Kinetic Investigation on the Photochemical Degradation of Brilliant Orange in the Presence of Hydrogen Peroxide

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Abstract

The degradation of Brilliant Orange from aqueous solution was investigated by advanced oxidation process. Such oxidation process using H_2O_2 in the presence of UV light is a feasible and efficient alternative for wastewater treatment from recalcitrant compounds such as reactive dyes. H_2O_2 acts as an oxidant, produces ·OH radical on irradiation by UV light. ·OH radical oxidizes the dye. The disappearance of Brilliant Orange was monitored on the basis of decolorization, determined by UV-absorption analysis. The extent of decolorization depends on the relative ratio of initial concentrations of H_2O_2 to BO. The kinetic study of the degradation was investigated, by varying the initial concentrations of BO and H_2O_2.

I. Introduction

Brilliant Orange H2R (BO), one of the most important azo dyes, is frequently used in the textile industry. Reckless dumping of untreated water from textile and leather industries is making river water unusable. Pollution is now a threat to aquatic life, crops and greenery. Dyes in the effluents undergo chemical as well as biological changes in the aquatic system, consume dissolved oxygen and thus disturb the aquatic eco-system. It is necessary to treat the textile and leather effluents before discharge. Use of conventional physical and chemical methods of effluent treatment, e.g. adsorption, electrical coagulation, and reverse osmosis, has brought a certain positive result on discolouration

process, but in these methods effluent contaminants transfer to a solid phase from aqueous phase creating a problem of disposal. Therefore, attention has to be focused on techniques that lead to complete destruction of dye molecules. Advanced Oxidative Processes (AOP)[1-7] is very effective for degradation of recalcitrant substance and has presented good results in respect of discolouring reactive dye-containing wastewaters. These processes involve the production of hydroxyl (·OH) radical, a highly reactive, nonselective oxidizing agent capable of destroying recalcitrant pollutants. One of the best known advanced oxidative methods is the use of H_2O_2 in the presence of UV light. The process is efficient and easy to operate. ·OH radicals can oxidize a large variety of pollutants such as aliphatic acids, dyes, phenols, pesticides etc[8].

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \quad (1)$$

$$\cdot OH + dye \rightarrow (dye)^* \quad (2)$$

$$\cdot OH + (dye)^* \rightarrow products + CO_2 + H_2O \text{ etc} \quad (3)$$

II. Experimental

Materials and Methods

Brilliant Orange H2R (Reactive Orange 13, reddish orange, obtained from commercial market), H2O2 (30%) and absolute ethanol were used as received. 5×10^{-4} M and 2 M

solutions of dye and H2O2, respectively, were prepared with double distilled water as stock solutions. Concentration ranges used for BO and H2O2 were 2×10^{-5} M to 10×10^{-5} M and 0.04 M to 0.08M, respectively.

To investigate the photochemical degradation, 100 mL solution of 7×10^{-5} M of BO and 0.08 M of H2O2 was used. pH of the solution was recorded and the solution was placed under UV lamp enclosed in a wooden box with continuously stirred by a magnetic stirrer. The solution was irradiated for an hour. During irradiation, a definite volume of irradiated solution was withdrawn after a definite interval of time to determine the concentration of dye. This was continued until 5 or 6 samples were collected. The samples were analyzed by UV-Visible spectrophotometer (UV-160A, Shimadzu, Japan). The results are shown in Fig.1. The percentage of degradation (%) has been calculated as:

Percentage of decolourization = $(A_o - A_t) \times 100/A_o$ (assuming degradation follows the same trend as that of decolourization). Where A_o is the absorbance at t = 0 minute and A_t is the absorbance at t minute. Absorbance was measured at 488 nm which corresponds to the λmax of BO.

To investigate the role of .OH radicals during photodegradation, a mixture of 7×10^{-5} M BO solution and 8.0×10^{-5} M H_2O_2 were irradiated using aqueous ethanol of different concentrations starting from 1% to 6%. Results have been shown in Fig.2. To observe the effect of initial concentration of dye on degradation, the initial concentration of dye was varied from 5×10^{-5} M to 1.0×10^{-4} M using 0.08 M H_2O_2 in each case. The results have been shown in Fig.3. To investigate the effect of initial concentration of H_2O_2 on photodegradation, the initial concentration of H_2O_2 was varied from 0.04 M to 0.08 M. The result in the Fig.4 shows that three different experiments were done with three initial concentrations of dye. The irradiation was continued for 50 minutes.

III. Results and Discussion

Fig.1 shows the change in the spectra of BO solution with time. After one hour, the peak corresponding to 488nm

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disappeared and the solution became colourless suggesting the oxidation of BO molecules. Peak corresponding to ~270 nm also disappeared, indicating the complete oxidation of BO molecules during one hour of irradiation.
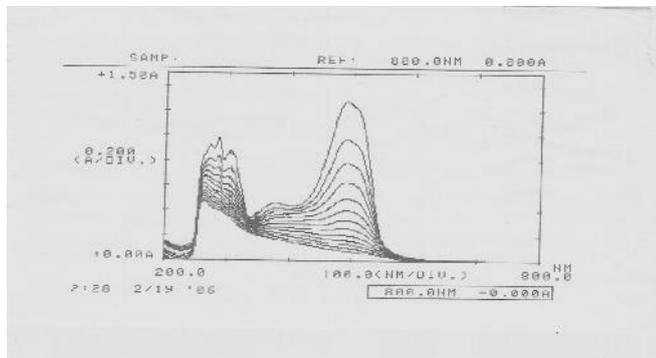

Fig.1. Overlay spectra of Brilliant orange H2R (BO) after photo-degradation by UV light in the presence of H_2O_2 at different time intervals; (from top) 0 min, 5 min, 10 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45 min, 50 min, 55 min, and 60 min. [conc. of BO = 7.0×10^{-5} M, pH = 4.10 Reference: water]

The $\cdot$OH radicals produced from H_2O_2 in the presence of UV light may directly involve into the photodegradation or may undergo reaction with aerial oxygen to produce some secondary radicals as proposed for semi conducting oxide mediated photodegradation of dyes [9-11]. The effect of ethanol concentration on the photodegradation of BO supported the direct involvement of $\cdot$OH radicals (Fig.2). No photodegradation was found either in the dark or in the presence of visible light suggesting that the energy required for the production of $\cdot$OH radical can not be supplied from ordinary light.
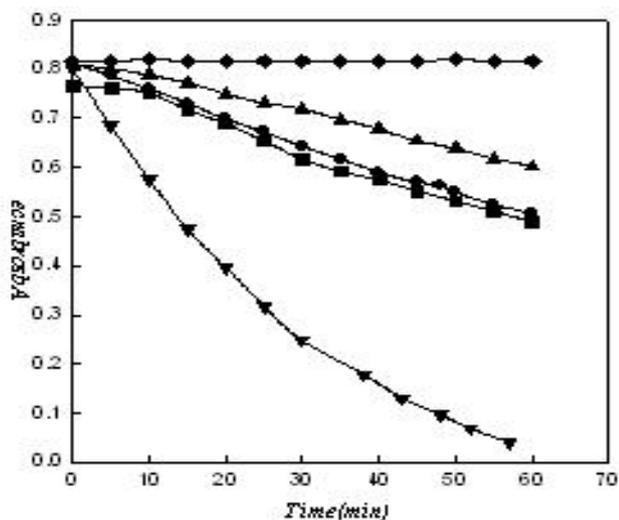

$\blacklozenge$=6% Ethanol ▲ =4% Ethanol ● =2% Ethanol ■ =1% Ethanol
►=No Ethanol

Fig.2. Effect of ethanol concentration on Photodegradation of BO solutions under UV irradiation in the presence of 8.0×10^{-5} M H_2O_2.

Effect of the concentration of BO

In order to observe the effect of concentrations of BO on its photodegradation, the initial concentrations of BO used, were 5×10^{-5} M, 7×10^{-5} M and 1.0×10^{-4} M, respectively. It was observed that the rate of degradation increased linearly with decreasing the initial concentration of BO (Fig.3). The percentage of degradation of BO increases from 77% to 100% on increasing the ratio of concentrations of H_2O_2 over BO. When the concentration of H_2O_2 is 1600 times higher than the initial concentration of BO, degradation was maximum.
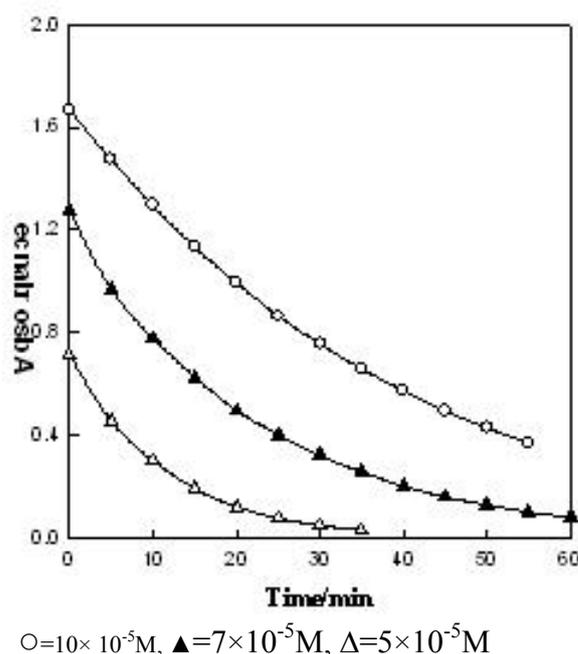

$\bigcirc$=10× 10^{-5}M, ▲=7×10^{-5}M, $\triangle$=5×10^{-5}M

Fig.3. Effect of initial concentrations of BO on its photodegra-dation in the presence of 8×10^{-2} M hydrogen peroxide.

Effect of the concentrations of H_2O_2

The effect of concentration of H_2O_2 on the photodegradation of BO was investigated by varying the ratio of [H_2O_2] to [BO] from 800 : 1 to 1600 : 1. Three different initial concentrations of BO were selected for three concentrations of H_2O_2. The rate of photodegradation increases with increasing the above ratio (Fig.4). The highest rate was observed when the ratio of [H_2O_2] to [BO] was 1600:1.

Above results suggested that the rate of degradation depends on the ratio of [H_2O_2] to [BO]. The higher is the ratio, the more is the degradation of BO.
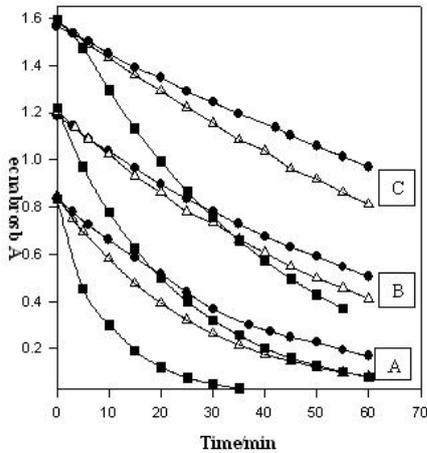
[BO] A $=5\times10^{-5}$M, B $=7\times10^{-5}$M,C $=10\times10^{-5}$M

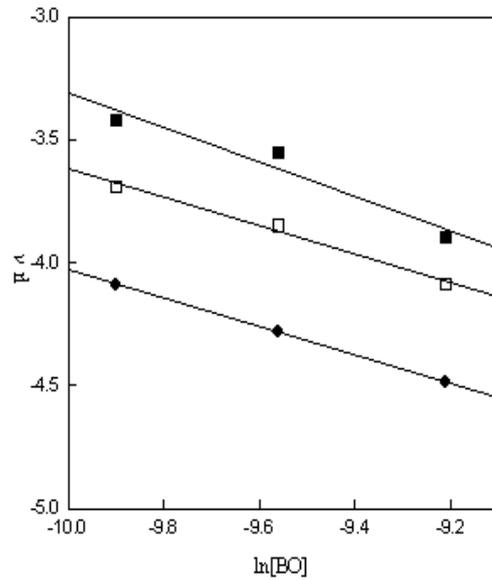[H_2O_2] ■ $= 8\times10^{-2}$M, $\Delta = 6\times10^{-2}$M, ● $=4\times10^{-2}$M

Fig.4. Effect of concentrations of H_2O_2 on the photodegradation of BO.

Kinetics of Photodegradation

The rate of photodegradation was investigated at constant H_2O_2 concentration with the various concentrations of BO (fig.4). Using initial rate method, the order with respect to BO was determined from the plot of ln$v$ vs ln[BO] (Fig.5) and the value is 0.62±0.05. This is in agreement with the result obtained by Mohey[12].

[BO] $=5\times10^{-5}$/M, $=7\times10^{-5}$/M, $= 10\times10^{-5}$/M

Fig.5. A plot of ln$v$ vs. ln[H_2O_2] for different concentration of BO

Table. 1. shows data for the determination of order.

Initial oncentration of $H_2O_2 \times10^2$ /M	No of obs.	Initial Conc. of BO$\times10^5$/M	[H_2O_2]:[BO]	Initial rate, $v \times10^2$	ln [BO]	ln v	α
4	1	5	800:1	1.67	-9.90	-4.09	
	2	7	1200:1	2.49	-9.56	-4.28	0.58
	3	10	1600:1	3.27	-9.21	-4.49	
6	1	5	570:1	1.48	-9.90	-3.69	
	2	7	860:1	2.35	-9.56	-3.85	0.58
	3	10	1140:1	3.01	-9.21	-4.09	
8	1	5	400:1	1.12	-9.90	-3.42	
	2	7	600:1	1.67	-9.56	-3.55	0.69
	3	10	800:1	2.02	-9.21	-3.90	

IV. Conclusions

H_2O_2 does not oxidize BO in the dark or in the presence of visible light. Oxidation occurs in the presence of UV light. The percentage of degradation was found to increase linearly with increasing the ratio of $[H_2O_2]$ to $[BO]$. When the photodegradation was carried out with constant initial concentration of H_2O_2, the rate of photodegradaton decreased with the increase of initial concentration BO. The highest rate was found when the ratio of H_2O_2 to BO was 1600 to 1. This concludes that the oxidation depends on the ratio of $[H_2O_2]$ to $[BO]$. The order of photodegradation of BO was determined by estimating the initial rate under different initial concentrations of BO (Fig.5). This was found to be 0.62 ± 0.05.

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