Decolourisation of C.I. basic yellow 1 by photo-oxidation method

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ABSTRACT

The decolourisation of C.I. basic yellow 1 in aqueous medium was studied using a 25W low-pressure ultra-violet (UV) lamp along with H$_2$O$_2$ as an oxidant. It was observed that when H$_2$O$_2$ was used with UV radiation, the decolourisation rate became faster and 98.1% of colour removal was occurred in 20min at 20mg/L of initial dye concentration. It was also observed that decolourisation is dependent on initial concentration of H$_2$O$_2$, initial concentration of dye solution, UV dosage and pH. The decolourisation rate followed pseudo-first order kinetics with respect to the dye concentration. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Decolourisation; C.I. basic yellow 1; Hydrogen peroxide; UV radiation; Pseudo-first order; Advanced oxidation process.

INTRODUCTION

The residual colour present in textile wastewater is one of the major problems faced by the textile industry. Basic dyes are some of the most widely used dyes in India but normally are considered as a problematic waste. In this work, the target compound C.I. basic yellow 1 is one of the dyes, which are utilized extensively in versatile textile dyeing and paper industry.

The removal of colour from the textile wastewater is achieved by several techniques[1]. There are three methods for treatment of coloured materials, including physical methods employing precipitation, adsorption, and reverse osmosis; chemical methods via oxidation (using air oxygen; ozone, NaOCl, and H$_2$O$_2$ as oxidants) and the reduction (e.g., Na$_2$S$_2$O$_4$); and biological methods including aerobic and anaerobic treatment[2]. The disadvantage of precipitation methods is sludge formation. The disadvantage of adsorption is that the adsorbent needs to be regularly regenerated. This is associated with additional costs and sometimes with very time-consuming procedures. Biological treatment is ineffective in cases where complicated aromatic compounds are present.

Advanced oxidation processes(AOPs) provide a promising treatment option for textile wastewater compared to other treatment methods[3-7]. H$_2$O$_2$/UV process is the most widely used AOP technology for the treatment of hazardous and refractory pollutants in wastewaters, mainly because no sludge is formed and a high colour removal in a short retention time is achieved[8]. UV/H$_2$O$_2$ is frequently applied to degrade refractory of organics in aqueous phase[9]. The process in general depends on the generation of OH radicals in solution in the presence of UV light. These radicals can then react with the dye molecules to undergo a serious
of reactions in which the organic molecule is finally destroyed or converted into a simple harmless compound.

Mohey EL-Dein et al.\cite{10} reported that C. I. reactive black 5 was decolourised by UV/H$_2$O$_2$ process while an optimum molar ratio of H$_2$O$_2$/dye. Colonna et al.\cite{11} reported that UV irradiation in the presence of H$_2$O$_2$ leads to complete decolourisation and mineralisation of sulphonated azo and anthraquinone dyes.

The aim of this study was to evaluate the feasibility of decolourisation of C.I. Basic Yellow 1 by UV/H$_2$O$_2$ process. The operating parameters such as hydrogen peroxide dosage, UV dosage, initial dye concentration and pH were determined to find the suitable operating conditions for the best efficiencies of decolourisation. Besides, the decolourisation rate followed pseudo-first order kinetics with respect to the dye concentration was determined.

**EXPERIMENTAL**

**Materials**

The dye, C.I. basic yellow 1 was obtained from Aldrich Chemical and used without further purification. Hydrogen peroxide (30% w/w) was obtained from Qualigens, Chennai. The pH of the dye solution was measured with a PE-138 Elico pH meter; pH was adjusted to the desired value by using HCl and NaOH (Fine chemicals, Chennai). The characteristic of the C.I. Basic yellow 1 is given in TABLE 1.

**Photo-reactor and irradiation experiments**

Experiments were carried out in a batch mode cylindrical glass reactor made of boro-silicate glass, which is shown in figure 1. The effective volume of the reactor was around 2 liters. The inner tube was made of quartz with a 500W, 254nm UV lamp placed inside it to provide the irradiation source. Air was bubbled into the reactor through the air diffusers in order to mix the dye solution uniformly by using an air pump.

A total of 1000ml of dye solution in the reactor was used for the treatment. The liquid inside the column was exposed to 500W UV lamp. 20mg/L of initial dye concentration was selected. The selected amount of dye was dissolved in deionized water prior to use. The different initial H$_2$O$_2$ dosages were added to dye solution to prepare the reaction mixture. Samples were periodically withdrawn from the reactor, and changes in absorbance were measured. For the dye studied in this work the action of UV alone or H$_2$O$_2$ in the absence of UV radiation was negligible after two days of treatment.

**Analytical methods**

Absorbance in the UV and visible range were measured with a Shimadzu-1061 UV-visible spectrophotometer. Periodically, H$_2$O$_2$ concentration was determined calorimetrically using potassium titanium oxalate solution at 398.9nm\cite{12}, and no depletion of the reagent was found in any case.

**RESULTS AND DISCUSSION**

In the photochemical reactor, the decolourisation of dye solution was conducted using the UV/H$_2$O$_2$ process under initial hydrogen peroxide concentration. In this process, UV irradiates the hydrogen peroxide to produce the strongest oxidizing free radicals such as hydroxyl and peroxyl radicals, which attack the organics instantaneously as soon as the reaction starts, to degrade the dye solution. Besides, the decolourisation rate expression of C.I. basic yellow 1 can be simplified as a pseudo-first order kinetic model as follows\cite{8}.

<table>
<thead>
<tr>
<th>CI no.</th>
<th>$M_w$ (g/mol)</th>
<th>$\lambda_{max}$ (nm)</th>
<th>M.F</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>49005</td>
<td>318.87</td>
<td>412</td>
<td>C$<em>{17}$H$</em>{19}$ClN$_2$S</td>
<td>[8]</td>
</tr>
</tbody>
</table>

![Figure 1: Photochemical reactor](image-url)
-dC_A/dt = k_{obs} C_A  

\[ \text{(1)} \]

Where \( k_{obs} \) denotes a pseudo-first order kinetic constant, \( C_A \) the concentration of dye solution and \( t \) represents time.

**Effect of initial \( \text{H}_2\text{O}_2 \) concentration**

Experimental studies were carried out with the 500W lamp along with \( \text{H}_2\text{O}_2 \) of different doses. The results show that the dye solution oxidation depends on the initial concentration of \( \text{H}_2\text{O}_2 \). The increase in \( \text{H}_2\text{O}_2 \) concentration from 90mg/L to 450mg/L significantly shortened the time necessary to decolourise the solution. The results are shown in figure 2. It was inferred that 450 mg/L \( \text{H}_2\text{O}_2 \) was the optimum dose in this process. If more than this dose of \( \text{H}_2\text{O}_2 \) is used then less reactive hydroperoxy radicals are produced (reaction 2) and moreover \( \text{OH}^- \) will readily dimerise to \( \text{H}_2\text{O}_2 \) according to reaction (3). These hydroperoxy radicals are less reactive and do not appear to contribute to the oxidation process. It is also reported that these hydroperoxy radicals undergo a chain termination reaction (reaction 4) and in aqueous solution, \( \text{H}_2\text{O}_2 \) dissociates to form the \( \text{HO}_2^- \) anion and \( \text{O}_2 \) in a chain reaction.

\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  

\[ \text{(2)} \]

\[ \text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O}_2 \]  

\[ \text{(3)} \]

\[ \text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  

\[ \text{(4)} \]

\[ \text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{OH} + \text{H}_2\text{O} \]  

\[ \text{(5)} \]

\[ \text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{OH}^- + \text{H}_2\text{O} \]  

\[ \text{(6)} \]

The existence of an optimum dose of \( \text{H}_2\text{O}_2 \) has been described by several investigators earlier while working on photo-oxidation of other organic compounds. Galbraith et al.\[16\] pointed out that there is an upper limit to the amount of \( \text{H}_2\text{O}_2 \) that can be added above which peroxide scavenges the hydroxyl radicals. Shu et al.\[17\] investigated the decolourisation of C. I. acid red 1 and C. I. Acid Yellow 23 by the UV/\( \text{H}_2\text{O}_2 \) process. They found an optimum dose of 9.8 mmol dm\(^{-3}\) \( \text{H}_2\text{O}_2 \) for a \( 2.35 \times 10^{-6} \) of acid red aqueous solution. Similar observations on optimal dose of \( \text{H}_2\text{O}_2 \) have been reported by various research groups\[18-22\].

**Effect of UV light power**

Experiments were carried out under various UV input powers, i.e. 300, 400 and 500W, respectively. The quantity of \( \text{H}_2\text{O}_2 \) added in each experiment was 450mg/L and 20mg/L of initial dye concentration. It was observed that with increasing UV power the rate of decolourisation also increased. Theoretically, the higher decolourisation rate form by the higher UV powers owing to the faster formation of free radical formation. As shown in figure 3, the decolourisation efficiency was 98.1, 93.7, and 89.4% at 30min of reaction time for UV power at 300, 400 and 500W, respectively.
In our study, the dye concentrations were chosen in the range of typical concentration in textile wastewater. The decolourisation of C.I. basic yellow 1 by UV/H$_2$O$_2$ process is shown in figure 4 for different initial dye concentration within 20.0-80.0mg/L, while 450mg/L of the H$_2$O$_2$ concentration and 500W of UV power. The decrease of the decolourisation with the increase of the initial dye concentration has been observed. From the figure, the lower concentration of dye solution accomplished the better decolourisation that almost 98.1% and 86.5% of decolourisation was observed by 20 and 40mg/L concentration of dye solution at 20min. Reversely, 66.3% and 52.4% of decolourisation was observed by 60 and 80mg/L concentration of dye solution at 80 min.

Effect of pH

Since the dyes to be removed can be at different pHs in coloured effluents, we have studied the effect of pH on the rate of decolourisation reaction in the pH range between 1 to 11. Comparative irradiation experiments were performed following the evolution of the absorbency with time. The dye solution was adjusted to the desired pH by addition of HCl or NaOH. The different concentrations of acid or base have been chosen in order to add the minimum quantity of these species to avoid the volume change of the reaction mixture. The decolourisations of dye solution as a function of the pH are shown in figure 5. The decolourisation rate increases from pH 1 to 3 and then remains almost constant up to pH 5. After this value, a remarkable decrease was observed.

These observations at different pH can be explained by taking into account the following parameters. (1) In the acidic pHs concomitant with acidification of the wastewater by HCl, increasing amounts of conjugated base were added to the wastewater. The anion Cl$^-$ is able to react with hydroxyl radicals leading to inorganic radical ions (reaction 7).

$$\text{Cl}^- + \cdot\text{OH} \rightarrow \text{ClO}^- + \cdot\text{H} \quad k=4.3\times10^9 \text{ mol}^{-1} \text{s}^{-1} \quad [23]$$

(2) At alkaline pH, the conjugate base of H$_2$O$_2$ increases (reaction 8).

$$\text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ \quad \text{pK}_a=11.6 \quad (8)$$

HO$_2^-$ has a higher cross-section (240mol cm$^{-1}$) at 254nm than H$_2$O$_2$ (18.6mol cm$^{-1}$), which favors the absorption of light by the reactive and should normally increase the *OH production (reaction 9)$^{[25]}$.

$$\text{HO}_2^- + \text{H}^+ + \text{hv} \rightarrow 2 \cdot\text{OH} \quad (9)$$

In alkaline medium, H$_2$O$_2$ undergoes decomposition leading to dioxygen and water, rather than producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of *OH is lower than expected.

$$\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \cdot\text{OH} \quad (10)$$

Furthermore, the deactivation of *OH is more important when the pH of the wastewater is high. The reaction of *OH with HO$_2^-$ is approximately 100 times faster.

$$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \cdot\text{OH} \quad k=7.5\times10^9 \text{ mol}^{-1} \text{s}^{-1} \quad (11)$$

$$\cdot\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O} + \cdot\text{OH}^* k=2.7\times10^9 \text{ mol}^{-1} \text{s}^{-1} \quad (12)$$

The reactivity of O$_2^*$ and HO$_2^*$ with the organic pollutants is very low.$^{[26]}$

(3) The self-decomposition rate of hydrogen peroxide is strongly dependent on pH. In practice, H$_2$O$_2$ is supplied in slightly acid condition (pH=5) because of its high self-decomposition rate at high pH. The first order reaction rate constants of this self-decomposition were determined to be $2.29\times10^{-2}$ and $7.40\times10^{-2}\text{min}^{-1}$ at pH
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=7 and 10.5 respectively[27].

\[2 \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \] (13)

In most cases, hydroxyl radicals react with dye through hydrogen abstraction mechanism (reaction 14)[7].

\[•\text{OH} + \text{RH} \rightarrow •\text{R} + \text{H}_2\text{O} \] (14)

In the deprotonated form, dye exhibits low reactivity due to the absence of a labile hydrogen atom. Indeed, in the molecule of C.I. basic yellow 1, the nitrogen atom carries an H atom and this labile H atom makes the molecule of C.I. basic yellow 1 especially vulnerable to attack •OH radicals[24]. The decrease of the colour removal rate at high basic solution (pH higher than 10) is probably due to the dissociation of the N-H bonds.

On the whole, our results demonstrate that the maximum decolourisation (98.1%) was occurred at pH 3.

Kinetics of decolourisation

The kinetics of disappearance of C.I. basic yellow 1 is represented in figure 6. First-order kinetic model was utilized as follows:

\[\ln \frac{C_0}{C} = kt \] (15)

where \(C_0\), \(C\), \(t\) and \(k\) are the initial dye concentration, dye concentration in \(t\), decolorization time (min) and the global reaction apparent rate constant(min\(^{-1}\)), respectively.

The linear fit between the \(\ln \frac{C_0}{C}\) and irradiation time under pH 3 and different concentrations of initial dye solution can be approximated as pseudo-first order kinetics.

CONCLUSIONS

The experimental results showed that the UV/H\(_2\)O\(_2\) process was a feasible pre-treatment method for decolourisation of C.I. basic yellow 1 under the suitable operating conditions. The decolourisation of C.I. basic yellow 1 was determined at different operational conditions such as UV dosage, hydrogen peroxide dosage, initial dye concentration and pH. The 98.1% of dye decolourisation can be achieved within 20 min, while UV power of 500 W, H\(_2\)O\(_2\) concentration of 450 mg/L, 20 mg/L of initial dye concentration and pH 3.0. The decolourisation rate followed pseudo-first order kinetics with respect to the dye concentration.

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REFERENCES