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# Kinetics and optimization of photolytic decoloration of carmine by UV/$H_2O_2$

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## Abstract

Carmine (C.I. name is Natural Red 4), a naturally occurring important dye, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically. The apparent rate of decoloration was calculated from the observed absorption data and was found to be of first order. A systematic study of the effect of dye concentration as well as $H_2O_2$ concentration on the kinetics of dye decoloration was carried out. Additionally, the effect of various additives on the decoloration of this dye was also investigated. Most of the anions tested had an inhibitory effect on the decoloration of the dye, with the most pronounced effect seen with sulfite ion as compared to carbonate, sulphate, nitrate and chloride ions. Examination of the effect of pH showed that the dye could be efficiently decolorized in a basic media. A plausible explanation involving the probable radical initiated mechanism was given to explain the dye decoloration. Lastly, we used HPLC analysis to show that the decoloration of carmine observed during the UV/$H_2O_2$ photolysis treatment was in fact due to the degradation of the dye.

*Keywords:* Carmine; Photolytic decoloration; Hydrogen peroxide

## 1. Introduction

Dye degradation/decoloration has drawn considerable attention by many workers in the last few years due to the fact that dye related pollution causes many environmental problems [1–3]. Moreover these dyes are toxic in nature due to the fact that they all have aromatic groups[4]. In fact many of these dyes have been shown to have hazardous properties [5]. On passage to water bodies at large, these chemicals may pose a health concern to all marine life as well as human life at the end of the food chain. Recently, many different techniques have been suggested in the literature to address the situation by causing the complete decoloration of dyes in industrial effluents prior to their entering the water bodies. These suggestions include photo-catalytic, photolytic and bio-decoloration of various dye solutions [6–9]. Advanced oxidation process based on UV/$H_2O_2$ photolytic decoloration is not only simple and homogeneous, but has also shown promising results in degrading many other organic compounds [10–12]. 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 series of reactions in which the organic molecule is finally destroyed or converted into a simple harmless compound. Carmine is a representative example of an organic dye which belongs to the ‘‘natural’’ class of dyes, and in food coloring, cosmetics, and paints. Since dyes are suspected to be carcinogenic in nature, any presence of them in waste water would have detrimental effects on marine and human life. In this paper an attempt is made to look at the decoloration of this dye in aqueous solution in the presence of $H_2O_2$ and UV light. The data are interpreted in terms of kinetic parameters. Furthermore, the effect of solution pH and the presence of various

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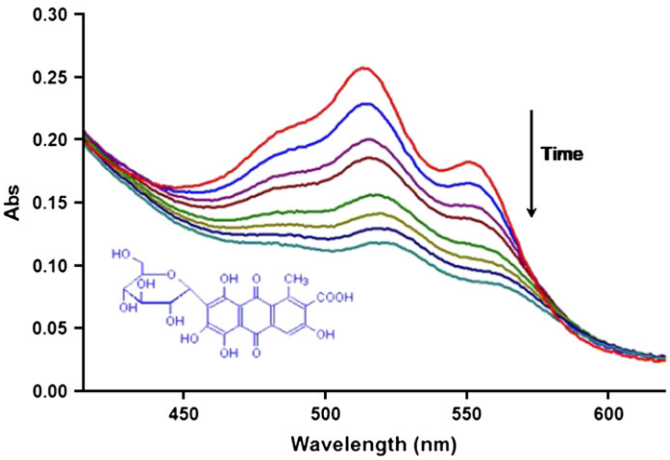

Fig. 1. Chemical structure of carmine and visible spectra showing photolytic degradation of carmine using UV/$H_2O_2$. Scans were taken at 0, 3, 5, 10, 15, 20, 25, and 30 min after photolytic treatment.

additives in the form of anions on the decoloration of the dye solution were also investigated.

## 2. Experimental

Carmine (C.I. name Natural Red 4) was obtained from Fluka and was used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and was diluted in water right before use. UV–vis studies were done on a CARY 50 UV/VIS spectrophotometer, using a 1 cm cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm.

### 2.1. Preparation of samples and decoloration studies

Carmine stock solution of $1 \times 10^{-3}$ M was prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of $H_2O_2$ and the mixture was irradiated with UV light. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of apparent decoloration rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

For studying the effect of pH on dye decoloration, the pH of the dye solution was altered by adding incremental amounts of either dilute HCl or diluted NaOH. For experiments examining the effects of different ions on the decoloration of carmine, a final concentration of 0.5 mg/ml of various salts was added to the dye solution before the addition of $H_2O_2$. None of the salts used had any effect on the dye spectra in the absence of UV light. The solution was then subjected to UV light and change in absorbance value was noted to calculate the apparent decoloration rate constant.

### 2.2. HPLC analysis of the discoloration/degradation samples

For HPLC analysis of the dye decoloration/degradation, 50 ml of dye solutions were taken either at time zero (right after addition of $H_2O_2$ and no UV irradiation) or at 30 min of UV irradiation after addition of $H_2O_2$, and the organic component of the mixture was extracted using chloroform. The organic layer was extracted again for a second time with chloroform, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% methanol and then used for HPLC analysis. The samples were run on $C_8$-Eclipse column (Agilent) using a 0–100% methanol (water as the base mobile phase) gradient over 30 min, at 1 ml/min, and analyzed by measuring the absorbance at 280 nm.

## 3. Results and discussion

In the present work, the kinetics of $H_2O_2$ assisted photochemical oxidation of carmine was investigated. The structure of the dye as well as the UV–vis spectra of the dye is given in Fig. 1. The decoloration studies were attempted by observing changes in the absorbance value of the dye at 500 nm. Initially, experiments were carried out with either UV light or $H_2O_2$. The results showed that mere UV light or $H_2O_2$ alone did not result in any significant decoloration of this dye. However, when the dye solutions of various concentrations were mixed with $H_2O_2$ prepared in aqueous media and subjected to UV

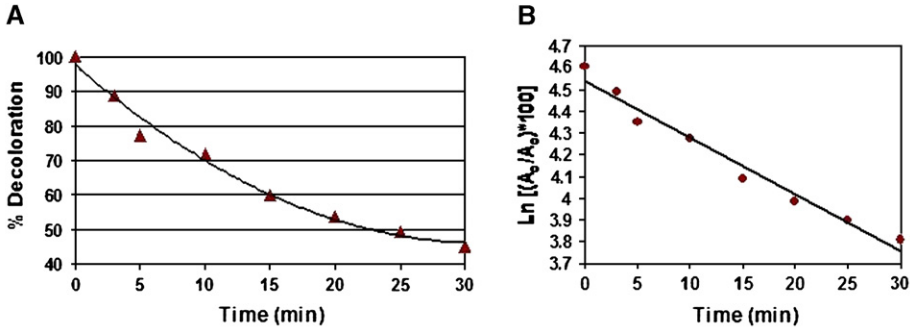

Fig. 2. (A) Photolytic degradation of carmine using UV/$H_2O_2$ [carmine] = 80 μM and [$H_2O_2$] = 3.3 mM. Scans were taken at 0, 3, 5, 10, 15, 20, 25, and 30 min after photolytic treatment. (B) First order curve fitting of carmine decoloration data.

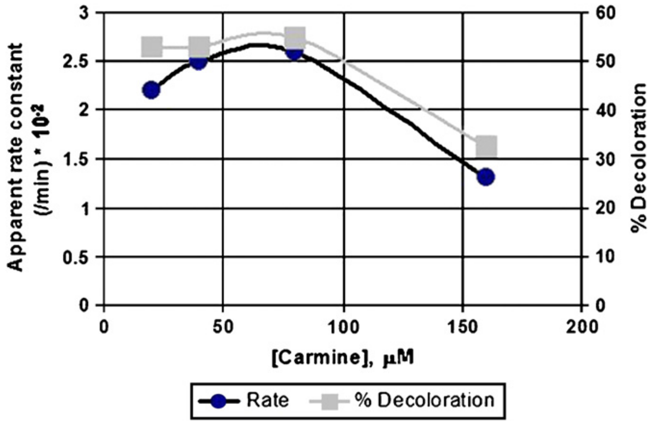

Fig. 3. Effect of carmine concentration on the % decoloration and apparent rate constant of the decoloration reaction. Hydrogen peroxide concentration was kept constant at 3.3 mM.

light, the dye started degrading immediately in the presence of $H_2O_2$ and the UV radiation. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows

$$\%\text{decrease in absorption} = [\{A(\text{initial}) - A(\text{final})\}/A(\text{initial})] \times 100$$

The change in absorption value which is a measure of its decoloration, as a function of irradiation time is depicted in Fig. 2. The kinetics of dye decoloration with respect to its change in absorption values fitted well into a first order rate equation.

$$\mathrm{Ln}(A_0) - \mathrm{Ln}(A_t) = \boldsymbol{k}t \tag{1}$$

where $\boldsymbol{k}$ is the apparent rate constant, $t$ is the irradiation time and $A_0$ and $A_t$ are the initial and the final absorbance values of the dye solution, respectively. The decoloration of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light [13]

$$H_2O_2 \rightarrow 2^{\bullet}OH \tag{2}$$

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decoloration of the original solution

$$^{\bullet}OH + \text{dye} \rightarrow {}^{\bullet}P \tag{3}$$

Table 1
Effect of $H_2O_2$ concentration on carmine decoloration (carmine = 80 μM)

| $[H_2O_2]$ mM | $k$ (min$^{-1}$) × $10^{-2}$ | % Decoloration |
|---|---|---|
| 0.83 | 1.42 | 34.02 |
| 1.7 | 1.91 | 43.76 |
| 3.3 | 2.6 | 55.02 |
| 66.4 | 3.03 | 59.18 |

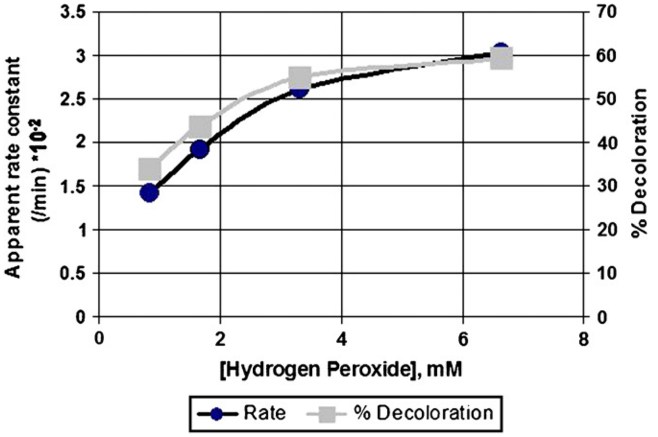

Fig. 4. Effect of hydrogen peroxide concentration on the % decoloration and apparent rate constant of the decoloration reaction. Carmine concentration was kept constant at 80 μM.

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the decoloration reaction of the dye molecule [14].

To optimize the decoloration kinetics of the dye, we carried out a systematic study by varying the concentration of both $H_2O_2$ and carmine. Fig. 3 and Table 1 show the effect of varying carmine concentration on the kinetics of dye decoloration. Unexpectedly we found that the apparent rate of carmine decoloration appears to be the same between 20 and 80 μM concentrations of carmine. Only at carmine concentration of 160 μM a lower apparent rate of carmine decoloration and a slower apparent rate of decoloration were observed. Similarly, Fig. 4 and Table 2 show the apparent rate constants and % decoloration of carmine at different $H_2O_2$ concentrations. It can be seen that the apparent rate of dye decoloration was directly proportional to $H_2O_2$ concentration; however, at high concentrations of $H_2O_2$ the increase in dye decoloration was not linear. As expected, at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of $H_2O_2$ to produce $HO_2^{\bullet}$ radicals [15].

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \tag{4}$$

For subsequent decoloration studies, the concentration of $H_2O_2$ was kept at an optimum level of 33.2 mM, and the carmine was maintained at 80 μM.

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the

Table 2
Effect of carmine concentration on its photolytic decoloration ($H_2O_2$ = 3.3 mM)

| [Carmine] μM | $k$ (min$^{-1}$) × $10^{-2}$ | % Decoloration |
|---|---|---|
| 20 | 2.2 | 53 |
| 40 | 2.5 | 53 |
| 80 | 2.6 | 55 |
| 160 | 1.3 | 32.6 |

Table 3
Effect of pH on carmine decoloration (carmine = 80 μM; $H_2O_2$ = 3.3 mM)

| pH value | $k$ ($\text{min}^{-1}$) × $10^{-2}$ | % Decoloration (30 min) |
|---|---|---|
| 2 | 10.1 | 57.17 |
| 6 | 2.6 | 55.02 |
| 10 | 4.88 | 74.48 |

dye solution in the presence of UV/$H_2O_2$. Table 3 and Fig. 5 show the % change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more at alkaline pH and less at acidic pH. This enhancement in dye decoloration in basic conditions is most likely due to the fact that at alkaline pH, peroxide anions ($HO_2$) are produced in solution by UV radiation, which in turn can generate more OH radicals [16]

$$HO_2^- + h\nu \rightarrow OH^{\bullet} + O^{\bullet -} \tag{5}$$

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye decoloration [17]. Therefore, we tested the effects of various anions on the photolytic decoloration of carmine (Table 4). The kinetics of dye decoloration in the presence of these ions is also shown in Fig. 6. It can be seen from the table and the figure that carbonate and chloride ions did not have any effect on dye degradation. Also surprisingly, nitrate and sulphate ions caused a small but significant increase in the apparent rate of dye decoloration. Most surprising result we observed was the dramatic effect of sulfite anions. Under conditions where more than 50% carmine would normally be degraded, sulfite ions reduced this to only 10%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below [18].

$$^{\bullet}OH + SO_3^2 \rightarrow H_2O + {}^{\bullet}SO_3^- \quad k = 5.1 \times 10^9\ (\text{L mol}^{-1}\ \text{s}^{-1}) \tag{6}$$

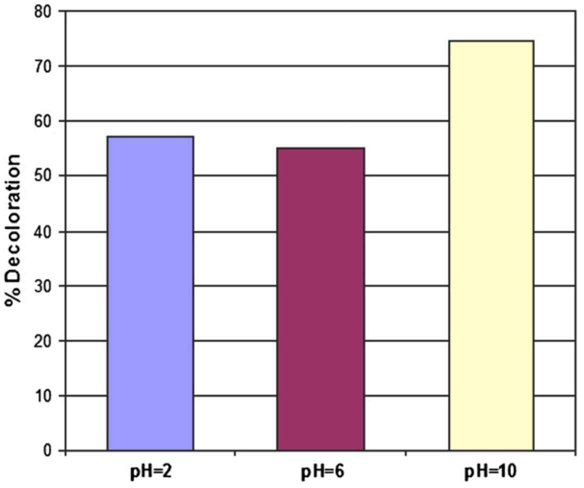

Fig. 5. Effect of pH on the decoloration of carmine. Samples were exposed to UV/$H_2O_2$ for 30 min before measuring the resultant dye concentrations. [Carmine] = 80 μM and [$H_2O_2$] = 3.3 mM.

Table 4
Effect of various ions on carmine decoloration (carmine = 80 μM; $H_2O_2$ = 3.3 mM)

| Ions | $k$ ($\text{min}^{-1}$) × $10^{-2}$ | % Decoloration |
|---|---|---|
| | 2.6 | 55.02 |
| $CO_3^{2-}$ | 4.52 | 55.02 |
| $SO_4^{2-}$ | 3.54 | 65.51 |
| $NO_3^-$ | 3.34 | 62.7 |
| $Cl^-$ | 2.63 | 55.89 |
| $SO_3^{2-}$ | 0.21 | 10.76 |

Lastly in order to confirm that the actual degradation was occurring during the photolytic treatment, samples of dye solution were taken at specific intervals and subjected to HPLC analysis. Fig. 7 shows the HPLC analysis of the dye solution after 30 min of photolytic treatment. As can be seen from this figure, a significant amount of dye was degraded within 30 min and additional peaks (presumably by-products) were produced. Hence, the loss of color (decoloration) we were observing was most likely due to actual dye degradation.

## 4. Conclusion

Photolytic oxidation of carmine dye was carried out in the presence of hydrogen peroxide. The decoloration of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well into the decoloration scheme of the dye. The decoloration of the dye was less in the presence of sulfite ions. Thus for effective decoloration of the dye, this ion should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution. Lastly, HPLC analysis of the reaction mixture showed that the decoloration observed during the photolytic oxidation process was in fact due to carmine degradation.

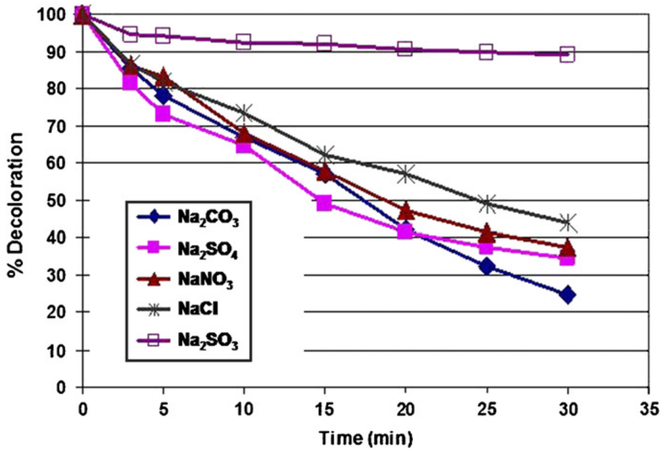

Fig. 6. Effect of various ions on the decoloration of carmine. [Carmine] = 80 μM, [$H_2O_2$] = 3.3 mM, and [ions] = 0.5 mg/ml.

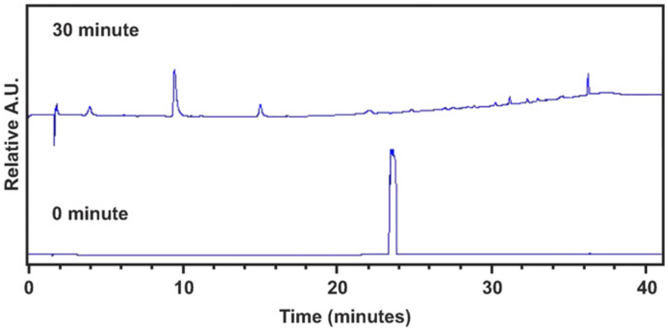

Fig. 7. HPLC analysis of the decoloration/degradation of carmine by the UV/$H_2O_2$ photolytic process. Samples were taken either at 0 min (no UV or $H_2O_2$) or after 30 min of UV/$H_2O_2$ exposure. Samples were prepared and analyzed as described in Section 2.

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