Advanced oxidation processes for decolorization of aqueous solution containing Acid Red G azo dye

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Received 5 February 2004; accepted 26 May 2004

Abstract: Some investigations concerning the decolorization of Acid Red G azo dye by photooxidation with hydrogen peroxide were performed. The influences of pH, oxidant concentration, and the presence of Fe$^{2+}$ or other metal ions (Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Mn$^{2+}$) as potential catalysts, were investigated. The best results were obtained in the presence of ferrous ions in acid and neutral media. The other ions are not as effective as Fe$^{2+}$ for dye decolorization. Co$^{2+}$ and Cu$^{2+}$ ions have a catalytic action, at low concentration, within a wide range of pH. Ni$^{2+}$ and Mn$^{2+}$ ions have no catalytic effect in photooxidation with hydrogen peroxide at acid pH values, but show a weak action in alkaline media.

Keywords: Acid Red G azo dye, hydrogen peroxide, UV radiation, decolorization, metal ions

1 Introduction

Significant quantities of wastewaters with various pollutants are generated by industry: organic substances, suspended solids, metal ions etc.

Among organic substances ever-present in wastewaters from the textile industry, dyes bring additional problems when they encounter natural waters: they can overload self-purification mechanisms, they can reduce or prevent photosynthetic processes, and they can have toxic or carcinogenic effects on the aquatic environment.

To solve environmental problems, wastewater treatment is stringently necessary. Besides decreasing wastewater volume, dye removal and decolorization in receiver basins before discharge is an indispensable aspect of the treatment.

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The best known and most commonly applied treatment is destruction of the dye by oxidation. In recent years, there has been considerable interest in the use of advanced oxidation processes (AOP), particularly those based on the UV-H$_2$O$_2$ system [5, 8, 21] that offer an increased efficiency in degrading various compounds. Moreover, H$_2$O$_2$ may be considered a friendly oxidant since it decomposes to water and oxygen. Some difficulties that may arise as a result of the presence of ozone in the water [26] can be avoided by oxidation with hydrogen peroxide activated by UV light.

In the presence of UV radiation, hydrogen peroxide photodissociates to generate hydroxyl radicals, which are strong oxidants (oxidation potential of 2.8 V). Hydroxyl radical oxidations are not specific. A wide variety of target compounds react at high rates [25].

Many studies have shown that unreactive organic compounds like dyes can be oxidized more quickly in these conditions if ferrous ions (Fenton reagent) are added [2, 3, 14, 22, 24]. A few studies have also focused on the intervention of some other metal ions in the degradation of various azo dyes, but only in heterogeneous photocatalysis systems [11, 13].

The purpose of this work was to study the decolorization of aqueous solutions containing Acid Red G azo dye by AOP, using hydrogen peroxide in the presence of Fe$^{2+}$ or other metal ions (Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Mn$^{2+}$) as catalyst. The influences of operational conditions, such as the pH, the oxidant concentration, and catalyst presence and concentration were studied.

2 Experimental

2.1 Materials and methods

The azo dye, Acid Red G, was obtained from COLOROM Codlea Company (Romania) and used without further purification. Aqueous solutions of this dye (0.05 mg/mL), used as a synthetic wastewater sample, were prepared by dilution of a dye stock solution (0.5 mg/mL). Analytical grade 30 % hydrogen peroxide was used without additional purification. The pH of the aqueous solution was adjusted with HNO$_3$ or NaOH 2M. For each metal studied, a stock solution of sulfate with a cation concentration of 0.25 mg M$^{2+}$/mL was used as catalyst. All reagents used were of analytical grade.

2.2 The reactor and irradiation experiments

A laboratory annular photoreactor with an useful capacity of over 300 cm$^3$ was used. It included quartz cooling jacket for keeping the temperature constant (Fig. 1). The photoreactor uses a medium pressure mercury vapor lamp (length 12 cm, diameter 20 mm), placed centrally. The lamp emits radiation over a large wavelength range (180-400 nm). The irradiation experiments were performed using 250 cm$^3$ of dye solution (C = 0.05 mg/mL) treated with hydrogen peroxide, with and without catalyst, in suitable conditions. Solutions to be photolyzed were freshly prepared before irradiation, and
samples were periodically withdrawn from the photoreactor (at 5 minute intervals) to determine the extent of decolorization. The photochemical experiments were carried out at room temperature (20 ± 3 °C).

Reagents

Dye solution

Fig. 1 Schematic drawing of the photoreactor: 1, UV lamp; 2, quartz cooling jacket; 3, reaction mixture.

The progress of the decolorization process was followed by measuring the optical density decrease at \( \lambda = 456 \) nm. The color intensity at this wavelength may be converted into Hazen units [6, 17]. The decolorization degree (DD) as an expression of the extent of color removal at 456 nm was calculated with the relationship:

\[
DD(\%) = \frac{A_i - A_t}{A_i} \cdot 100
\]  

where \( A_i \) is the initial absorbance of the dye sample and \( A_t \) the absorbance at time \( t \).

2.3 Analytical methods

The UV-VIS absorption spectra of the Acid Red G azo dye, at different pH values, were recorded by a SPECORD M42 spectrophotometer.

The absorbance of samples taken from the photoreactor was determined with a DRELL 2000 spectrophotometer, HACH Company.

The pH measurements were accomplished by means of a LPH 430T (Tacussel électronique) pH-meter.

3 Results and discussion

The chemical structure of Acid Red G dye (MW=698) is shown in Fig. 2.
Fig. 2 Chemical structure of Acid Red G azo dye.

3.1 The influence of hydrogen peroxide concentration

Kinetic studies of photooxidation were carried out for different hydrogen peroxide concentrations. Samples of 250 mL of azo dye solution treated with different volumes of hydrogen peroxide were irradiated inside the photoreactor.

The results are presented in Fig. 3. As was expected, the Acid Red G decolorization rate increased with increasing hydrogen peroxide concentration.

This can be explained by the photolysis of $\text{H}_2\text{O}_2$ by UV light, which generates $\text{HO}^*$

$$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO}^*$$

with very much higher oxidative capacity than any other available oxidants [12]. The combination of $\text{H}_2\text{O}_2$ and UV light is more effective in the decolorization of Acid Red G azo dyes than UV alone because the dyes are attacked both by UV photons and by hydroxyl radicals [21].

Nevertheless, a high concentration is neither useful nor a disadvantage. When hydrogen peroxide is in excess, and with the associated high $\text{HO}^*$ concentrations, competitive reactions take place, producing an inhibitory effect on the degradation [4, 7]:

Fig. 3 Effect of $\text{H}_2\text{O}_2$ concentration on the decolorization of Acid Red G azo dye. Initial conditions: $C_{\text{dye}}=50 \text{ mg/L}$, $\text{pH}=5.68$, $t=20^\circ\text{C}$. 
\[ HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \]  
\[ HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2 \]  
\[ 2HO_2^\bullet \rightarrow H_2O_2 + O_2 \]  
\[ HO_2 + HO^\bullet \rightarrow H_2O + O_2 \]  

The question of an optimum dose of hydrogen peroxide to achieve a high decolorization degree after 10 minutes of irradiation was considered. Our results indicate a concentration of 600 mg/L (17.318 mmole/L) and a hydrogen peroxide to dye mole ratio close to 246:1.

3.2 Effect of the initial pH

To establish the influence of pH on the decolorization of Acid Red Gazo dye some experiments, at different initial pH values, using the optimum dose of hydrogen peroxide were carried out. The pH was regulated by adding H_2SO_4 or NaOH to the aqueous solution of the dye. The results are presented in Fig. 4 and Table 1.

As can be seen in Fig.4, little difference in color removal is evident at different pH values. In all cases, the reaction rates are satisfactory. However, the acid medium appears slightly favored. After 10 minutes of irradiation, the calculated decolorization degree was 89.16% in the acid medium, 81.03% in the neutral medium and 82.48% in the alkaline medium. This observation is in good agreement with the results of Azbar et al. [3], but in disagreement with those of other researchers [5, 7]. In our opinion these differences could result both from the chemical structure of dyes and the nature of the acid used. Thus, if an acid medium was obtained by adding HCl, a decrease in decolorization rate occurs, due to the fact that Cl\(^-\) ions are HO\(^\bullet\) radical scavengers [18]. As the chloride concentration increases, hydroxyl radical is scavenged more effectively, resulting in a lower steady state radical concentration [19]. About the influence of NO_3\(^-\) ions in the homogenous photocatalyse we have no information.

During the photooxidation, a steady change in pH values can be noticed, in all experiments and for all the hydrogen peroxide concentrations (Table 1). During the first part of the photooxidation process, in alkaline and neutral medium, a decrease in pH is observed which can be explained by the formation of acidic species [1].

In an alkaline medium, the following reaction is favored:

\[ H_2O_2 \rightarrow HO^- + H^+ \]  

The conjugate base anion of hydrogen peroxide generates HO_2^\bullet and then HO^\bullet radicals. Because HO_2^\bullet radicals are less reactive than HO^\bullet, increasing HO_2^\bullet does not significantly contribute to the dye destruction [10]. In the latter part of the process the pH values slowly increase. Because this pH increase occurs at the end of reaction, when the destruction of dye is almost complete, it might be attributed to secondary (termination) reactions of hydrogen peroxide, which generate hydroxyl anion [9, 27]:

\[ H_2O_2 + O_2^- \rightarrow HO^\bullet + HO^- + O_2 \]
The release of CO$_2$ into the gas phase, and the formation of alkaline products such as NH$_3$, may also be considered.

In an acid medium the pH variations are irregular. The strong acidity of the reaction mixture probably minimizes the variations caused by acid species resulting from photodegradation.

| Time, min | Acid medium | Neutral medium | Alkaline medium |
|-----------|-------------|----------------|-----------------|
| 0         | 2.552       | 6.313          | 11.003          |
| 5         | 2.603       | 4.784          | 10.914          |
| 10        | 2.578       | 4.285          | 10.893          |
| 15        | 2.531       | 4.169          | 10.892          |
| 20        | 2.552       | 4.202          | 10.870          |
| 25        | 2.539       | 4.231          | 10.886          |
| 30        | 2.559       | 4.380          | 10.924          |

**Table 1** pH variation in photooxidation process.

### 3.3 Effect of ferrous ions

Because hydrogen peroxide alone cannot achieve decolorization of the dye within reasonable time periods, it is used in association with UV radiation or Fe$^{2+}$ ions (Fenton reagent). Under UV radiation, the photolysis of hydrogen peroxide occurs and, consequently, very reactive hydroxyl radicals are rapidly generated. The addition of ferrous ions has a similar effect. By using hydrogen peroxide, UV radiation and ferrous ions at
the same time, the rate of dye decolorization can be further increased.

In Fig. 5 the progress of dye decolorization is compared for the following systems: \( \text{H}_2\text{O}_2/\text{UV}/\text{Fe}^{2+} \); \( \text{H}_2\text{O}_2/\text{UV} \) and \( \text{UV}/\text{Fe}^{2+} \).

![Graph showing the decolorization variation in different AOPs](image)

**Fig. 5** The decolorization variation in different AOPs. Initial conditions: \( C_{\text{dye}}=50 \text{ mg/L} \), \( \text{pH}=6.12 \), \( [\text{H}_2\text{O}_2]= 17.318 \text{ mM} \), \( [\text{Fe}^{2+}]= 7.03\times10^{-2} \text{ mM} \).

In the presence of ferrous ions and the absence of hydrogen peroxide, the decolorization process is very slow. This can be explained by the low concentration of hydroxyl radicals formed from the following reactions [16, 24]:

\[
\begin{align*}
\text{H}_2\text{O} + h\nu & \rightarrow \text{H}^\bullet + \text{HO}^\bullet \\
\text{Fe}^{2+} + \text{HO}^\bullet & \rightarrow \text{Fe}^{3+} + \text{HO}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O} + h\nu & \rightarrow \text{Fe}^{2+} + \text{HO}^\bullet + \text{H}^+
\end{align*}
\]

(9) \hspace{2cm} (10) \hspace{2cm} (11)

In the presence of hydrogen peroxide the reaction is much faster, with the higher hydroxyl radical concentrations generated by photolysis; the decolorization is appreciable and almost instantaneous when ferrous ions are added.

At fixed pH and initial concentrations of dye and \( \text{H}_2\text{O}_2 \), the decolorization rate changes with the amount of ferrous ion added into solution. Fig. 6 shows how the reactions progress for increasing initial ferrous concentrations. After 15 minutes of photooxidation the decolorization degree was greater than 99 % in the presence of ferrous ions.

The catalytic effect of ferrous ions is accounted for by their contribution to the generation of supplementary hydroxyl radicals, additional to those formed in the photocleavage of hydrogen peroxide by UV radiation. The following reactions can be considered [28]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^\bullet \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^\bullet
\end{align*}
\]

(12) \hspace{2cm} (13)
This process, known as photo-Fenton, is favored by an acidic medium [15, 20]. This reaction scheme suggests that the decolorization rate will increase with increasing ferrous ion concentration because more radicals are formed. Nevertheless, dye decolorization can be improved by increasing the initial concentration of Fe$^{2+}$ only to a certain limit, beyond which further addition becomes useless.

3.4 The influence of other metal ions as catalysts

Dissolved inorganic ions are frequently present in dye-containing textile wastewaters [23].

To investigate any catalytic effect of other metal ions on dye decolorization by photo-oxidation with hydrogen peroxide, experiments using aqueous solutions of Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Mn$^{2+}$ were done. The same operational conditions as for Fe$^{2+}$ ions were maintained.

The experimental results for Co$^{2+}$ are presented in Fig. 7, Fig. 8 and Fig. 9 (for acidic, neutral and alkaline media).

The Co$^{2+}$ ions have a good catalytic activity on the dye decolorization at all pH values and concentrations used. The decolorization degree decreases for concentration values higher than 8.48·10$^{-3}$ mmol/L.

The effect of Cu$^{2+}$ ions on Acid Red G azo dye decolorization is presented in Fig. 10, Fig. 11 and Fig. 12 (for acidic, neutral and alkaline medium).
Fig. 7 Effect of Co$^{2+}$ ions on AOP in acidic medium. Initial conditions: $C_{dye}=50$ mg/L, $[H_2O_2]=17.318$ mM.

Fig. 8 Effect of Co$^{2+}$ ions on AOP in neutral medium. Initial conditions: $C_{dye}=50$ mg/L, $[H_2O_2]=17.318$ mM.

Like Co$^{2+}$, copper ions have catalytic activity at all pH values and concentrations used. The decolorization degree decreases with increasing concentration; the best results have been obtained for concentrations lower than $3.39 \times 10^{-3}$ mmol/L.

In Fig. 13, Fig. 14 and Fig. 15 the influence of Ni$^{2+}$ ions on dye decolorization is depicted.

Nickel ions are not catalysts for the photooxidation process in acidic medium. At
low concentrations ($<1.7\cdot10^{-2}$ mmol/L) in neutral medium and at high concentrations ($>1.7\cdot10^{-2}$ mmol/L) in alkaline conditions they have a catalytic on dye decolorization.

Experimental results regarding the influence of Mn$^{2+}$ ions are presented in Fig. 16, Fig. 17 and Fig. 18.

It can be observed that Mn$^{2+}$ ions exhibit a weak catalytic activity only in alkaline medium at concentrations lower than $3.64\cdot10^{-2}$ mmol/L and that decolorization degree decreases with increasing concentration.
Fig. 11 Effect of Cu\textsuperscript{2+} ions on AOP in neutral medium. Initial conditions: $C_{\text{dye}}=50\text{ mg/L}$, $[\text{H}_2\text{O}_2]=17.318\text{ mM}$.

Fig. 12 Effect of Cu\textsuperscript{2+} ions on AOP in alkaline medium. Initial conditions: $C_{\text{dye}}=50\text{ mg/L}$, $[\text{H}_2\text{O}_2]=17.318\text{ mM}$.

4 Conclusions

AOP using hydrogen peroxide and UV radiation provides a rapid, easy and efficient procedure to decrease the sample color and/or dye concentration under a range of different operational conditions. The pH value has no major influence on the rate of dye decolorization by AOP ($\text{H}_2\text{O}_2$/UV) but it seems that acidic media are slightly favored. For
many conditions, a decrease in pH occurs during the oxidative process. The addition of ferrous ions considerably increases reaction rate, and decolorization time is shorter for high ferrous ion concentrations. Photooxidation with H₂O₂/UV/Fe²⁺ requires an acid pH to prevent Fe³⁺ precipitation.

The influences of other metal ions such as Co²⁺, Cu²⁺, Ni²⁺, and Mn²⁺ were studied.
Their effect on dye decolorization by photooxidation with H$_2$O$_2$ is less than that of Fe$^{2+}$ ions. For all pH values, Co$^{2+}$ and Cu$^{2+}$ ions have a catalytic action at low concentrations. Ni$^{2+}$ and Mn$^{2+}$ ions do not have a catalytic effect on dye decolorization, especially at acidic and neutral pH values.
Fig. 17 Effect of Mn$^{2+}$ ions on AOP in neutral medium. Initial conditions: $C_{dye}=50$ mg/L, $[\text{H}_2\text{O}_2]=17.318$ mM.

Fig. 18 Effect of Mn$^{2+}$ ions on AOP in alkaline medium. Initial conditions: $C_{dye}=50$ mg/L, $[\text{H}_2\text{O}_2]=17.318$ mM.

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