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Photolytic oxidation of Safranin-O with H_2O_2

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Abstract

Safranin-O (C.I name is Basic Red 2), a histologically important dye for counterstaining cartilages, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically. The rate of degradation was calculated from the observed absorption data and was found to be first order. A systematic study of the effect of dye concentration as well as H_2O_2 concentration on the kinetics of dye degradation was carried out. Additionally, the effect of various additives on the degradation of this dye was also investigated. Most of the anions tested had a minor inhibitory effect on the degradation of the dye, with the most pronounced effect seen with Cl^-, Br^-, CH_3COO^-, and SO_3^{2-} ions. Addition of cations did not significantly affect the dye degradation, except for Cd^{2+}, Cu^{2+}, and Ag^+, all of which inhibited dye degradation, and Fe^{3+}, which dramatically enhanced the rate of dye degradation. Examination of the effect of pH showed that the dye could be efficiently degraded over a wide pH range. A plausible explanation involving the probable radical initiated mechanism was given to explain the dye degradation.

Keywords: Safranin; Photolysis; Degradation

1. Introduction

Dyes are an important class of chemicals which are widely used in many industrial processes in the leather, textile and printing industries. The discharge of these dyes in the effluents by these industries may cause a major environmental problem [1–4]. Many of these dyes are of major concern because of their known carcinogenic properties [5]. On passage to water bodies at large, these chemicals may pose a health concern to all forms of marine life and also to human life at the end of the food chain. Recently, many different techniques have been suggested in the literature to tackle the situation by causing the complete degradation of dyes in industrial effluents prior to entering the water bodies. These suggestions include photocatalytic, photolytic and biodegradation of various dye solutions [6–9]. Advanced oxidation process based on UV/H_2O_2 degradation is not only simple and homogeneous, but has also shown promising results in degrading many other organic compounds [10–12]. The process in general demands the generation of OH radicals in solution in the presence of UV light. These radicals can then attack the dye molecules to undergo a series of reactions in which the organic molecule is finally destroyed or converted into a simple harmless compound. Safranin-O (C.I name is Basic Red 2) is a representative example of an organic dye, which belongs to the Quinone–Imine class, and is widely used for counterstaining purposes, for example, as a metachromatic method for cartilages which is stained yellow. Since the dye is known to be carcinogenic in nature, any presence of this dye in wastewater would have detrimental effects on marine life. In this paper, an attempt is made to look at the degradation 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 additives in the form of anions and cations on the degradation of the dye solution were also investigated.

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2. Experimental

Safranin-O (C.I name is Basic Red 2, F. wt = 350.8) was obtained from Fluka and 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 used in this work. Its concentration in all the dye solutions for this work was kept constant at 1.67 mM unless otherwise specified. UV/VIS studies were done on a CARRY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm.

2.1. Preparation of samples and degradation studies

Safranin-O stock solution of 1×10^{-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 a UV light of 254 nm. 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 degradation rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

For studying the effect of pH on dye degradation, the pH of the dye solution was altered by adding incremental amounts of either concentrated HCl or concentrated NaOH. For experiments examining the effects of different ions on the degradation of Safranin, 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 degradation rate constant.

3. Results and discussion

In the present work, the kinetics of H_2O_2-assisted photochemical oxidation of Safranin-O was investigated. The structure of the dye is given in Fig. 1. The initial investigation of the dye revealed a major peak at 520 nm as shown in Fig. 2. The degradation studies were attempted by observing changes in the absorbance value of the dye at this wavelength. Initially, experiments were carried out in the absence and presence of either UV light or H_2O_2 alone. The results showed that mere UV light or H_2O_2 alone was not sufficient for degradation of this dye.

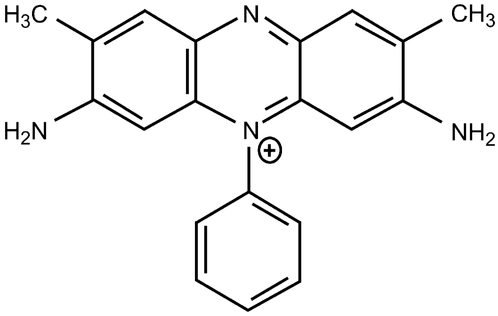

Fig. 1. Structural formula for Safranin-O.

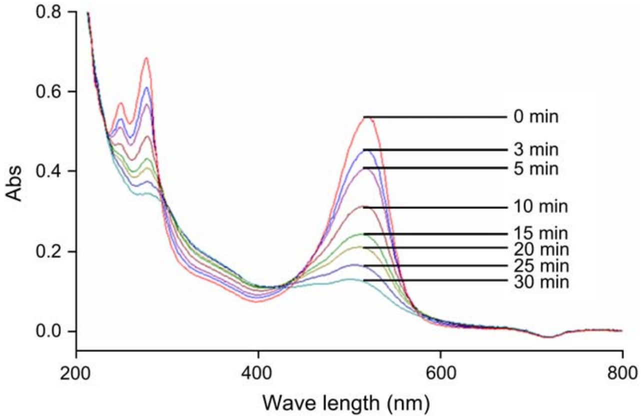

Fig. 2. Time dependent degradation of SO by UV/H_2O_2 within 30 min. [SO] = 20 μM, [H_2O_2] = 1.67 mM.

Dye solutions of various concentrations in the presence of 1.67 mM H_2O_2 were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H_2O_2 and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. 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:

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

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

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

where k is the 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.

To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both H_2O_2 and SO. Fig. 3 and Table 1 show the rate constants and % degradation of SO at different H_2O_2 concentrations. As it can be seen, the rate of dye degradation was directly proportional to H_2O_2 concentration. Similarly, Table 2 shows the effect of varying SO concentration on the kinetics of dye degradation. The rate of SO degradation appears to be inversely proportional to the dye concentration.

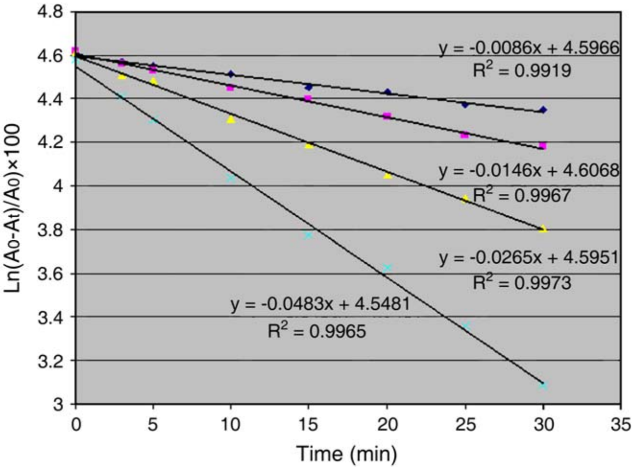

Fig. 3. Effect of H_2O_2 concentration on the kinetics of SO degradation. [SO] = 20 μM, $[H_2O_2]$ was 0.21, 0.42, 0.84, or 1.67 mM.

The degradation of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light [13].

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

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

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

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 degradation reaction of the dye molecule [14]. The concentration of H_2O_2 was kept at an optimum level (in this case at 1.67 μM) due to the fact that at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of H_2O_2 to produce $HO_2^{\bullet}$ radicals.

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

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways [15]. Thus one can assume that H_2O_2 acts as a pseudo catalyst in this case.

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/H_2O_2. Surprisingly, pH did not appear to have any significant effect on the kinetics of dye degradation (Fig. 4). This is contrary to what we have observed with other dyes, where photolytic dye degradation appears to be best at alkaline pH, and slowest at acidic pH (manuscript submitted for publication). Perhaps, the well-documented pH effect on dye degradation is dye-dependent. We did, however, see a slight increase in the degradation of SO at pH 9. This slight enhancement in dye degradation 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].

Table 1
Effect of H_2O_2 concentration on the kinetics of SO degradation (30 min)

$[H_2O_2]$ (mM)	$K \times 10^{-2}$ (min^{-1})	% Degradation
0.21	0.86	23
0.42	1.46	36
0.84	2.65	55
1.67	4.83	77

[SO] = 20 μM.

Table 2
Effect of SO concentration on the kinetics of dye degradation (30 min)

[SO] (uM)	$K \times 10^{-2}$ (min^{-1})	% Degradation
5	5.62	81
10	4.59	76
20	4.83	77
30	1.79	41
40	1.17	28
50	0.95	25

$[H_2O_2]$ = 1.67 mM.

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

We and others have previously shown that ions that are normally present in textile wastewater streams can have dramatic effects on the kinetics of dye degradation [17]. Therefore, we tested the effects of various cations and anions on the photolytic degradation of SO (Table 3). It can be seen from this table that the % degradation of the dye solution substantially decreased in the presence of bromide, chloride, bicarbonate, acetate, and sulfite ions. The inhibitory effect of halides on dye degradation has been previously shown and explained by us and by others [17]. However, the effect of acetate and sulfite was unexpected. Perhaps these ions somehow scavenge the OH radicals that are produced by the photolysis of H_2O_2.

We also examined the effects of various cations on the kinetics of SO degradation. As can be seen in Table 3, additions

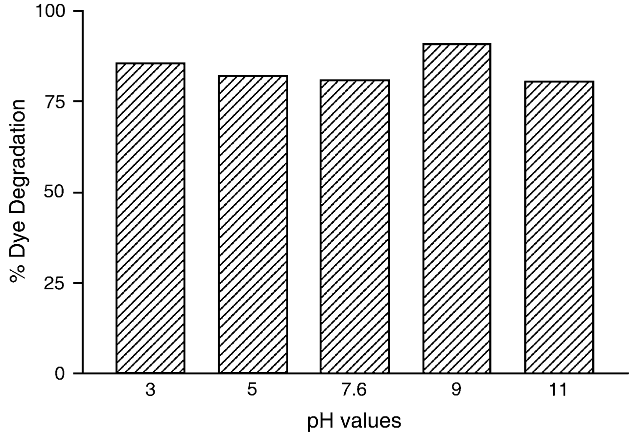

Fig. 4. Effect of pH on SO degradation. [SO] = 20 μM, $[H_2O_2]$ = 1.67 mM.

Table 3
Effect of various ions on SO degradation (30 min)

Ions	$K \times 10^{-2}$ (min^{-1})	% Degradation
–	5.9	84
Anions		
NO^{3-}	4.35	72
SO_4^{2-}	3.96	69
CO_3^{2-}	3.7	68
Cl^-	2.84	57
Br^-	2.7	56
CH_3COO^-	1.15	30
SO_3^{2-}	0.52	14
Cations		
Fe^{3+}	38.85	98 (10 min)
K^+	6.19	85
NH_4^+	5.88	83
Ni^{2+}	5.63	82
Co^{2+}	5.12	79
Ca^{2+}	4.84	77
Mg^{2+}	4.99	77
Pb^{2+}	4.09	72
Cd^{2+}	3.9	72
Cu^{2+}	1.89	44
Ag^+	0.17	3

[SO] = 20 μM, [H_2O_2] = 1.67 mM.

of cations did not significantly effect the dye degradation, except for Cd^{2+}, Cu^{2+}, and Ag^+, all of which inhibited dye degradation. Addition of Fe^{3+} to the dye solution caused a very dramatic enhancement in the degradation of SO (Fig. 5, Table 3). This is most likely due to the ''photo-Fenton'' mediated degradation of the dye. These significant results underscore the importance of testing the effects of various ions for effective degradation of dyes.

4. Conclusion

Photolytic oxidation of Safranin-O dye (also called as Acid Red 2) was carried out in the presence of hydrogen peroxide. The degradation of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the degradation scheme of the dye. The degradation of the dye was less in the presence of bromide, chloride, acetate, sulfite, silver and bicarbonate ions. Thus for effective degradation of the dye, these ions 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.

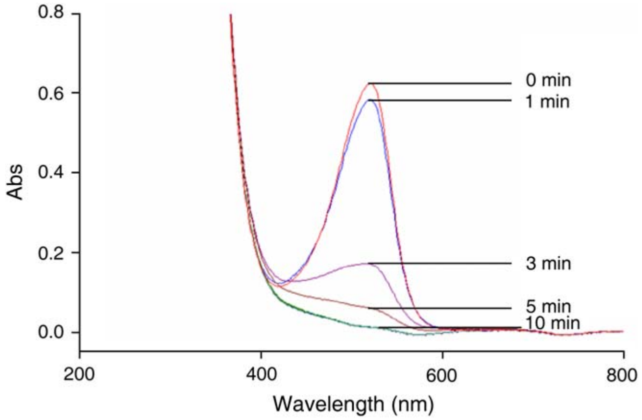

Fig. 5. Photolytic (UV/H_2O_2) degradation of SO in the presence of 2.5 mg/mL of Fe^{3+}. [SO] = 20 μM, [H_2O_2] = 1.67 mM.

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