treatment. Target pollutant used in this study was Eriochrome red G azo dye (C.I. mono sulphonic Mordant red 17) azo dye (MR17 dye) purchased from Ciba-Geigy LTD Basel, Switzerland. The chemical structure of MR17 is shown in TABLE 1. All other reagents were analytical grade and used as received. All solutions were prepared with deionized (DI) water.

**TABLE 1 : Characteristics of eriochrome red G azo dye (Mordant red 17 azo dye or MR 17).**

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Molecular Formula</th>
<th>( \lambda ) max (nm)</th>
<th>Mw (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>C(<em>{17}) H(</em>{10})N(_4)NaO(_5)S</td>
<td>430</td>
<td>411.39</td>
</tr>
</tbody>
</table>

**Methods**

**Apparatus**

**Photochemical reactor**

The photoreactor used for the photodegradation of MR17 dye was purchased from ACE glass. ACE glass photoreactor comprised of a quartz tube surrounded with a water cooling jacket and immersed in a Pyrex cylinder as a solution container. The container has inlets for feeding reactants and ports for measuring temperature and withdrawing samples.

**Radiation source**

A 20W low-pressure mercury vapor lamp (maximum emission at 254 nm) was the UV irradiation source. The lamp was surrounded with a water-cooling jacket to remove the heat and to maintain a constant temperature. The lamp tube was immersed in the reaction solution. The incident photonic flux (light intensity) was measured by the photolysis of ferrioxalate as an actinometer. The value of the incident photonic flux was determined as \((I_o = 1.46 \times 10^6 \text{ Ein.} / \text{L min})\).
Procedures

Experiments of photodegradation of MR17 dye were performed as described elsewhere\textsuperscript{13}. Aqueous solutions of MR17 dye were prepared in distilled water by dissolving the necessary quantity of the dye and fed into the photoreactor. The content of the photoreactor was mixed with magnetic stirrer and the temperature was maintained at $25 \pm 2^\circ\text{C}$ by circulation of water through an internal cooling tube. The pH of the solution was measured by an Orion pH-Meter and adjusted by using dilute nitric acid or aqueous sodium hydroxide. The lamp was started to initiate the reaction after 3 min of premixing and samples were taken at regular time intervals.

Analysis

As mentioned previously\textsuperscript{18}, the change in the concentrations of MR17 dye due to the photodegradation were determined and their UV-Vis spectra were recorded with a Perkin Elmer UV-Vis spectrophotometer. Qualitative information related to the degradation of both parent dye and intermediates formed during the photodegradation process was obtained by monitoring the absorbance in the region between 200 and 800 nm. In addition, decolorization of the dye was followed quantitatively by measuring the decrease in absorbance at $\lambda_{\text{max}} = 430$ nm for the dye chromophore. The decolorization ratio, expressed as a percentage, ($\%$) was calculated by\textsuperscript{19} the following Equation:

$$\text{Decolorization} \, (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where $C_0$ is the initial concentration of MR17 dye in the solution and $C_t$ is the final concentration of MR17 at time $t$.

Chemical oxygen demand (COD), was determined by closed reflux method. Samples were oxidized with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ in 50% $\text{H}_2\text{SO}_4$ solution. Then the excess of $\text{K}_2\text{Cr}_2\text{O}_7$ was determined by standard solution of ferrous ammonium sulfate in presence of ferrion indicator.

RESULTS AND DISCUSSION

The primary step in these experiments was the determination of the maximum absorbance ($\lambda_{\text{max}}$) for MR17 dye using different concentrations. At pH 3 (at which the experiments were carried out) the spectrum of MR17 dye represents absorption bands at 430 and 260 nm. The band at 430 nm (attributed to $n > \pi^*$ transitions of N = N, C = N and C = O chromophore groups) is responsible for the color of the dye solution and is thus used to monitor the rate of decolorization of the dye. Absorbance band at 260 nm ($\pi > \pi^*$ transition in aromatic rings) represent aromatic character of the dye, hence decreases in the absorbance at this wavelength correspond to loss of aromaticity of the dye during photodegradation\textsuperscript{20}.

The effect of pH of the dye solution on decolorization efficiency

Changing the solution pH has an important effect on the structure and characteristics of the dyes\textsuperscript{19}. Thus the degradation of (0.05 mM) MR17 was studied at various initial pHs (3, 5, 7 and 9) to investigate its effect on the decolorization process as shown in Figure 1. The results indicate that the decolorization efficiency of MR17 dye at the same dose of $\text{H}_2\text{O}_2$ under both acidic and alkaline conditions were different and appear to be dependent on the initial pH. It can be noted that the largest decolorization rate with almost 100% disappearance of the parent MR17 dye in the first 50 min of photolysis was observed at pH 3.0 with a $\text{H}_2\text{O}_2$ concentration of 2.5 mM.

While increasing the pH value to a strong alkaline medium decreased the decolorization ($\%$). The lowest degradation rate was observed in alkaline medium as the decolorization ($\%$) decreased from 100 to 73.4% at pH 9 at the same concentration of $\text{H}_2\text{O}_2$ in the same photoperiod as shown in Figure 1. This may be due to the efficient generation of hydroxyl radicals with strong oxidizing potential ($E^0 = 1.8$ V at neutral pH to 2.7 V in acidic pH) under acidic conditions\textsuperscript{21,16}.

Figure 1 : Dependence of the decolorization ($\%$) on the pH value of MR17 dye under the conditions: [dye]$_0 = 5 \times 10^{-2}$ mM, [H$_2$O$_2$]$_0 = 2.5 \times 10^{-3}$ M and $T = 25 \pm 2^\circ\text{C}$. 

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Furthermore, decolorization (%) of MR17 dye was monitored by measurement of the pH within the irradiation time. The pH of the solution decreases slowly at the initial stage of the photooxidation, dropping by less than one pH unit in acidic medium (from 5.00 - 4.61) while the neutral and alkaline medium lead to dropping by more than one pH unit (7.00 - 5.15 and 9.00 - 7.40) except in the case of high pH (pH3) it remains almost constant within the 60 min of irradiation as shown in Figure 2. This slight drop in the pH indicates the formation of organic acid compounds during the degradation process as a result of degradation and cleavage of the azo group in the dye\(^{22}\). Decreasing the pH values during the photodegradation process using H\(_2\)O\(_2\) was also observed for different dyes such as Reactive red 120, Reactive black 5, Reactive yellow 84 in aqueous solution\(^{6}\). However, remaining the pH value almost constant at initial high pH (pH3), indicating that although the organic acid compounds are formed during the degradation process of the dye they are still at such very small concentration supporting the mineralization of MR17 dye under the present conditions. Since hydroxyl radicals are generated efficiently under acidic conditions\(^{23}\), also, the results indicated that MR17 degraded significantly at pH3, subsequent experiments were performed at pH 3.

Effect of initial hydrogen peroxide (H\(_2\)O\(_2\)) concentration

Photodegradation process is mainly dependent on the amount of ‘OH radicals. However, production of ‘OH radicals is a function of the concentration of H\(_2\)O\(_2\). Several experiments were performed to investigate the effect of H\(_2\)O\(_2\) concentration on the effectiveness of the photodegradation of MR17 dye. Aqueous solutions of MR17 dye (0.05mM) were irradiated in the absence and presence of H\(_2\)O\(_2\) as shown in Figure 3. It was found that while direct photolysis (in the absence of H\(_2\)O\(_2\)) of MR17 day solution was very slow and resulted in about 5% of dye decolorization in 60 min. Also, in the same period of the experiment, dark reaction (MR17 dye/H\(_2\)O\(_2\)/dark) was found to have about 5% of dye decolorization which was in agreement with the literature\(^{24}\).

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]  \hspace{1cm} (2)

It was reported that the dosage of H\(_2\)O\(_2\) is a critical parameter of advanced oxidation processes (AOPs)\(^{25}\). Also, the results of the decolorization of MR17 depends mainly on the concentration of H\(_2\)O\(_2\). When H\(_2\)O\(_2\) reacts with dye molecules, theoretically an excess of H\(_2\)O\(_2\) is needed to produce more ‘OH radicals. However, increase both the concentration of H\(_2\)O\(_2\) and ‘OH radicals result in competitive reactions, which would inhibit the decolorization rate of MR17 according to Eq. 3-7\(^{19}\).

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  \hspace{1cm} (3)

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

\[ \text{HO}_2^- + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (5)

\[ 2 \cdot \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (6)

\[ 2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (7)
The previous reactions show that •OH radicals consumed by reactions (3), (5) and (7). Therefore an optimum concentration of H$_2$O$_2$ in the reaction course must be reached. As described previously$^{[13]}$, a pseudo-first-order rate equation can be used to illustrate the photodegradation reaction rate ($r$) of MR17 dye using different concentrations of H$_2$O$_2$ (2.5x10$^{-5}$, 2.5x10$^{-3}$, 2.5x10$^{-1}$ and 5x10$^{-3}$M). Linear regression of first-order plots of ln C$_{0}$/C$_{t}$ versus time provide $k_{app}$ from slopes.

The results in Figure 4 indicated that the decrease in dye concentration as a function of exposure time was mainly dependent on the concentration of H$_2$O$_2$. The data were in good agreement with the pseudo-first-order kinetic model providing apparent pseudo-first-order rate constants ($k_{app}$, min$^{-1}$) for each experiment.

![Figure 4: Dependence of the decolorization (%) of MR17 dye on the H2O2 concentration under the conditions: [dye]0 =5x10-2 mM, pH 3 and T=25±2°C.](image)

**TABLE 2 :** Photodegradation kinetics data [half-lives time (t$_{1/2}$), apparent rate constant ($k_{app}$), the coefficient of determination ($R^2$)] and initial reaction rate for degradation of (0.05 mM) MR17 dye using different concentrations (mM) of H$_2$O$_2$. Presented in TABLE 2.

<table>
<thead>
<tr>
<th>[H$_2$O$_2$], mM</th>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>t$_{1/2}$ (min)</th>
<th>$R_{initial}$ (mol L$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.0007</td>
<td>99</td>
<td>1.75E-07</td>
<td>0.9884</td>
</tr>
<tr>
<td>2.5</td>
<td>0.088</td>
<td>7.87</td>
<td>2.2E-06</td>
<td>0.9958</td>
</tr>
<tr>
<td>250</td>
<td>0.022</td>
<td>31.5</td>
<td>5.5 E-07</td>
<td>0.9934</td>
</tr>
<tr>
<td>500</td>
<td>0.0007</td>
<td>99</td>
<td>3.5E-07</td>
<td>0.9815</td>
</tr>
</tbody>
</table>

It can be seen that the largest degradation rate of the dye was observed with a H$_2$O$_2$ concentration of 2.5 mM with apparent rate constant of 0.088 min$^{-1}$. Increasing the concentration of H$_2$O$_2$ to 500 mM lead to high inhibition of the reaction as noted by more decrease in the rate constant to 0.007 min$^{-1}$. Furthermore, the degradation rate constant of the dye at the lower H$_2$O$_2$ concentration (0.007 min$^{-1}$) was the same as the degradation rate at higher concentration (0.007 min$^{-1}$). At lower H$_2$O$_2$ concentration (0.025 mM), the decolorization rate decreases due to the presence of insufficient •OH radicals. While increasing the concentration of H$_2$O$_2$ to 500 mM, resulted in high scavenging rate of high reactive •OH radicals by H$_2$O$_2$ to produce less reactive radicals such as HO$_2$• (Eq. 3). It is interesting to note that the photodegradation process in the presence of H$_2$O$_2$ is more efficient when using the optimum dose of H$_2$O$_2$ as reported previously by numerous authors$^{[27]}$. Since the highest degradation rate was observed by using 2.5 mM H$_2$O$_2$, therefore, in all subsequent experiments an initial H$_2$O$_2$ concentration of 2.5 mM was used.

**Effect of dye initial concentration (C$_{o}$) on efficiency of the process**

Effect of initial dye concentration on the photodegradation rate was investigated by irradiation of solutions with different concentrations (0.1 and 0.05 mM) of MR17 dye. pseudo-first-order kinetic model was used to represent the data as shown in Figure 5.

![Figure 5: Effect of initial concentration of the MR17 dye on photodegradation under the conditions: [H$_2$O$_2$]$_{0}$ = 2.5x10$^{-3}$ M, pH 3 and T= 25 ± 2°C.](image)

**TABLE 3 :** Kinetics data for effect of initial dye concentrations on photodegradation of MR17 dye using 2.5x10$^{-3}$ M [H$_2$O$_2$], pH 3 and T= 25 ± 2°C.

<table>
<thead>
<tr>
<th>[MR17 dye], mM</th>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>t$_{1/2}$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0115</td>
<td>60.27</td>
<td>0.9944</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0884</td>
<td>7.840</td>
<td>0.9888</td>
</tr>
</tbody>
</table>
Results indicated that the lowest decolorization rate (50%) was observed at high concentration of dye (0.1 mM) in the first 40 min with apparent rate constant of 0.0115 min$^{-1}$ and half-life of 60.27 min. However, using low initial concentration of the dye (0.05 mM) resulted in large enhancement of the degree of decolorization to reach 93% which lead to increase the apparent rate constant more than 7 times to be 0.0884 min$^{-1}$ and the half-life decreased to 7.84 min. This is due to the absorption of major illuminated light by dye molecules, at high initial concentrations, which act as filters limiting the penetration of light through the solution[28] thus decreasing the generation of •OH radicals available for photodegradation of MR17 dye[29]. Also, these results suggest that oxidation occurs on the chromophore rather than on the dye molecular skeleton. Because of this, H$_2$O$_2$/UV would be more effective for dilute solutions of MR17 dye.

Effect of inorganic anions on photodegradation process

To investigate the effect of inorganic anions on the decolorization of MR17 dye, experiments were performed in presence of (1.145 g/L) nitrate (NO$_3^-$), chloride (Cl$^-$) and carbonate (CO$_3^{2-}$) ions. TABLE 4 presented the results of varies the decolorization % at different times with the studied inorganic anions.

TABLE 4: Effect of (1.145 g/L) different inorganic anions (NO$_3^-$, Cl$^-$ and CO$_3^{2-}$) on the photodegradation of MR17 under the conditions: [dye]$_0$ = 5x10$^{-3}$mM, [H$_2$O$_2$]$_0$ = 2.5x10$^{-3}$M, pH 3 and T = 25 ± 2°C, (control = absence of anions).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Decolorization (%)</th>
<th>NO$_3^-$</th>
<th>Cl$^-$</th>
<th>CO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>34.00</td>
<td>29.77</td>
<td>31.51</td>
<td>16.28</td>
</tr>
<tr>
<td>10</td>
<td>55.00</td>
<td>46.51</td>
<td>42.92</td>
<td>26.98</td>
</tr>
<tr>
<td>15</td>
<td>72.50</td>
<td>66.05</td>
<td>64.38</td>
<td>41.40</td>
</tr>
<tr>
<td>20</td>
<td>84.00</td>
<td>75.81</td>
<td>76.71</td>
<td>46.98</td>
</tr>
<tr>
<td>25</td>
<td>91.50</td>
<td>83.72</td>
<td>86.30</td>
<td>61.86</td>
</tr>
<tr>
<td>30</td>
<td>93.50</td>
<td>90.70</td>
<td>89.95</td>
<td>69.77</td>
</tr>
<tr>
<td>40</td>
<td>96.50</td>
<td>96.28</td>
<td>94.52</td>
<td>79.53</td>
</tr>
<tr>
<td>50</td>
<td>100.00</td>
<td>100.00</td>
<td>96.80</td>
<td>86.98</td>
</tr>
<tr>
<td>60</td>
<td>100.00</td>
<td>100.00</td>
<td>98.17</td>
<td>90.23</td>
</tr>
</tbody>
</table>

It was reported that presence of inorganic anions in the photodegradation solutions may induce or reduce the rate of photooxidation[30]. The kinetic data (TABLE 5) showed that the rate of photodegradation of MR17 was differ in the presence of different inorganic anions. Presence of NO$_3^-$ ions lead to slight decrease in the photodegradation rate as shown by increase the half-life ($t_{1/2}$) of degradation process from 7.88 (in the absence of NO$_3^-$) to 8.45 min. Although previous reports[31] showed that the presence of NaNO$_3$ had negligible effect on the photodegradation process. Furthermore, presence of Cl$^-$ ions significantly decreased the decolorization rate constant of dye and the $t_{1/2}$ increased from 7.88 to 10.19 min. However, the rate decreased dramatically from 0.088 min$^{-1}$ in the absence of CO$_3^{2-}$ to 0.040 min$^{-1}$ due to the addition of CO$_3^{2-}$ ions which lead to increase the $t_{1/2}$ by 2.2 fold (from 7.88 to 17.33 min). This behavior may be attributed to •OH radical scavenging by CO$_3^{2-}$ ion[32].

TABLE 5: Photodegradation kinetics data [apparent rate constant ($k_{app}$), half-lives time ($t_{1/2}$) and the coefficient of determination ($R^2$)] for degradation of (2.5 x10$^{-5}$ M) MR17 in the presence of (1.145 g/L) different inorganic anions (control = absence of anions).

<table>
<thead>
<tr>
<th>Anions</th>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>$t_{1/2}$ (min) = ln (2)/$k_{app}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.088</td>
<td>7.88</td>
<td>0.988</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.082</td>
<td>8.45</td>
<td>0.992</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.068</td>
<td>10.19</td>
<td>0.990</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>0.040</td>
<td>17.33</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Since the experiments were performed at pH 3 under H$_2$O$_2$/UV, carbonate ions were present mainly as H$_2$CO$_3$. Presence of bicarbonate ions in the course of photooxidation may decrease the decolorization rate due to scavenging of •OH by HCO$_3^-$ as shown in Eq. 8.

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (8)
\]

Production of CO$_3^{2-}$ which is less reactive than hydroxyl radical[33] lowered the levels of •OH during the course of the reaction hence decreasing the decolorization rate as shown in TABLE 4. In general, the presence of inorganic anions in the wastewater tends to inhibit the photodegradation of MR17 dye as shown in TABLE 5.

Effect of temperature of aqueous medium

Effect of temperature on MR17 dye degradation was investigated. Figure 6 represent the effect of temperature on the photodegradation process.
According to the apparent kinetic rate constants at different temperatures, the apparent activation energy $E_a$ for the decolorization of MR17 dye by $\text{H}_2\text{O}_2$/UV was computed with Arrhenius Equation:

$$k = A \exp \left( -\frac{E_a}{RT} \right)$$

(9)

Taking the natural logarithm of both sides yields:

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

(10)

where, $A$ is the pre-exponential (or frequency) factor; $E_a$ is the apparent activation energy (J mol$^{-1}$), $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the reaction absolute temperature (K). The Arrhenius plot of $\ln k$ versus $1/T$ for MR17 (Figure 7) has a linear relationship and allow to obtain $E_a$ from its slope. The apparent activation energy $E_a$ obtained from the Arrhenius type plot in Figure 7 was found to be 24.91 kJ mol$^{-1}$. Generally, the reaction activation energy of ordinary thermal reactions is usually between 60 kJ mol$^{-1}$ and 250 kJ mol$^{-1}$,[33] the result implies that the decolorization of MR17 dye in aqueous solution by $\text{H}_2\text{O}_2$/UV process requires lower activation energy ($E_a$) and can be easily achieved.

**Mineralization of MR7 azo dye**

The extent of the mineralization of the dye was determined on the basis of chemical oxygen demand (COD) measurements. The mineralization efficiency was calculated by Eq. 11.

$$\text{Mineralization} (\%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

(11)

where COD$_0$ corresponds to the initial value of COD and COD$_t$ is the value of COD obtained at time $t$.

Chemical oxygen demand (COD) is the amount of oxygen equivalent to the amount of organic and inorganic matter present in the sample. Decreasing COD is evidence for the oxidation and/or decrease in the car-
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The extent of degradation of MR17 dye was determined by measuring the decrease in COD values due to the photodegradation of MR17 dye using $\text{H}_2\text{O}_2$/UV over a 3.0 h photoperiod as shown in Figure 8. The results indicating that the $\text{H}_2\text{O}_2$/UV process was very efficient and mineralizes about 85.57% of MR17 dye in period of 3.0 h.

CONCLUSION

The results have shown that UV/$\text{H}_2\text{O}_2$ treatment is very effective and can be a suitable pre-treatment method for the degradation of MR17 dye. Using a 20W low-pressure mercury vapor lamp in presence of 2.5x10$^{-3}$ M $\text{H}_2\text{O}_2$ lead to about 100% decolorization in the first 50 min and 85.57% mineralization of MR17 dye in about 3.0 hr. Also, the results indicated that presence of inorganic anions such as NO$_3^-$, Cl$^-$ and CO$_3^{2-}$ ions inhibited the removal of the dye from solution. The decreasing order of dye removal in presence of inorganic anions was; CO$_3^{2-} > \text{Cl}^-> \text{NO}_3^-$ ions. The decolorization rate was found to increase by increasing the temperature of aqueous medium from 283 to 318K. The lower value of $E_a$ obtained from the slope of the linear relationship of Arrhenius Equation indicated that the decolorization of MR17 dye in aqueous solution by $\text{H}_2\text{O}_2$/UV process requires lower activation energy and can be easily achieved. The investigations should be continued in order to identify the evaluation of the intermediates during the oxidation process.

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