PHOTOCATALYTIC DEGRADATION OF SOME REACTIVE AZO DYES BY FENTON, PHOTO-FENTON AND SOLAR PHOTO-FENTON PROCESSES

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ABSTRACT

Nowadays, wastewater effluents from various dye industry has become a serious environmental problem such as vat dyes, reactive dyes and azo dyes. In textile industry, different reactive dyes are extensively used in the last years, but they are highly hazardous to the environment and difficult to treat effectively. In this study, the photocatalytic degradation of three commercial textile azo dyes, namely Reactive orange M2R (ROM2R), Reactive Yellow 18(RY18) and Reactive Yellow ME-4GL (RYME-4GL) by photo Fenton reagent has been evaluated under irradiation of visible light and solar light in an aqueous medium. The degradation process was carried out by hydroxyl free radicals, which were the most reactive chemical species of the whole process. The effects of different reaction parameters such as initial dye concentration, Fe²⁺, H₂O₂ and pH of the experimental solution on the initial rate and photodegradation of the dye were assessed and optimized. Kinetic studies reveal that the photobleaching process follows first order kinetics.

Key words: Reactive azo dye, Solar irradiation, Photo-Fenton reaction, Decolorization, Mineralization

1.0 Introduction

Nowadays, organic dyes are consumed very large amount in textile industries and which one of the main group of pollutants in wastewater (1,2). In the last two decades, azo dyes are produced and consumed very large amount in textile industries. It is calculated that more than 750,000 t of approximately10,000 dyes are released per annum and around 50-60 % of all dyes are azo dyes, which are represented by azo groups (-N=N-)(3,4,5). The discharge of azo dyes containing waste water without any treatment has
affected aesthetic quality of water and threats to human health by highly toxic and carcinogenic compounds (6,7). Also the dyes in water various methods have been proposed to deal with azo dye wastewater such as chemical coagulation (8), activated carbon adsorption (9), biodegradation (10) and advanced oxidation processes (AOPs) (11,12).

AOPs represent one of the most promising technologies for the degradation of organic contaminants in water (13). Among the available AOPs, Fenton and photo-Fenton are of special interest because they involve the application of ferrous ions to react with H₂O₂ producing hydroxyl radicals (OH*) with powerful oxidizing ability to degrade organic pollutants (14).

The efficiency of the photo-Fenton process can be explained by the increased amount of OH* generated through the catalytic cycle of iron ions (Fe²⁺ & Fe³⁺) combined with H₂O₂ and UV- vis photons (15). The main reactions involved in Fenton process are described as follows (16).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \\
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \\
\text{OH}^- + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \\
\text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \\
\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]

The above mentioned reactions are very important involving different ions and also radicals. The scheme of this reaction is more significant because H₂O₂ and Fe²⁺ or Fe³⁺ are relatively inexpensive and ecofriendly.

The purpose of the present study is to evaluate the efficiency of the photo-Fenton process for the decolourization and photodegradation of the azo dyes. The efficiency of degradation was compared using solar and artificial irradiation. The photo Fenton reaction under solar irradiation was studied with the aim to propose a lower cost alternative for the treatment of wastewaters dye contamination, becoming more attractive for industrial applications.
2.0 MATERIALS AND METHODS

2.1 Reagents

ROM2R, RY18 and RYME-4GL azo dyes are used in the present work. The dye solutions were prepared by dissolving minimum quantity of the dye without further purification in distilled water. The hydrogen peroxide solution (33%) of analytical grade, FeSO₄·7H₂O were obtained from Merck. Several concentrations of sulphuric acid and NaOH (Merck) solutions were prepared for maintaining pH at any stage of experiment.

Table 1. Physical Properties of azo dyes

<table>
<thead>
<tr>
<th>S.No</th>
<th>Dye</th>
<th>Chemical formula</th>
<th>Molar Mass</th>
<th>Structure</th>
<th>λ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ROM2R</td>
<td>C₂₅H₂₂Cl₂N₂O₁₀S₅</td>
<td>715.52</td>
<td><img src="image" alt="ROM2R Structure" /></td>
<td>488</td>
</tr>
<tr>
<td>2</td>
<td>RY18</td>
<td>C₂₅H₁₆ClN₀Na₄O₁₃S₄</td>
<td>906.12</td>
<td><img src="image" alt="RY18 Structure" /></td>
<td>410</td>
</tr>
<tr>
<td>3</td>
<td>RYME-4GL</td>
<td>C₂₅H₂₂ClN₀Na₂O₁₂S₃</td>
<td>818.13</td>
<td><img src="image" alt="RYME-4GL Structure" /></td>
<td>420</td>
</tr>
</tbody>
</table>

2.2 Experimental procedure and analysis

All experiments were carried out in a 1 litre thermostated bath glass photoreactor equipped with magnetic stirrer. A known volume of the dye solution was taken in the reactor. Predetermined amount of Fe²⁺ ion solution and H₂O₂ solution were added into the dye solution. The pH of the dye solution was adjusted by adding dil. H₂SO₄ or NaOH. The solution was then illuminated by UV light with magnetic stirring. The photodegradation was carried under 125W UV mercury lamp. At a given time of intervals, the analytical samples withdrawn from the reaction mixture and then stored in the dark for needed
analysis. The absorbance spectrum was determined with ELICO SL-218 Double Beam UV-visible spectrophotometer and the degradation of the dyes (ROM2R, RY18 & RYM4-4GL) were monitored by recording the absorbance as a function of illumination time. The decolourization degree percentage (DD%) and rate constant values were calculated as follows (17, 18).

$$\text{DD} \% = \left(\frac{A_0 - A_t}{A_0}\right) \times 100$$

Where, \( A_0 \) is the initial intensity of colour

\( A_t \) is the intensity of colour at ‘t’. The rate constant \( k \) was calculated from the expression \( k = 2.303 \times \text{slope} \).

3.0 RESULTS AND DISCUSSION

3.1 Effect of initial H\(_2\)O\(_2\) dose on photodegradation

To investigate the effect of different initial concentrations of hydrogen peroxide (H\(_2\)O\(_2\)) on the degradation of azo dyes were studied by keeping all other factors constant. The Fig.1-6 shows that, the degradation of the dyes were rapidly increases with increase the amount of H\(_2\)O\(_2\). Further increase in H\(_2\)O\(_2\), the degradation rate was decreased. This is due to, the H\(_2\)O\(_2\) act as a scavengers of *OH radicals (eqn.11) to produce *O\(_2\)H which has lower oxidation potential than *OH.

$$\text{OH} + *\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (10)$$

$$*\text{OH} + \text{H}_2\text{O}_2 \rightarrow *\text{OOH} + \text{H}_2\text{O} \quad (11)$$

$$*\text{OOH} + *\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (12)$$

From the fig.1&3, it was reveal that, no measurable effect on the degradation of the dye in the absence of light irradiation (Dye+Fe(II)+H\(_2\)O\(_2\)+Dark). However, from the literature [19,20], and from our previous report [21] we concluded that, the [H\(_2\)O\(_2\)] may increase or inhibit the decolourization rate depending on concentration. The results are shown in Table 2 and Fig. (5&6) illustrate that RYM4-GL dye degradation was excellent for solar photo-Fenton process instead of photo-Fenton proces.
Table 2. The rate constant variation in different dye degradation

<table>
<thead>
<tr>
<th></th>
<th>ROM2R</th>
<th></th>
<th></th>
<th>RY 18</th>
<th></th>
<th></th>
<th>RYME-4GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$_2$O$_2$]$_0$ M</td>
<td>k sec$^{-1}$ x 10$^{-4}$</td>
<td>[H$_2$O$_2$]$_0$ M</td>
<td>k min$^{-1}$</td>
<td>[H$_2$O$_2$]$_0$ mM</td>
<td>k min$^{-1}$</td>
<td>Photo-Fenton</td>
<td>Solar Photo-Fenton</td>
</tr>
<tr>
<td>2</td>
<td>0.0891</td>
<td>2.022</td>
<td>1x10$^{-1}$</td>
<td>0.2980</td>
<td>0.9205</td>
<td>2</td>
<td>1.4988</td>
</tr>
<tr>
<td>0.5</td>
<td>2.152</td>
<td>10.321</td>
<td>1x10$^{-2}$</td>
<td>0.5117</td>
<td>1.1764</td>
<td>1</td>
<td>1.2942</td>
</tr>
<tr>
<td>0.1</td>
<td>6.984</td>
<td>18.718</td>
<td>1x10$^{-3}$</td>
<td>0.2749</td>
<td>0.9722</td>
<td>0.1</td>
<td>0.3097</td>
</tr>
<tr>
<td>0.01</td>
<td>6.083</td>
<td>16.524</td>
<td>1x10$^{-4}$</td>
<td>0.2094</td>
<td>0.5781</td>
<td>0.05</td>
<td>0.3062</td>
</tr>
<tr>
<td>0.001</td>
<td>1.986</td>
<td>9.658</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig.1. The degradation efficiency of ROM2R with different initial concentrations of H$_2$O$_2$ by the Fenton process.

Fig.2. The degradation efficiency of ROM2R with different initial concentration of H$_2$O$_2$ by the photo-Fenton process.

Fig.3. The degradation efficiency of RY18 with different initial concentrations of H$_2$O$_2$ by the Fenton processes.

Fig.4. The degradation efficiency of RY18 with different initial concentration of H$_2$O$_2$ by the photo-Fenton processes.
3.2 Effect of Fe$^{2+}$ concentration

The addition of ferrous ion is one of the important parameter on the decolourization of azo dyes has been studied by using photo-Fenton and Solar photo-Fenton processes. According to the previous report [14], increasing Fe$^{2+}$ ion concentration, dye degradation rate of azo dyes also increases, to optimum level where further addition of ferrous salt becomes inefficient [22].

In this study, different concentration of Fe$^{2+}$ (1x10$^{-5}$ - 3 mmol) were used for the dye degradation process and keeping all other factors constant. As shown in Fig.12, the maximum decolorization percentage was 97% for YME-4GL dye within 30 min reaction time whereas the decolorization rate of RY18 is very low. From the literature many researchers have reported (23,24) that at higher concentration of ferrous ion (Fe$^{2+}$) leads to lowering the degradation efficiency. This is due to self scavenging of hydroxyl radical (’OH) by converting into OH$^{-}$ ion during the oxidation process of Fe$^{2+}$ according to eqn. (12)

\[ \cdot \text{OH} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} \] (13)
3.3 Effect of pH on degradation of dyes

In order to investigate the effects of pH on the rate of degradation of dyes and the generation and consumption of OH radical, dye solutions were irradiated at different initial pH values (2-4). The results (Fig.7-12) shows that pH plays a predominant role with the generation of *OH in the degradation of the dyes. Therefore, the initial pH value has to be in the acidic range (2-4) to generate the maximum amount of *OH to oxidize organic compounds. At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the possibility to react with dyes [25,26].
As illustrated in Table 2 almost no significant photo Fenton discoloration took place with above 3.5 and below 2.5 of initial solution pH. Almost 95% of the dyes were degraded within 30 minutes and the discoloration rate k, also much faster at pH=3. The low activity determined for high pH has been reported (22,27,28) and can be explained by the formulation and precipitation of Fe(OH)₃. Also, the results indicated that the dyes were degraded significantly at pH 3, subsequent experiments were carried out at pH 3.

Fig. 13 The degradation efficiency of ROM2R at different pH by the Fenton process.

Fig. 14 The degradation efficiency of ROM2R at different pH by the Photo-Fenton process.

Fig. 15 The degradation efficiency of RY18 at different pH in Fenton process.

Fig. 16 The degradation efficiency of RY18 at different pH in Photo-Fenton process.
3.4 Effect of concentration of dye

The effect of initial concentration of dyes on the percentage degradation was studied at different concentrations varying from $1 \times 10^{-4}$ to $5 \times 10^{-4}$M keeping all other factors identical. It can be seen in Fig.19-24 that the rate of photocatalytic degradation decreases with increasing initial concentration of the dye. At low concentration of dye the percentage conversion is higher compared to that at higher concentration [23]. At high concentration of dye, the generation of $^\cdot$OH available for photobleaching process decreases, because of the most of the UV light will be absorbed by the dye molecules instead of H$_2$O$_2$. From the results the fenton system would be more effective for dilute solutions of the dye.

Table 3. The effect of pH on the rate constant of the dye degradation process.

<table>
<thead>
<tr>
<th>pH</th>
<th>ROM2R $k$ sec$^{-1} \times 10^{-4}$</th>
<th>RY 18 $k$ min$^{-1}$</th>
<th>RYME-4GL $k$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fenton</td>
<td>Photo-Fenton</td>
<td>Fenton</td>
</tr>
<tr>
<td>2</td>
<td>1.18</td>
<td>2.53</td>
<td>2.6</td>
</tr>
<tr>
<td>2.5</td>
<td>2.02</td>
<td>5.56</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>2.86</td>
<td>10.28</td>
<td>3</td>
</tr>
<tr>
<td>3.5</td>
<td>1.43</td>
<td>6.84</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>0.57</td>
<td>4.32</td>
<td>3.4</td>
</tr>
</tbody>
</table>
At the optimum conditions for the degradation of three azo dyes, the maximum degradation occurs at 1x10^-4 M solution. The colour removal for ROM2R and RY18 are 32.35% and 35.8 for Fenton processes while, the removal are 69.1% and 86.3% for photo-Fenton processes for the two dyes respectively. In case of RYME-4GL the color removal is 87.3% for photo-Fenton process and 98% for solar photo-Fenton process (Fig 13&14).

Fig. 19 The degradation efficiency of different initial concentrations of ROM2R dye in Fenton system

Fig. 20 The degradation efficiency of different initial concentrations of ROM2R dye in photo-Fenton system

Fig. 21 The degradation efficiency of different initial concentrations of RY18 in Fenton system

Fig. 22 The degradation efficiency of different initial concentrations of RY18 in photo-Fenton system
3.5 Mineralization of three azo dyes

The amount of chemical oxygen demand (COD) is equivalent to the total amount of inorganic and organic matter present in the compound. So, the decreasing value of COD is evidence for the degradation of the sample by oxidation and also the decrease the carbon content present in the sample. By using Fenton, photo-Fenton and solar photo-Fenton processes, the degradation of the dyes were evaluated by measuring the COD values. In Table 4, the results shows that, the order of mineralization is Solar photo-Fenton > photo-Fenton>Fenton processes.

Table 4. The photocatalytic mineralization of dyes at optimum condition

<table>
<thead>
<tr>
<th>Dye</th>
<th>Fenton</th>
<th>Photo-Fenton</th>
<th>Solar photo-Fenton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Final COD</td>
<td>% Degradation</td>
<td>Final COD</td>
</tr>
<tr>
<td>ROM2R</td>
<td>278</td>
<td>28.5</td>
<td>42</td>
</tr>
<tr>
<td>RY18</td>
<td>196</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>RYME-4GL</td>
<td>-</td>
<td>-</td>
<td>62</td>
</tr>
</tbody>
</table>
3.5 Conclusion

In the present work, the photocatalytic degradation of some azo dyes in aqueous solution by Fenton oxidation process has been studied at various operational parameters. At pH 3, the degradation of the dye is high in both photo-Fenton and solar photo-Fenton. But comparing these two, solar photo-Fenton is best for degradation of dye. Thus, the effect of photocatalytic degradation, strongly depend on the concentration of dye, pH of the solution, Fe²⁺ dosage and H₂O₂ dosage. The decolourization of RYME-4GL was achieved greater than 90% within 30 min. of solar irradiation. From the results, we have concluded that the solar photo-Fenton process is feasible and cost-effective for the mineralization of dyes at low hydrogen peroxide concentration, and is appropriate method for removal of color, COD and detoxification of azo dye solutions. Therefore, the photo-Fenton process is most eminent method for wastewater treatment using solar energy, can be a effective method for industrial applications.

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3.6 REFERENCES


