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Comparative efficiencies of the degradation of Crystal Violet using UV/hydrogen peroxide and Fenton's reagent

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Abstract

The kinetics of the photo-decoloration of Crystal Violet (CV) imparted by UV/H_2O_2 process and also by Fenton's reagent were investigated. Negligible effects were observed in the presence of either UV light or H_2O_2 alone. As expected, the Fenton-mediated decoloration occurred much faster than the photolytic process. The effects of dye concentration, hydrogen peroxide concentration, pH and the presence of various ions on the decoloration rate were also studied. The extent of decoloration of the dye was found to be independent of pH. The rate of decoloration of the dye that occurred in both the photolytic as well as in the Fenton's methods was found to fit first-order kinetics. A mechanism is suggested for the degradation of the dye. The effect of anions that are normally present in dye effluent on the degradation of the dye was also investigated. Unexpectedly, hydrogen phosphate ions were found to dramatically inhibit the Fenton-mediated decoloration of the dye, whereas they had a minor effect on the photolytic degradation system. The other ions tested had equal minor inhibitory effects on dye degradation by both the methods.

Keywords: Crystal Violet; Decoloration; Photolytic oxidation; UV/H_2O_2; Fenton's reagent

1. Introduction

Many different types of synthetic dyes such as azo, vat, nitro, indigo, etc., are widely used for different purposes in paper and pulp manufacturing, plastics, printing and textile industry [1–3]. The effluent from these industries, when it contains substantial amounts of such dyes, causes not only coloration of water, but also poses a threat to aquatic life [4]; furthermore, their presence in drinking water constitutes a potential human health hazard [5,6]. It is therefore essential either to remove the dyes from water or to treat them in such a way so as to minimize their effects on the environment and also to decolorize the water.

Different approaches have been suggested to remove dyes from aqueous solution including adsorption, biological decoloration, coagulation, advanced oxidation processes (AOP), photo-Fenton reaction, ozone treatment and hypochlorite treatment [7–14]. A very simple approach which can be commonly utilized is the photolytic oxidation of such solutions. In many cases, this method is readily applicable due to the UV content of sunlight. On the other hand, the decoloration of dye using Fenton's reagent has been reported in the literature and has shown promising results [15–17]. In this paper, we wanted to examine the relative efficiencies of two different AOP methods, namely UV/H_2O_2 and Fenton's for the degradation of the triarylmethane dye, Crystal Violet (CV); many of the parameters that affect dye decoloration rate, such as dye concentration, H_2O_2 concentration, and pH were also evaluated. Since many electrolytes are present in dye effluent, the kinetics of dye decoloration in both the presence and absence of various ions were determined.

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2. Experimental

2.1. Reagents

Crystal Violet (Fig. 1) was procured from Fluka and was used as received. Deionized water was used for all dye solutions. Hydrogen peroxide (35% w/w) was obtained from Merck and used at a final concentration of 1.67 mM, unless otherwise stated.

2.2. Preparation of samples and decoloration studies with UV/H_2O_2

Crystal Violet used in all the experiments was at a concentration of 22 μM in water (unless otherwise indicated). UV/vis studies were carried out using a CARY 50 UV/vis spectrophotometer, using a 1-cm quartz cell. All experiments were carried out in a 4-ml quartz cuvette as follows: 3 ml of 22 μM Crystal Violet solution was mixed with 50 μl of 0.1 M H_2O_2, and the mixture was then subjected to UV light (254 nm) produced using an Upland UVGL-58 lamp.

For experiments examining the effects of different ions on the decoloration of Crystal Violet, a final concentration of 0.5 mg/ml of three salts (sodium chloride, sodium sulphate, and sodium hydrogenphosphate) was added to the cuvette before the addition of H_2O_2. None of the electrolytes used had an effect on the pH or on the UV/vis spectra of Crystal Violet in the absence of UV light.

2.3. Preparation of samples and decoloration studies by Fenton's process

All experiments reported were carried out in a 4-ml quartz cuvette as follows: 3 ml of 50 μM Crystal Violet solution was mixed with 30 μl of 0.1 M $FeSO_4$/1 mM H_2SO_4. The Fenton chemistry reaction was initiated by the addition of 15 μl of 1 M H_2O_2 after which, absorbance scans were collected every 6 s, for a total of 2 min. The effects of different ions on the degradation of Crystal Violet were studied via the addition of a final concentration of 0.5 mg/ml of various salts to the cuvette before the addition of H_2O_2; none of the electrolytes had an effect on the Crystal Violet spectra in the absence of H_2O_2.

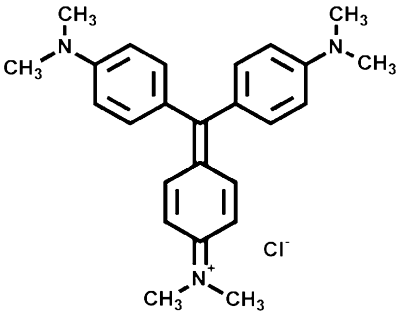

Fig. 1. Structure of Crystal Violet.

2.4. HPLC analysis of the discoloration/degradation samples

For HPLC analysis of the dye decoloration/degradation, 50 ml of dye solutions was taken either at time zero (right after the addition of H_2O_2 and no UV irradiation) or at 30 min of UV irradiation after the 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

Initially, experiments were carried out in the presence of either UV light or H_2O_2 alone; neither of these treatments had an effect on the absorption maxima of the dye solution and imparted no decoloration. However, decoloration of the dye occurred when it was subjected to UV light in the presence of H_2O_2, presumably due to the production of hydroxyl radicals, as shown below:

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \tag{1}$$

The hydroxyl radicals can in turn react with the dyes and lead to dye degradation:

$$^{\bullet}OH + Dye \rightarrow {}^{\bullet}Dye + H_2O \tag{2}$$

Further reactions in solution can then take place as a part of the overall scheme:

$$^{\bullet}Dye + O_2 \rightarrow Dye{-}O_2^{\bullet} \tag{3}$$

$$2Dye{-}O_2^{\bullet} \rightarrow 2Dye{-}O^{\bullet} + O_2 \tag{4}$$

$$Dye{-}O^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + \text{products} \tag{5}$$

Additionally the peroxy radicals can also further react with the dye as follows:

$$HO_2^{\bullet} + Dye \rightarrow {}^{\bullet}Dye + H_2O_2 \tag{6}$$

For the decoloration studies, we monitored the decrease in the absorption peak at 582 nm; the time-dependent decrease in the dye concentration is shown in Fig. 2. The absorption data of the dye solution was fitted to the first-order rate equation.

$$\ln(A_t) - \ln(A_0) = -kt,$$

where k is the rate constant, t is the reaction time and A_0 and A_t are the initial and the final absorbance values of the dye solution, respectively. A plot of $\ln(A_t)$ versus time generated

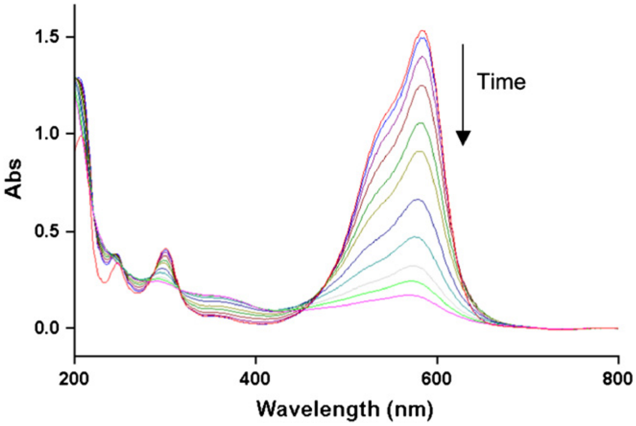

Fig. 2. Time-dependent decrease of CV visible region spectra by UV/H_2O_2 within 30 min.

a straight line with a negative slope. The slope of this line corresponds to the rate constant value for the decoloration of the dye. For the application of the UV/H_2O_2 initiated decoloration of dye effluent, it was necessary to initially change both the initial dye concentration and hydrogen peroxide concentration so as to optimize the conditions of maximum decoloration. Table 1 and Fig. 3 show the effect of increasing hydrogen peroxide concentrations on decoloration rate, with the most rapid decoloration occurring at the highest H_2O_2 concentration tested. However, it can be seen that the apparent rate seemed to be reaching a plateau at higher H_2O_2 concentrations. For example, doubling the H_2O_2 concentration from 3.33 mM to 6.66 mM, resulted in only a 13% increase in the apparent rate constant. This can be explained to be due to the self-quenching reaction of $^{\bullet}OH$ radicals with H_2O_2:

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k = 3.3 \times 10^7\ M^{-1}\ s^{-1} \tag{7}$$

Therefore, 1.67 mM was selected as the optimum concentration of H_2O_2 for subsequent study. Similarly, the initial concentration of the dye affected the decoloration of the dye; Fig. 4 shows that as the dye concentration increased, an almost linear decrease in the decoloration rate of the dye was observed. However, as we were unable to find an optimum concentration of Crystal Violet that would give the best decoloration of the dye, it therefore appeared that the apparent decoloration rate was independent of dye concentration in the range of 5–27 μM.

Table 1
Effect of H_2O_2 concentration on photolytic degradation of Crystal Violet

Conc. of H_2O_2 (mM)	Rate constant (min^{-1}) × 10^{-2}
0.33	2.6
0.83	4.7
1.67	7.0
3.33	9.1
6.66	10.3

[CV] = 22 μM.

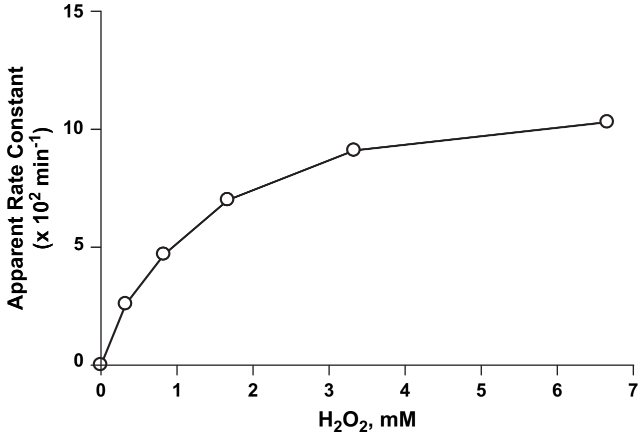

Fig. 3. Effect of H_2O_2 concentration on Crystal Violet decoloration. [CV] = 22 μM, [H_2O_2] was either 0.33, 0.83, 1.67, 3.33, or 6.66 mM.

Examination of the effect of pH on dye decoloration revealed that dye decoloration was not affected in acidic media. The apparent rate constants of the dye decoloration at neutral pH and at pH 2 were 0.07 min^{-1} and 0.072 min^{-1}, respectively. We could not examine the effect of alkaline pH on dye decoloration, as Crystal Violet reacts with hydroxide anions to produce a colorless, non-conjugated form of the dye.In order to optimize the Fenton-mediated degradation of Crystal Violet, the concentrations of dye, hydrogen peroxide and Fe^{2+} were varied; the results are summarized in Tables 2–4. The Fenton's reagent involves reaction of ferrous ions with hydrogen peroxide to produce hydroxyl radicals, which are strong oxidizing reagents that react with the dye solution and degrade it [18]:

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad k = 70\ M^{-1}\ s^{-1} \tag{8}$$

The hydroxyl radical propagates the reaction by reacting with the organic dye to produce further radicals, which can then react in many different steps.

$$^{\bullet}OH + Dye \rightarrow H_2O + Dye^{\bullet} \quad k = 10^9 - 10^{10}\ M^{-1}\ s^{-1} \tag{9}$$

$$Dye^{\bullet} + H_2O_2 \rightarrow Dye{-}OH + HO^{\bullet} \tag{10}$$

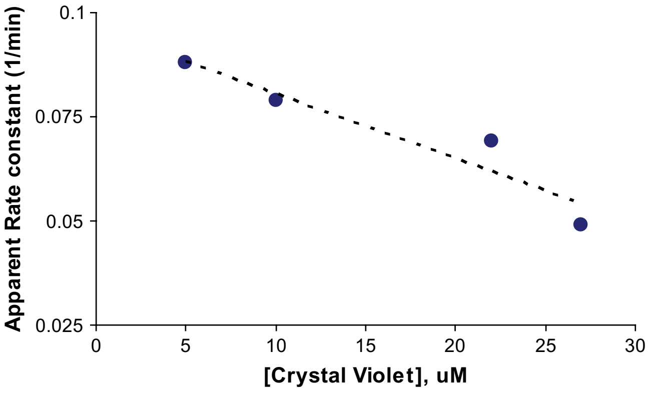

Fig. 4. Effect of Crystal Violet concentration on the photolytic decoloration of the dye. Hydrogen peroxide concentration was kept constant at 1.67 mM, and different concentrations of the dye (5 μM, 10 μM, 22 μM, or 27 μM) were used as described under Section 2.

Table 2
Effect of H_2O_2 concentration on CV decoloration in the Fenton process

Concentration of H_2O_2 (μM)	Rate constant (min^{-1})
83	0.26
333	0.66
667	1.2

$[CV] = 22$ μM, $[Fe^{2+}] = 333$ μM.

Table 4
Effect of Fe^{2+} concentration on CV decoloration in the Fenton process

Concentration of Fe^{2+} (μM)	Rate constant ($\times 10^{-2}$, s^{-1})
83	4.4
333	11
667	20

Concentration of $[H_2O_2] = 333$ μM, $[CV] = 22$ μM.

Additionally many other reactions are also possible, which include the radical–radical reaction or the reaction of the OH radical with H_2O_2.

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (11)$$

The peroxide radicals ($HO_2^{\bullet}$) produced in the above case can further oxidize other species present in the solution [17].

$$HO_2^{\bullet} + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^+ \quad k = 1.26 \times 10^6\ M^{-1}\ s^{-1} \qquad (12)$$

The rapid depletion of H_2O_2 that is often observed with Fenton's reagents is probably due to the combined reactions (8)–(12). However, since reaction (9) has the highest rate constant, it is responsible for the degradation of the dye. Also, it is possible for Fe^{2+} to be auto-regenerated in this system, and act as a catalyst [11].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad (13)$$

One can see from Table 2 that the rate of CV degradation in the Fenton process was proportional to the amount of H_2O_2. This can be explained on the basis that at higher concentrations of H_2O_2, more OH radicals are available which can degrade more dye molecules. Similarly, at a fixed concentration of H_2O_2, the extent of dye degradation decreased with increasing concentration of the dye solution (Table 3). Lastly, Table 4 shows that as the amount of the Fe^{2+} increased, the apparent rate of dye degradation increased proportionally, presumably because of more OH radicals being generated.

It seems that unlike the photolytic process, the Fenton-mediated degradation of CV is not as sensitive to CV and H_2O_2 concentrations.

In addition to dyes, textile waste streams also have elevated levels of other salts and ions [19] derived from the many different types of auxiliaries that are employed in coloration processes. To investigate the decoloration of Crystal Violet in the presence of certain anions, electrolytes were added to the dye solution in fixed quantities, all other experimental conditions being kept the same as for the Crystal Violet alone decoloration study. Among the anions chosen for this purpose were the sodium salts of chloride, sulphate and hydrogen phosphate ions; the results are given in Table 5 for both the processes investigated. Each of these added salts imparted a change to the rate of decoloration of the dye. For the photolytic process, in the absence of electrolyte, the dye degraded by 90% within 30 min at room temperature with a rate constant of 7.0×10^{-3} min^{-1}. However, in the presence of electrolyte, the rate constant decreased; for example, in the presence of chloride ions, the rate constant was found to be 4.1×10^{-3} min^{-1}. This change can be explained on the basis of the following chemical reaction involving chloride ions [20].

Table 3
Effect of CV concentration on its decoloration in the Fenton process

Concentration of CV (μM)	Rate constant (min^{-1})
5	1.6
22	0.66
27	0.54

Concentration of $[H_2O_2] = 333$ μM, $[Fe^{2+}] = 333$ μM.

$$Cl^- + {}^{\bullet}OH \rightarrow HOCl^{\bullet}- \qquad (14)$$

Similarly, for the Fenton process, about 50% of the dye could be degraded within 1 min, whereas the addition of various ions (e.g. Cl^-) negatively affected the decoloration rate. Table 5 shows a comparison of the effects of various anions on the decoloration rate of Crystal Violet by the two processes. Unexpectedly we found that the electrolytes affected the extent of degradation differently depending on the method in use. For example hydrogen phosphate ions almost completely inhibited the Fenton-mediated dye degradation, whereas they caused only a 30% decrease in the photolytic mediated degradation rate.

Finally, we used HPLC to confirm that the dye decoloration was in fact due to dye degradation. HPLC analyses of dye solutions after 30 min of UV/H_2O_2 photolytic treatment showed that the parent dye was significantly diminished and additional product peaks were detected. Although the new product peaks were not identified, the results nevertheless show that the dye molecules were being broken down.

4. Conclusions

The present work investigated the photolytic decoloration of Crystal Violet in the presence of UV/H_2O_2 and with Fenton's reagent. CV was found to degrade rapidly and efficiently

Table 5
Effect of various ions on the decoloration of Crystal Violet by the two degradation processes

Anion	Apparent rate constants ($\times 10^{-2}$, min^{-1})	
	Photolytic process ($[CV] = 22$ mM, $[H_2O_2] = 1.67$ mM)	Fenton process ($[CV] = 22$ μM, $[H_2O_2] = 0.33$ mM, $[Fe^{2+}] = 333$ μM)
–	7	66
Cl^-	4.1	44
SO_4^{2-}	3.7	40
HPO_4^{2-}	4.8	1.2

in H_2O_2/UV, but was even better degraded by the Fenton process. The decoloration kinetics fitted a first-order mechanism. Optimization studies revealed that the decoloration using the photolytic (UV/H_2O_2) approach was most efficient using 1.67 mM H_2O_2, but was found to be independent of the dye concentration used in the range 5–27 μM. The apparent rate of dye decoloration provided by the Fenton process was found to be proportional to H_2O_2 concentration as well as the concentration of Fe^{2+} used. It is suggested that the photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in the solution. The effect of various anions commonly found in waste streams, on the decoloration of CV was also studied. It was found that hydrogen phosphate ions completely inhibited the Fenton process, whereas it decreased the photolytic rate by only 30%.

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