Decolourisation of textile dyeing Wastewater by modified solar
Photo-Fenton Oxidation
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ABSTRACT

In a laboratory study, decolourisation of real textile dyeing wastewater by modified solar
photo-Fenton (Steel scrap/ H₂O₂) process under irradiation with sunlight was examined.
Batch experiments were conducted to determine optimal operating conditions. The optimal
doses of H₂O₂ and steel scrap were 15 mL/L and 1 g/L, respectively at pH 3. Colour removal
of 89% was obtained under optimum conditions. These results suggest that, the modified
solar photo-Fenton process proved to be efficient for decolourisation of the real textile dyeing
wastewater. A simplified mechanism of hydroxyl radical production in the presence of steel
scrap as a catalyst has been proposed. The morphologic analysis and mapping of the
elementary composition of Steel scrap used as a catalyst was determined by scanning
electronic microscopy.

Keywords: Textile dyeing wastewater, Steel scrap, Decolourisation, Solar light, Hydrogen
peroxide, Modified solar photo-Fenton process.

1. Introduction

More than 10,000 dyes are used in the textile industry and 280,000 tonnes of textile dyes are
discharged every year world wide ( Hsueh et al., 2005), Textile dyeing and finishing
processes produce large quantities of wastewater that is highly coloured and contains large
concentration of organic matter( Mass et al.,2005), which is difficult to treat via classical
methods. Apart from the aesthetic problems created when coloured effluents reach the natural
water currents, dyes strongly absorb sunlight, thus impeding the photosynthetic activity of
aquatic plants and seriously threatening the whole ecosystem (Slokar et al.,1998),

The advanced oxidation processes (AOPs), are currently considered to be a potential
treatment method for the removal of colour which are characterized by production of the
hydroxyl radical (OH·) as a primary oxidant. Among the various AOPs, the use of Fenton
reagent (H₂O₂/Fe²⁺) is one of the most effective methods of organic pollutant oxidation. The
Fenton reagent has been found to be effective in treating various industrial wastewater
components including aromatic amines (Casero et al., 1997), and a wide variety of dyes [Kuo
et al., 1992; Nam et al., 2001), as well as many other substances, eg. Pesticide (Huston et al.,
1999; Barbusinski et al., 2001), and surfactants (Lin et al., 1999), Therefore, the Fenton
reagent has been applied to treat a variety of wastes such as those associated with the textile
and chemical industries.

The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen
peroxide (Barbusinski et al., 2003), Therefore, this method offers a cost effective source of
hydroxyl radicals, using easy to handle reagents. However, disadvantages in using the Fenton reagent include the production of a substantial amount of Fe (OH)\textsubscript{3} precipitate (Barbusinski, 2005), and additional water pollution caused by the homogeneous catalyst that is added as an iron salt, cannot be retained in the process (Malik et al., 2003). To solve these problems, the application of alternative iron sources as catalyst containing organic contaminants has been studied extensively. A number of researchers have investigated the application of iron oxide such as hematite, ferrihydrite and crystalline goethite (Kavitha et al., 2004; Montserra et al., 2002; Juan Mataias Chacon et al, 2006; Patricia et al., 2007). They generally have observed a greatly accelerated decomposition of hydrogen peroxide but variable amounts of contaminant were lost.

Another group of investigations consisted in the application of iron powder in the H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{0} system. Zero-valent iron metal (Fe\textsuperscript{0}) is a very promising reactive medium due to its low cost, effectiveness, ability to degrade contaminants and its accessibility (Nilesh Tantak et al., 2006; Meric et al., 2004). It was found that iron powder could be used to replace iron salts as a catalyst for the Fenton reaction (Jian-Hui Sun et al., 2010).

In this study a modified solar photo-Fenton process using heterogeneous catalyst (Steel scrap) was developed and applied to catalyze the oxidation reaction of textile dyeing wastewater. A batch process was conducted to demonstrate the feasibility of colour removal from textile dyeing wastewater by the newly developed oxidation technology.

2. Materials and Methods

2.1 Chemicals

H\textsubscript{2}O\textsubscript{2} (30w/w) (Merck). The double distilled water was used to prepare experimental solution. The pH of the reaction solutions was adjusted using 1N H\textsubscript{2}SO\textsubscript{4} and NaOH solutions.

![Figure 1: Schematic diagram of lab-scale Modified Solar Photo-Fenton reactor](image_url)
2.2. Modified Solar Photo-Fenton Reactor and Decolourisation Procedure

All modified solar photo-Fenton experiments were carried out at Anna University campus in Chennai (13°00.57' N; 80°14.12' E), Tamilnadu, India, using multiple borosilicate glass trays as reactor as shown in Fig.1. The experiments were conducted using solar light in the month of March 2010 (UV intensity 22±2 W/m²). Glass stirrer was used for mixing of wastewater with H₂O₂. The obtained solution was pumped with the help of a peristaltic pump to the reactor filled with a steel scrap as a catalyst. The experiments were conducted on 500mL wastewater samples (in duplicate). The time duration of experiments was 30 minutes. Samples were collected at every 5 minutes interval, NaOH solution was used to quench the oxidation by rising the pH to 7. At this pH further generation of hydroxyl radical is prevented then centrifuged at 3000 rpm in 3 min and were analysed for colour.

2.3 Analytical methods

The textile dyeing Wastewater samples were taken in polyethylene bottles from an industry at Tirupur, Tamilnadu, India. Samples taken were preserved in the refrigerator at 4° C in accordance with the standard methods for the Examination of Water and Wastewater (APHA, 2002). Textile wastewater samples were characterized in terms of the pH value as well as of BOD₃, COD, TDS, TSS, Chlorides and Sulphate Concentrations (APHA, 2002). All solutions were prepared with double distilled water. The pH of the solutions was measured using Elico LI 120 equipped with combined glass-calomel electrode. A Heraus-Sepatech Labofuge 200 centrifuge was used for the centrifuging of the samples at 3000 rpm for 3 minutes duration for removing turbidity before colour measurement. The detection of the colour value was determined using a Spekol UV-Vis Spectrophotometer according to Method 2120C in standard methods (APHA, 2002). The initial value of colour was 0.433 [absorbance at wavelength (λmax)=600nm, number of selected ordinates =10]. A Scanning Electron Microscopy instrument (HITACHI Model-S3400) was used for SEM-EDX analysis for finding the chemical composition of the steel scrap used as a catalyst, and the Lux meter was used for measurement of solar irradiation.

2.4. Mechanism of the Modified Solar photo-Fenton Process

In an aqueous solution, under acidic conditions, Fe²⁺ ions are released to the solution by the steel scrap. The steel scrap acts as a heterogeneous catalyst for the activation of hydrogen peroxide. When Steel scrap is used as a solid catalyst, Fe ions are leached from the solid material. Then, the iron ions act as homogeneous catalyst for the activation of H₂O₂ to generate hydroxyl radicals according to the Fenton reaction. (Barbusinski.,2005), Because the Steel scraps release Fe²⁺ ions to the solution under acidic conditions, iron dissolution is an initial step for the oxidation of contaminants by the H₂O₂/Steel scrap process. When textile dyeing wastewater oxidation occurs, the initial Fe²⁺ ions are consumed, and then the oxidation rate will depend on the dissolution rate of Fe²⁺. This mechanism has three stages: 1st stage - dissolution of scrap and release of Fe²⁺ ions, 2nd stage-the solar photo- Fenton reaction including formation of hydroxyl radicals OH⁺ and 3rd stage-oxidation of textile dyeing wastewater

3. Results and Discussion

3.1 Chemical Composition and Morphologic Analysis of Steel Scrap
The steel scrap is produced during metal sawing was washed and dried at 103°C. The heated Steel scrap was cooled and separated by a sieve to get uniform size. The particle size of steel scrap used in the study was in the range of 0.5-2 mm. The chemical composition of the Steel scrap used as a catalyst is shown in Table 1. The morphologic analysis of steel scrap used as a catalyst is shown in Fig.2. The solids present an irregular surface and the small particle aggregates are observed. The (Energy Dispersive X-Ray) EDX analysis showed presence of very high amount of Fe, C and O as shown in Figure 3.

Table 1: Chemical composition of the scrap used as a catalyst in percentage by weight

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>Ca</th>
<th>Mo</th>
<th>Al</th>
<th>Trace Elements</th>
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<td></td>
<td>41.39</td>
<td>8.77</td>
<td>45.91</td>
<td>1.20</td>
<td>0.46</td>
<td>0.50</td>
<td>0.35</td>
<td>0.31</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Figure 2: Morphologic analysis of Steel scrap used as catalyst

Figure 3: EDX analysis of the Steel scrap used as catalyst
3.2 Characterization of textile dyeing wastewater

The textile wastewater was obtained from a textile industry at Tirupur, Tamilnadu, India, during March 2010. Samples taken were preserved in the refrigerator at 4°C in accordance with the standard methods for the Examination of Water and Wastewater (APHA., 2002). The characterization of the raw effluent has been done by collecting raw effluent samples from equalization tank in the industry. The wastewater samples were characterized in terms of the pH value as well as of BOD₃, COD, TDS, TSS, Chlorides and Sulphate Concentrations (APHA., 2002). The characteristics of raw effluent are listed in Table 2.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Colour, Absorbance in nm</td>
<td>0.433</td>
</tr>
<tr>
<td>2</td>
<td>COD, mg/L</td>
<td>1706</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
<td>8.8</td>
</tr>
<tr>
<td>4</td>
<td>Chlorides, mg/L</td>
<td>396</td>
</tr>
<tr>
<td>5</td>
<td>BOD₃, mg/L</td>
<td>420</td>
</tr>
<tr>
<td>6</td>
<td>Sulphate, mg/L</td>
<td>450</td>
</tr>
<tr>
<td>7</td>
<td>Total suspended solids, mg/L</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>Total dissolved solids, mg/L</td>
<td>3460</td>
</tr>
</tbody>
</table>

3.4 Effect of initial pH variation

The aqueous pH has a major effect on the efficiency of modified solar photo-Fenton reaction. Fig 4 demonstrates the effect of pH on the decolourisation of the textile dyeing wastewater. The reactor was run for 30 min under controlled pH condition (3,4,5,6&7) with a constant dose of Steel scrap of 1 mg/L and H₂O₂ of 20 mL/L. It is apparent from the figure that the percentage decolorisation decreases with increase in pH, at pH 3 it is 89%. The observed decolourisation of 89% at pH 3 is also supported by previous studies., Kuo (Kuo., 1992) observed 93% of decolourisation of dye in 30 min. Malik and Saha (Malik et al., 2003), reported that the optimum pH was 3 for the decolourisation of dyes. Meric et al., showed that more than 99% of colour removal was possible in the pH range of 3-3.5.

![Figure 4: Effect of pH on decolourisation (catalyst=1g/L and H₂O₂=20mL/L)](image)

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3.5. Effect of Initial concentration of H$_2$O$_2$

The effect of concentration of H$_2$O$_2$ on the rate of decolourisation was carried out for duration of 30 min with real textile dyeing wastewater. The reaction was done at pH 3 with the constant dose of steel scrap 1mg/L. The concentration of H$_2$O$_2$ was varied from 5 to 20 mL/L. From the data shown in Fig. 5 it can be seen that the maximum efficiency of decolourisation was observed at 15 mL/L. The efficiency increased with the increased quantity of H$_2$O$_2$. The lower rate of H$_2$O$_2$ did not give significant reduction in colour removal. It may be due to that higher rate of reaction may not compensate the large amount of oxidants (Montserrat Perez et al., 2002). The decolourisation of textile dyeing wastewater was increased by increasing the concentration of H$_2$O$_2$. This can be explained by the effect of the additionally produced hydroxyl radicals. The decolourisation above certain ranges improvement was not obvious. This may be due to the recombination of hydroxyl radicals and also hydroxyl radicals reaction with H$_2$O$_2$ contributing to the hydroxyl radical scavenging capacity (Modirshala et al., 2006).

![Figure 5](image-url)

**Figure 5**: Effect of H$_2$O$_2$ on decolourisation (pH =3 and catalyst concentration =1g/L)

3.6 Effect of initial catalyst (scrap) dosage

The effect of dosage of catalyst (Steel scrap) on the rate of decolourisation was studied in the range of 0.5 to 2 g/L. The time vs percentage decolourization was plotted for all dosage of Steel scrap as shown in Fig. 6 In the study, maximum efficiency of decolourization of 89% was obtained at 1g/L. The decolourisation was decreased with increased quantity of steel scrap. The use of large quantities of Steel scrap in solution has a negative effect on decolourisation. An increase in the concentration of Steel scrap did not improve the oxidation process and Steel scrap acts only as a catalyst. In the presence of UV/Solar light, the concentration of Fe$^{2+}$ increased which is available for hydroxyl radical generation (Kavitha et al., 2004). Ferrous ion regeneration can be stopped since the organic matter can be a hydroxyl radical scavenger and hence can cause the interruption of the radical chain reaction (Bertanza et al., 2003).
4. Conclusions

The results confirm that steel scrap can be used as a source of Fe ions (catalyst) in the solar photo-Fenton process. It was observed that steel scrap acted as a heterogeneous catalyst for the activation of hydrogen peroxide. The modified solar photo-Fenton process was found to be very efficient for decolourisation of real textile dyeing wastewater. The optimal doses of H$_2$O$_2$ and steel scrap were 15 mL/L and 1 g/L, respectively at pH 3. These results suggest that, compared with both the classical solar photo-Fenton reaction and solar photo-Fenton reaction with alternative iron sources, the new modified solar photo-Fenton process (H$_2$O$_2$/Steel scrap) has clear advantages. This process is relatively economical because the steel scrap can be used as a discard material, e.g. from machining. The Modified Solar photo-Fenton process is easy to operate, allowing it to retain the catalyst in the process and thus the catalyst (steel scrap) can be used repeatedly. The Modified Solar photo-Fenton reaction with the use of steel scrap offers greater possibilities for practical application of solar photo-Fenton reagent.

5. References


