Disappearance of Basic yellow 28 from aqueous solution by Fenton’s reagent

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Abstract
The disappearance of Basic yellow 28 from aqueous solution has been investigated using Fenton’s reagent (Fe\(^{2+}\) and H\(_2\)O\(_2\)). The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ([H\(_2\)O\(_2\)]\(_0\)), the initial ferrous concentration ([Fe\(^{2+}\)]\(_0\)), the initial Basic yellow 28 concentration ([dye]\(_0\)) and the temperature on the disappearance of Basic yellow 28 have been assessed. The optimal reacting conditions were experimentally determined and it was found to be initial pH = 3.0, [H\(_2\)O\(_2\)]\(_0\) = 0.20 mM, [Fe\(^{2+}\)]\(_0\) = 0.14 mM for [dye]\(_0\) = 13 µM at temperature = 25 °C. Under optimal conditions, 90 % disappearance efficiency of dye from aqueous solution was achieved after 2 min of reaction.

Keywords: Fenton’s reagent, Basic yellow 28, Ferrous ion, Hydrogen peroxide, disappearance efficiency.

1. Introduction
Synthetic dyes are extensively used in many technologically important processes, e.g., in textile [1], leather tanning [2], paper production [3], food technology [4], agricultural research [5], light-harvesting arrays [6], photo-electrochemical cells [7], hair coloring [8], etc. It is estimated that over 10,000 tonnes of dyes are produced all over the world per year. About 1–2% dyes are lost during production and 1–10% is lost during the use [9]. Due to the large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and serious health hazards [10]. Traditional wastewater treatment technologies like activated sludge processes have proven to be markedly ineffective for handling wastewater containing synthetic textile dyes because of the chemical stability of these pollutants. A wide range of methods has been developed for degradation of synthetic dyes in water and wastewater [11]. The technologies involve adsorption on inorganic or organic matrices, decolorization by photocatalysis and/or by oxidation processes and microbiological decomposition [12]. Chemical oxidation is reported to be very effective but the efficiency strongly depends on the type of oxidant and the nature of dye [4].

Advanced oxidation process (AOP) is defined as the oxidation process, which generates hydroxyl radicals in sufficient quantity to effect wastewater treatment. AOP uses Fenton’s reagent to achieve high performance [13]. Presence of ozone and UV radiation enhances the performance of Fenton’s reagent [14]. Most of these processes have been associated with the generation of radical species mainly hydroxyl radicals \(\cdot\)OH. Hydroxyl radical is a strong oxidizing agent able to react with organics and causing the ring opening. Unlike many other radicals, hydroxyl radicals is non-selective and thus readily attacks a large group of organic chemicals to convert them to less complex and less harmful intermediate products [15].

In literature, Fenton (Fe\(^{2+}/\text{H}_2\text{O}_2\)) and Fenton-like (Fe\(^{3+}/\text{H}_2\text{O}_2\)) reactions are found to be efficient for decolorizing and detoxifying of textile effluents [16-23]. Fenton reactions and O\(_3\) oxidation are still the most basic and yet practical advanced oxidation processes for the treatment of industrial effluents including textile effluents [24,25].

AOPs have common principles in terms of the participation of hydroxyl radicals that are assumed to be operative during the reaction. Due to the instability of \(\cdot\)OH radical, it must be generated continuously in situ through chemical or photochemical reactions [26]. Hydroxyl radicals are generated by the reaction between H\(_2\)O\(_2\) and ferrous ions. The slow regeneration of Fe\(^{3+}\) to Fe\(^{2+}\) is the rate-determining step of the overall reaction. Thus, in AOP, rate of dye degradation is fast in the beginning due to high initial concentration of Fe\(^{2+}\). However, the rate drastically reduces due to the drop in the concentration of Fe\(^{2+}\) and poor rate of its regeneration [27].
The objective aim of this study is to determine the influence of some operational parameters (initial pH of solution, initial concentration of hydrogen peroxide, initial ferrous concentration, initial concentration of dye, temperature). The optimal experimental conditions for potential capability of disappearance dye were investigated.

2. Materials and Methods

2.1. Chemicals

The Basic Yellow 28 was prepared from a local textile factory in Casablanca (Morocco) and used without further purification. The structure of the dye and their characteristics are given respectively in Fig. 1 and Table 1.

![Molecular structure of Basic yellow 28](image)

**Figure 1:** Molecular structure of Basic yellow 28.

The chemicals used for AOP study are ferrous sulfate heptahydrate (FeSO4·7H2O) and hydrogen peroxide (30% w/w). The pH was adjusted with sodium hydroxide and sulfuric acid. All this chemicals are supplied by LobaChemie, India, and were used without further purification. Distilled water was used throughout this study.

**Table 1: Characteristics of the Basic yellow 28 [28].**

<table>
<thead>
<tr>
<th>Color index</th>
<th>Basic yellow 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td>Maxilon Golden Yellow GL 200%</td>
</tr>
<tr>
<td>Chemical class</td>
<td>Methine</td>
</tr>
<tr>
<td>CI number</td>
<td>48054</td>
</tr>
<tr>
<td>Type</td>
<td>Cationic</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>433 g/mol</td>
</tr>
<tr>
<td>(\lambda_{\text{max}})</td>
<td>438 nm</td>
</tr>
</tbody>
</table>

2.2. Experimental procedures

Disappearance of dye (%) against time was carried out with a UV-vis spectrophotometer. Dye solution pH values were adjusted to the desired level using dilute sulfuric acid and sodium hydroxide, which were measured by a pH meter (Knick). All experiments were carried out in spectrometric cell (1 cm path length), which were placed in a spectrophotometer. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of ferrous ion solution. The reactions were initiated by adding hydrogen peroxide to the cell. Each experiment was replicated three times.

2.3. Analytical methods

The UV-vis spectra of dye were recorded from 200 to 800 nm using a UV-vis spectrophotometer (BioMate 3, England) with a spectrometric cell (1 cm path length). The maximum absorbance wavelength (\(\lambda_{\text{max}}\)) of Basic yellow 28 could be found at 438 nm from the spectra. Therefore, the concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at \(\lambda_{\text{max}}= 438\) nm and from a calibration curve. The disappearance efficiency of Basic yellow 28 was defined as follows (Eq. (1)):

\[
\text{Disappearance efficiency (\%) = (1-C_t/C_0) \times 100}\%
\]

Where \(C_0\) is the initial concentration of Basic yellow 28, and \(C_t\) is the concentration of Basic yellow 28 at reaction time t (s).
3. Results and discussion

3.1. Effect of pH

The pH of the solution is an important parameter for Fenton oxidation process, which controls the production rate of hydroxyl radical. In order to find the optimal pH of reaction mixture for the disappearance of Basic yellow 28 in Fenton oxidation, a series of experiments were conducted at different pH values of 3.00, 3.50, 4.00, 5.00, 6.00, etc. The results are illustrated in Fig. 2.

The results indicated that the disappearance of Basic yellow 28 was significantly influenced by the pH of the solution and the optimal solution pH was observed at about 3.00.

Many studies have revealed that the solution pH can dramatically influence the degradation of synthetic dyes in water by Fenton oxidation and the optimal solution pH values were achieved at range 3.00-4.00 [29,30]. At low pH (below 3.00), the reaction according to Eqs. (2) and (3) could be slowed down because hydrogen peroxide can stay stable probably by solvating a proton to form an oxonium ion (e.g. H$_3$O$^+$, Eq. (4)). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [31]. At the same time, the formed complex species [Fe(H$_2$O)$_6$]$^{2+}$ and [Fe(H$_2$O)$_6$]$^{3+}$ also react more slowly with hydrogen peroxide [32]. In addition, the scavenging effect of the •OH radical by H$^+$ is severe (Eq. (5)) [33,34].

Fe$^{2+}$ + H$_2$O$_2$ + H$^+$ $\rightarrow$ Fe$^{3+}$ + •OH + H$_2$O

$K_2$ = 76 M$^{-1}$s$^{-1}$ (2) [35,36]

Fe$^{3+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{2+}$ + •OOH + H$^+$

$K_3$ = 0.01-0.02 M$^{-1}$s$^{-1}$ (3) [35,36]$

H$_2$O$_2$ + H$^+$ $\rightarrow$ H$_2$O$^+$

•OH + H$^+$ + e$^-$ $\rightarrow$ H$_2$O (4)

3.2. Effect of the initial H$_2$O$_2$ concentration

Hydrogen peroxide plays the role of an oxidizing agent in Fenton oxidation process. The selection of an optimal hydrogen peroxide concentration for the degradation of Basic yellow 28 by Fenton oxidation is important from a practical point of view due to the cost of hydrogen peroxide. Fig. 3 shows the effect of initial H$_2$O$_2$ concentration ([H$_2$O$_2$]$_0$) on the disappearance of Basic yellow 28 during Fenton treatment. As it can be seen, the effect of increasing [H$_2$O$_2$]$_0$ from 0.05 mM to 0.60 mM was first positive for the degradation of Basic yellow 28. This is due to the oxidation power of Fenton process which was improved with increasing •OH radical amount in solution obtained from the decomposition of increasing hydrogen peroxide.

![Figure 2](image-url)
According to the results are shown in Fig. 3, the optimal hydrogen peroxide concentration for the most effective disappearance of 13 µM Basic yellow 28 is about 0.20 mM.

3.3. Effect of the initial Fe$^{2+}$ concentration
To elucidate the role of initial concentration of Fe$^{2+}$ ([Fe$^{2+}$]$_0$) on the degradation of Basic yellow 28 by Fenton oxidation, a series of experiments were conducted with different [Fe$^{2+}$]$_0$ from 0.03 mM to 0.14 mM. Fig. 4 shows the effect of [Fe$^{2+}$]$_0$ on the disappearance of Basic yellow 28 by Fenton oxidation.

The results indicated that the disappearance of Basic yellow 28 is remarkably dependent on the [Fe$^{2+}$]$_0$ at fixed [H$_2$O$_2$]$_0$ and [dye]$_0$. At a low [Fe$^{2+}$]$_0$ (0.03 mM), the degradation efficiency was 16.84% after the 2 min reaction time. Both disappearance efficiency and disappearance rate were increased with increase of [Fe$^{2+}$]$_0$, the disappearance efficiency being 33.58%, 57.36% and 90.28% after the 2 min reaction time with [Fe$^{2+}$]$_0$ of 0.07 mM, 0.1 mM and 0.14 mM, respectively. This is because more •OH radicals are produced with the increase of [Fe$^{2+}$]$_0$ according to Eq. (2).

In the light of these results, the optimal Fe$^{2+}$ concentration was selected as 0.14 mM for the disappearance of 13 µM Basic yellow 28. Moreover, many studies have revealed that the use of a much higher concentration of
Fe^{2+} could lead to the self-scavenging of \('\cdot\text{OH} radical by Fe^{2+}\) (Eq. (6)) \([35,37]\) and induce the decrease in degradation rate of pollutants.

\[
\text{\('OH + Fe^{2+} \rightarrow Fe^{3+} + \cdot\text{OH}' \quad k_6 = 4.3 \times 10^8 \text{M}^{-1}\text{s}^{-1}}
\]

\(3.4.\) Effect of the initial basic yellow 28 concentration

To study the effect of initial Basic yellow 28 concentration ([dye]₀) on its degradation, the range 6.20-23.00 µM of [dye]₀ was investigated. Fig. 5 shows the changes of Basic yellow 28 concentration with the reaction time. It was observed that lower the [dye]₀ (< 13 µM), shorter is the reaction period needed to degrade Basic yellow 28 completely. At a higher [dye]₀ of 23.00 µM, the Basic yellow 28 concentration decreased quickly in the first 20 s and then slowed down as the time goes on. The disappearance efficiency was 69.83% after the 20 s reaction time. This is due to the fact that with constant [H₂O₂]₀ and [Fe^{2+}]₀, more hydrogen peroxide was consumed in the first 20 s because of a higher [dye]₀. After 20 s, the amount of hydrogen peroxide was smaller and the disappearance of Basic yellow 28 slowed down significantly.

\[\text{Figure 5: Effect of initial Basic yellow 28 concentration on the disappearance of dye during Fenton oxidation treatment. Reaction conditions: } [\text{Fe}^{2+}]_0 = 0,14 \text{mM}, [\text{H}_2\text{O}_2]_0 = 0.2 \text{mM, pH} = 3.00, \text{and temperature} = 25^\circ\text{C}\]

\[\text{3.5. Effect of temperature}\]

Temperature is critical to the reaction rate, the product yield and distribution. In order to determine the effect of reaction temperature on the disappearance of Basic yellow 28 a series of experiments were conducted by varying temperature from 15 °C to 45 °C. The results are illustrated in Fig. 6.

\[\text{Figure 6: Effect of temperature on the disappearance of Basic yellow 28 during Fenton oxidation treatment. Reaction conditions: } [\text{Fe}^{3+}]_0 = 0,14 \text{mM, [dye]}_0 = 13 \text{µM, [H}_2\text{O}_2]_0 = 0.2 \text{mM and pH} = 3.00\]
It can be seen that the temperature exerts a strong effect on the disappearance rate of Basic yellow and the disappearance was accelerated by a rise in temperature. This is because higher temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), thus increasing the rate of generation of oxidizing species such as ·OH radical or high-valence iron species.

**Conclusions**

Treatment of simulated wastewater containing Basic yellow 28 dye using Fenton oxidation process has been taken into consideration in the present study. Based on the experimental results presented above, it has been found that the solution pH, the initial H$_2$O$_2$ concentration, the initial Fe$^{2+}$ concentration, the initial dye concentration and the temperature are the main factors that have strong influences on the disappearance of Basic yellow 28 by Fenton oxidation process. The optimal operation parameters for the Fenton oxidation of Basic yellow 28 were 0.20 mM $[\text{H}_2\text{O}_2]$, 0.14 mM $[\text{Fe}^{2+}]$, for 13 µM [dye]$_0$ at an initial pH of 3.00 with 25 °C temperature. Under these conditions, 90 % disappearance efficiency of dye in aqueous solution was achieved after 2 min of reaction.

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**References**


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