



## Degradation of acidic Orange G dye using UV-H<sub>2</sub>O<sub>2</sub> in batch photoreactor

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### ABSTRACT

Degradation of Orange G dye has been investigated using UV irradiation with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a batch photoreactor. UV irradiation and H<sub>2</sub>O<sub>2</sub> resulted in significant photodegradation of the dye although the effect individual reaction was very little. The degradation was studied to elucidate the effect of various process parameters such as pH, concentration of dye, dose of H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> and light intensity/light source with reflecting or non reflecting surface of photoreactor. Results showed the efficient degradation of Orange G for typical process conditions.

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**Keywords:** Orange G, UV/H<sub>2</sub>O<sub>2</sub>, photoreactor, degradation, process parameters.

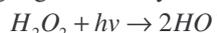
### INTRODUCTION

The discharge of color effluent is a common phenomenon in industries such as textile, leather, plastics, paper, food and cosmetics. According to an estimate, 700000 tons of dyes are produced annually. Out of the total production 60-70% of the dyes are used by textile industries and 10-15% of the total used colorants are discharged into effluent water during their synthesis and dyeing processes (Robinson et al., 2001; Sun et al., 2002; Silva et al., 2004; Alinsafi et al., 2007; Cho and Zho, 2007). Among several classes of dyes, azo dyes are about 60-70% of the dyes used in textile industry (Silva et al., 2004). During the dyeing process substantial amounts of dyes are not fixed and are released into the wastewater. This discharged color wastewater imposes a serious threat to the environment. Dyes are known to cause allergic dermatitis, skin irritation, cancer and mutation. Orange G is a typical acid azo dye used in many food and textile applications and is found in the discharged wastewater.

Different approaches have been used to remove dyes from effluents including

adsorption, coagulation, ozone treatment, photo-Fenton reaction, biological decolorization, hypochlorite treatment and advanced oxidation processes or AOPs (Wu and Law, 1998). In a broad way we can classify them in three categories: Chemical, Physical and Biological methods. Each method has its own advantages and disadvantages. In case of adsorption, the problem is only displaced and further treatments are indeed necessary in order to separate the purified effluents or to regenerate the adsorbents (Hoffmann et al., 1998; Hachem et al., 2001). High sludge production in case of coagulation and photo-Fenton reaction process is its major disadvantages. In methods involving ozonation, the half life of ozone causes operational difficulties and biological decolorization process is not suitable due to its long retention time and high cost. The photochemical or photocatalytic processes of degradation have been found to be effective for such chemicals (Gogate and Pandit, 2004a, 2004b). In the recent years, the use of advanced oxidation processes has been studied for the treatment of textile effluents

(Mohammad et al., 2005; Shu and Chang, 2005; Modirshla and Behanajady, 2006; Alshamsi et al., 2007; Sun et al., 2006; Behnajady et al., 2007; Cho and Zoh, 2007; Aleboyeh et al., 2008;). These processes were based on powerful oxidizing agents such as hydroxyl radicals. Most common AOP techniques involve the use of ultraviolet light in the presence of H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>, O<sub>3</sub> and Fenton's reagent. UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process has proved the capability of the complete degradation of the Direct Red 80 (DR80) by using fixed bed photoreactor (Mohammad et al., 2005). Hydrogen peroxide in presence of UV light generates hydroxyl radicals as



These radicals are capable of oxidizing organic compounds (RH) and producing organic radicals (R<sup>·</sup>), which are highly reactive and can undergo further oxidation (Georgiou et al., 2002; Modirshahla et al., 2006; Modirshahla and Behnajady, 2007). UV/H<sub>2</sub>O<sub>2</sub> process has advantage of no sludge formation during the treatment, process can be carried out under ambient conditions and the oxygen formed in this process is useful for aerobic biological decay process (Murugandham and Swaminathan, 2004; Marechal et al., 1997).

In the aqueous solution, the acid dye first gets dissolved and the sulphonate groups of the acid dye (D-SO<sub>3</sub>Na) dissociate and release anionic dye ions (Mall et al., 2006).



The -N=N- azo group present in OG dye is reported to get converted into gaseous dinitrogen with TiO<sub>2</sub>/UV photocatalysis at pH 3, 6 and 9, which is ideal for the elimination of nitrogen-containing pollutant dye effluent (Lachheb et al., 2002). Sun et al. (2006) studied the kinetics of orange G dye using nano-sized Sn(IV)/TiO<sub>2</sub>/AC photocatalyst at pH 2 and established that Langmuir-Hinshelwood kinetic model explains the degradation of the dye .

In the present article, it was attempted to determine the feasibility of the total degradation of orange G by a UV/H<sub>2</sub>O<sub>2</sub> treatment process. The degradation was studied to elucidate the effect of various operating parameters such as pH, different concentrations of dye, doses of H<sub>2</sub>O<sub>2</sub> , doses of TiO<sub>2</sub>, different light intensities/light

sources, different reaction chamber surfaces in a batch photoreactor.

## MATERIALS AND METHODS

### Materials

The test dye Orange G (OG) 90% (Fig. 1) and H<sub>2</sub>O<sub>2</sub> (30% w/v) was obtained from S. D. Fine Chemical Limited, Mumbai, India. TiO<sub>2</sub> (Product No.28375) containing 98% Ti was procured from Qualigens Fine Chemicals Limited, Mumbai, India. They were used without any further treatment.

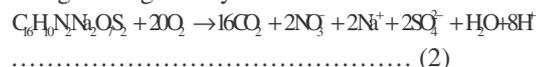
The physical and chemical characteristics of dye are given in Table 1.

### Photochemical Reactor

The photoreactor used for degradation is shown in Fig. 2. The reactor was of dimension 59 cm × 28.5 cm × 56 cm. Two 15W UV tubes (model F15T8/GL, maximum spectral intensity at 254 nm, radiant flux of 16 mW·cm<sup>-2</sup>) and one 125 W (model BLB-125W-E27) high pressure UV Bulb were used as radiation sources. The 15 W tubes were positioned on opposite sides of the cabinet interior nearer to the top and bulb was positioned at the center of the top. A temperature probe was fixed inside the chamber to record the reactor temperature. Small rotary fans were also provided to keep the temperature uniform inside the reaction chamber. For these experiments the working area of 38.5 cm × 19 cm in the chamber was used.

### Stoichiometric equations for total oxidation of Orange G dye

The stoichiometry of the oxidation of orange G is given by



### Analytical methods

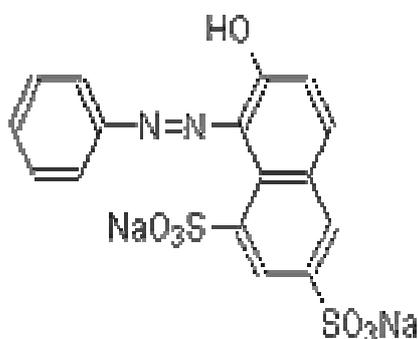
The UV-Vis smart spectrophotometer (Lamotte, Italy), single beam spectrometric quartz light, over a wavelength 350 to 1000 nm was used to record the absorbance.

The maximum absorbance wavelength, λ<sub>max</sub> for OG was 490 nm. The concentration of the dye at different reaction times were estimated by measuring the absorption intensity (at λ<sub>max</sub> = 490 nm).

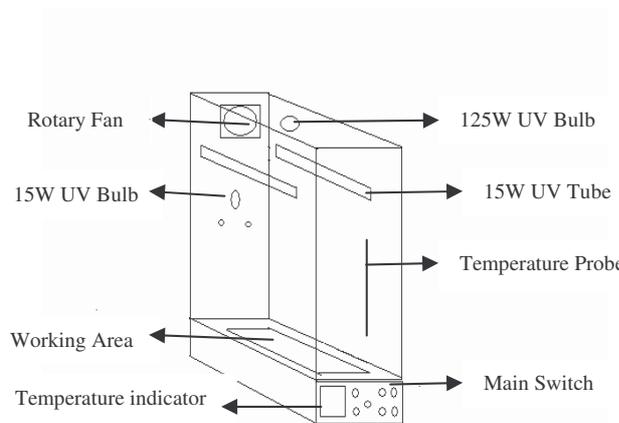
**Table 1:** Physical and chemical characteristics of dye.

S. No.	Title	Properties
1.	Dye name	Orange-G
2.	Abbreviation	OG
3.	Generic name	Acid orange 10
4.	Color Index (C.I.)	16230
5.	Appearance	Orange to red-orange powder
6.	Chemical formula	C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>
7.	Molecular Weight	452.37
8.	λ <sub>max</sub> , nm	490
9.	ε <sup>c</sup> , Abs ml/mg	46.9 (20,683)
10.	Toxic fumes	Carbon monoxide, carbon dioxide, nitrogen oxides, sulfur oxides.

<sup>c</sup>Extinction coefficient (Owusu-Apenten, 2002)



**Fig. 1:** Structure of dye: Orange G.



**Fig. 2:** Experimental Set-up of Photochemical Reaction Chamber.

The degradation of OG studied is reported as ‘η’, called photodegradation efficiency and defined as follows (Hachem et al., 2001; Lachheb et al., 2002; Sun et al., 2006):

$$\eta (\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \quad \dots \dots \dots (3)$$

Where C<sub>0</sub> is the initial concentration of OG, and C is the concentration of OG at reaction time t (min).

**RESULTS**

Experiments were conducted to find out the effect of different parameters involved

in the photodegradation. Except the parameter under study all others parameters were kept identical in different sets of experiments. The volume of dye solution was 20 ml for all the studies. The parameters studied have been discussed as under.

**Reflective surface and black surface**

The experiments were conducted at two different cabinet surfaces i.e. black painted surface and reflective surface (covered by aluminum sheet). It was observed that reflective surface cabinet was more effective for degradation of orange G dye than black painted surface. The percentage efficiency

was high with reflective surfaced reaction chamber, typically 100% against 85% for black painted surface under identical irradiation and experimental conditions after 180 min (Fig. 3).

#### Different light sources

It was found that corresponding to an increase in light intensity, there was an increase in the degradation of OG (Fig. 4). For a reflective surface reaction chamber, after 90 minutes the percent degradation efficiency was observed to be 83% with single 15 W UV tube, 88% with two identical 15 W UV tube, 95% with one 15 W UV tube and one 125 W UV bulb and 99.9% with two 15 W UV tubes and 125 W UV bulb.

#### UV-Vis spectrum

The progress in the absorbance spectra of the dye solution during the reaction was monitored with 0.5% dose of H<sub>2</sub>O<sub>2</sub> of reaction sample at pH 3. Results are shown in Fig. 5. It shows the change in absorption spectra of OG during UV/H<sub>2</sub>O<sub>2</sub> process at different irradiation time.

#### Dye concentration

A series of experiments were conducted with different concentrations of OG in the range of 50-300 ppm. The decolorization of dye was found to depend on the concentration of the dye (Fig. 6). The results indicated that the photodegradation efficiency of OG was higher at low concentration.

#### pH

To study the effect of pH on degradation of OG, experiments were conducted at different pH values ranging from 1.0 to 10.0. The hydrogen ion concentration affects the production rate of hydroxyl radical. Increase in pH of OG solution from 1.0 to 3.0 led to an enhanced OG degradation efficiency (Fig. 7).

#### H<sub>2</sub>O<sub>2</sub> doses

The experiments were conducted at different hydrogen peroxide doses from 0.125% to 5.0% of sample solution (Fig. 8). The results indicate that the rate of degradation of OG increased with increase in H<sub>2</sub>O<sub>2</sub> concentration up to 0.5% of sample

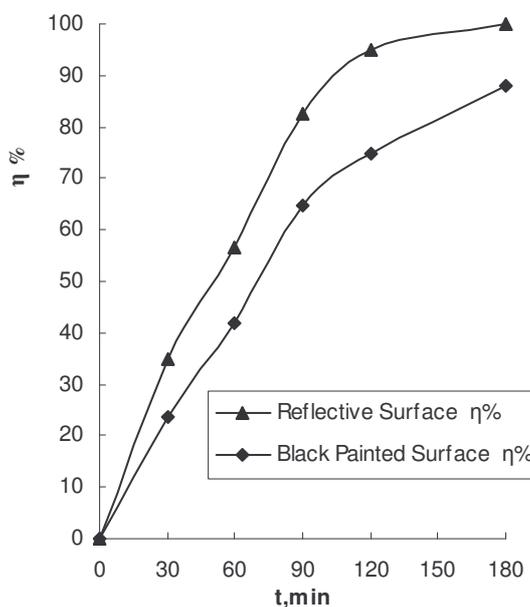
solution, but above it, there was a decrease in the degradation efficiency.

#### TiO<sub>2</sub> doses

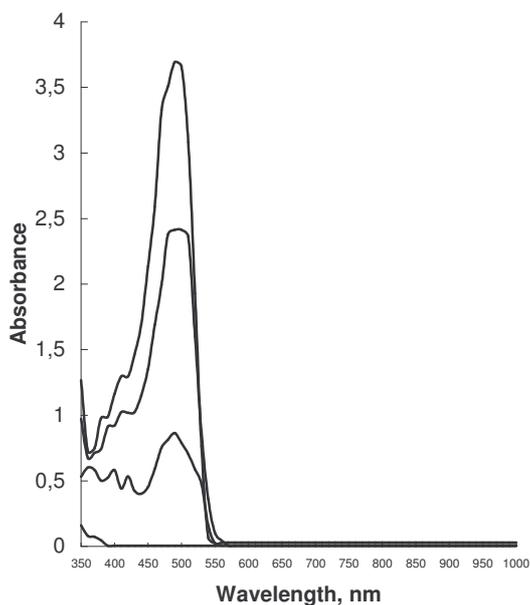
The effect of TiO<sub>2</sub> doses on the photodegradation rate of the dye was investigated by employing different doses of TiO<sub>2</sub> varying from 1 mg to 10 mg for 2 hr. It was found that there was no appreciable effect of TiO<sub>2</sub> (Qualigen Fine Chemicals) on the photocatalytic degradation rate of Orange G (Fig. 9).

#### DISCUSSION

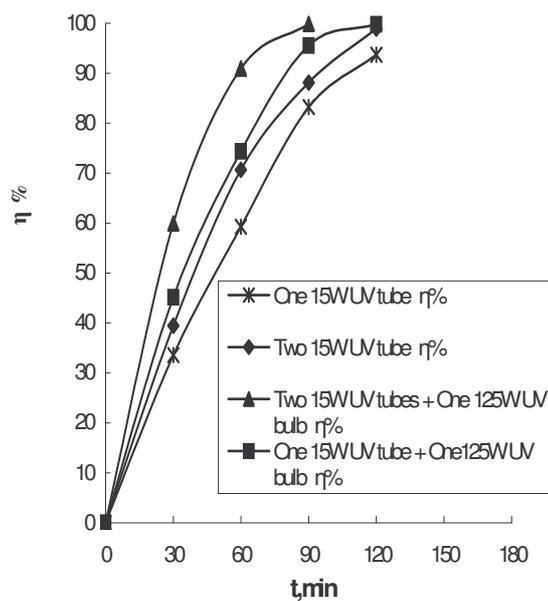
The effect of various parameters of practical importance on degradation of Orange G has been investigated in the present study. As expected the degradation was better using reflective surface chamber in comparison to black painted surface because of high resultant intensity of light with reflective surface. The results are in concurrence with those of Garcia et al. (2007), who used the reaction cabinet covered with aluminum foil to avoid radiation losses during irradiation process. Similarly, increasing the intensity of light the degradation increased. Sun et al. (2006) used 300 W high pressure mercury light in presence of Sn(IV)/TiO<sub>2</sub>/AC and observed 99.1% degradation in 60 min (Fig. 10), whereas in the present study 88% degradation has been observed with only UV/H<sub>2</sub>O<sub>2</sub> along with two 15 W tubes in 150 min. The degradation reached 99.9% in 90 min with additional source of 125 W bulb. The obvious better degradation achieved by Sun et al. (2006) has the disadvantage of using metal based catalyst Sn(IV)/TiO<sub>2</sub>/AC, which may increase the cost of the process. Further the adsorption process as incorporated by Sun et al. has its own inherited disadvantages. As such the present results appear to be more promising from the environment point of view. For higher concentration of OG (300 ppm) it took rather long time of approximately 6 hr for near total degradation in comparison to 3 hr for 50 ppm solution. Probably it happened because at the high initial concentration of dye, the color might have hindered the penetration of light into the bulk of the reaction sample (Lachheb et al., 2002). Consequently, the degradation of the dye decreased as the dye concentration increased.



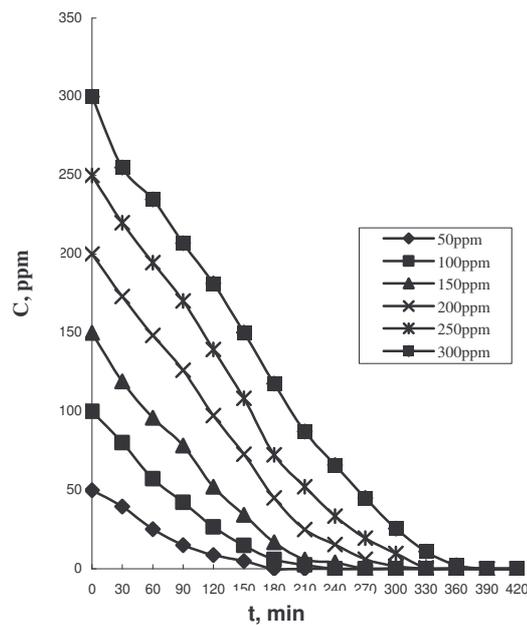
**Fig. 3:** Effect of reflective surface and black surface [pH = 3, Concentration of OG = 50ppm, H<sub>2</sub>O<sub>2</sub> = 0.5% of total sample].



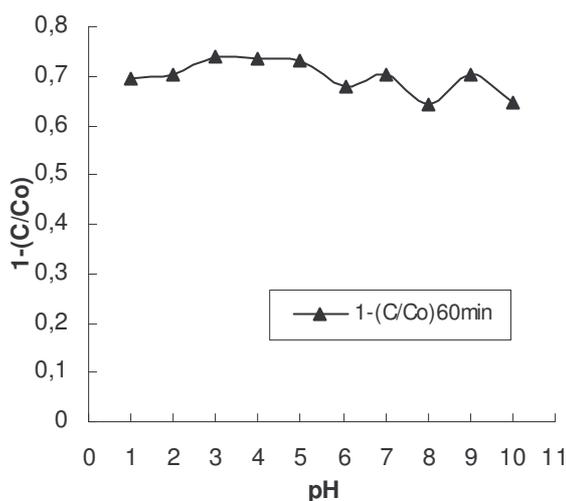
**Fig. 5:** UV-vis spectra of OG [pH = 3, Concentration of OG = 50 ppm, H<sub>2</sub>O<sub>2</sub> = 0.5% of total sample].



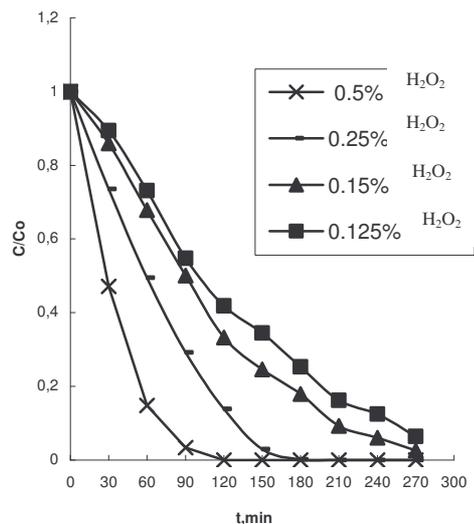
**Fig. 4:** Effect of different light sources [pH = 3, Concentration of OG = 50 ppm, H<sub>2</sub>O<sub>2</sub> = 0.5% of total sample].



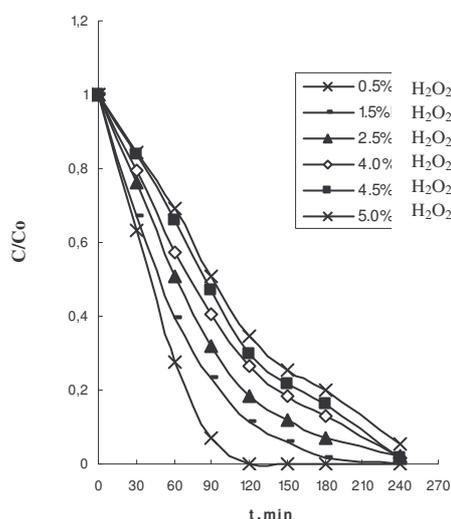
**Fig. 6:** Effect of different initial concentrations of OG [H<sub>2</sub>O<sub>2</sub> = 0.5% of total sample, pH = 3].



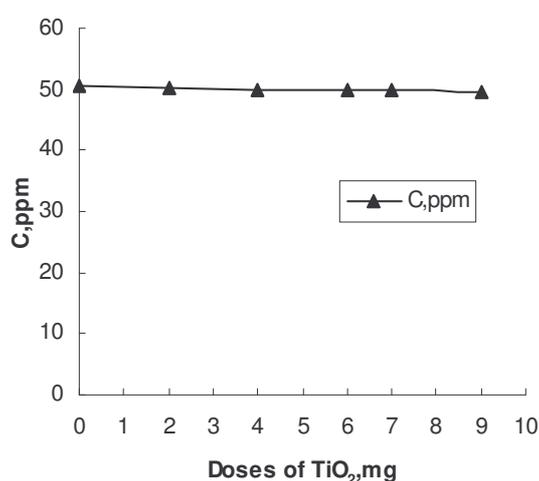
**Fig. 7:** Effect of different pH [ $H_2O_2 = 0.5\%$  of total sample, Concentration of OG = 50 ppm for 60 min].



**Fig. 8: (a)** Effect of different doses of  $H_2O_2$  (0.125-0.5%) [pH = 3, Concentration of OG = 50 ppm].



**Fig. 8: (b)** Effect of different doses of  $H_2O_2$  (0.5-5.0%) [pH = 3, Concentration of OG = 50 ppm].



**Fig. 9:** Effect of different doses of  $TiO_2$  [pH = 3, Concentration OG = 50 ppm].

The results indicated that the photodegradation of OG was more efficient in acidic medium. In alkaline medium the oxidizing species hydroxyl anion ( $HO_2^-$ ) is also formed ( $HO_2^-$  anion is the conjugated base of  $H_2O_2$ ). This  $HO_2^-$  anion reacts with  $\bullet OH$  radical and residual  $H_2O_2$  [Eq. (4), (5)] consequently lowers the degradation

efficiency of OG (Murugandham and Swaminathan, 2004)



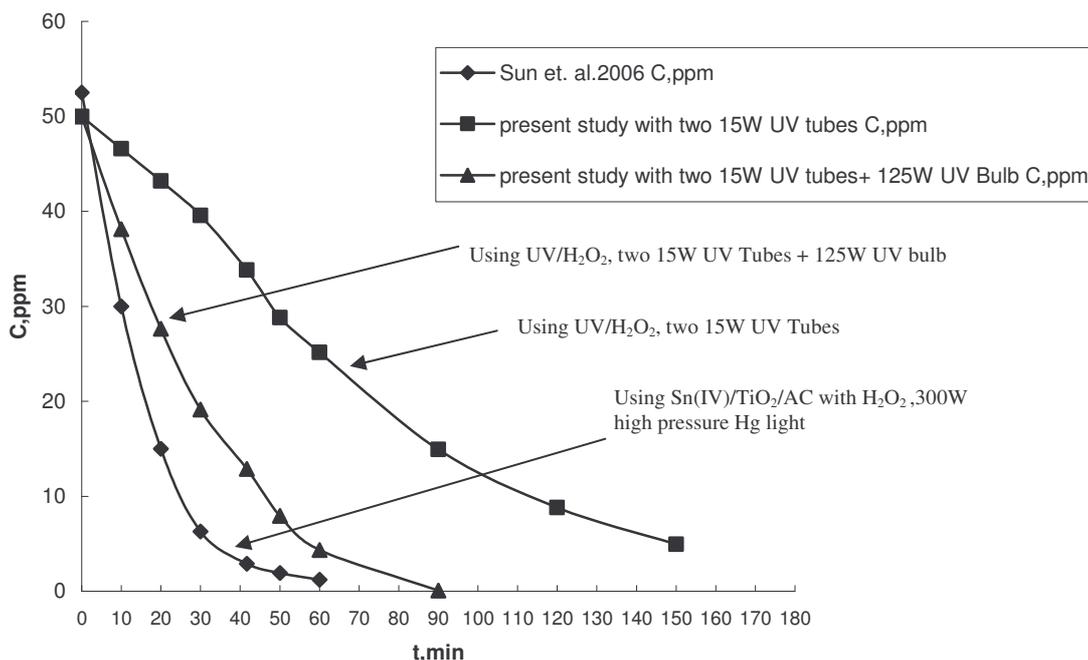


Fig. 10: Parity plot for present data with the data obtained by Sun et al. (2006).

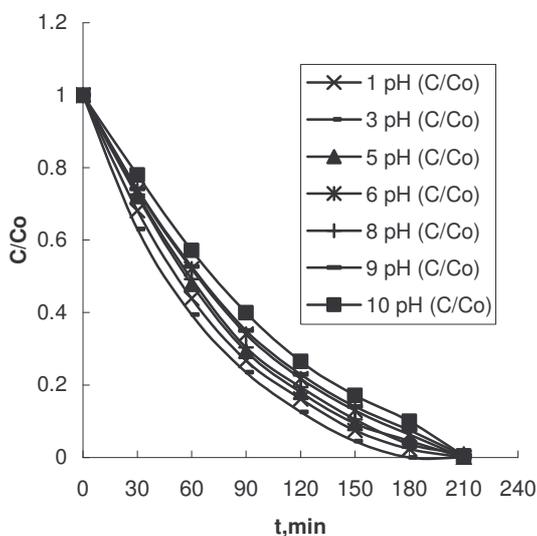


Fig. 11: Effect of pH and time on orange G Degradation [ $H_2O_2 = 2.5\%$  of total sample, Concentration of OG = 50 ppm].

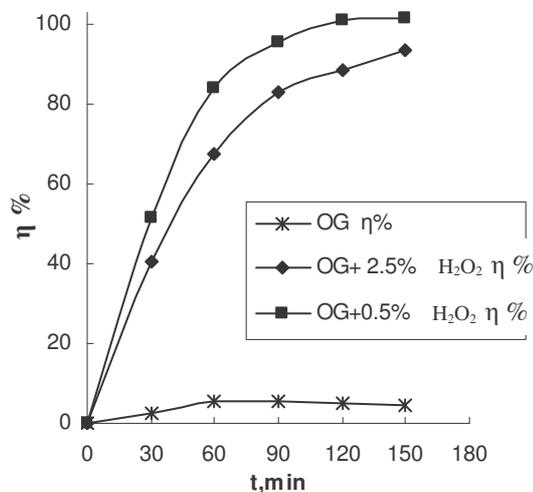
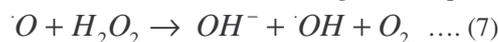


Fig. 12: % Degradation efficiency ( $\eta\%$ ) of Orange G Dye [OG +  $H_2O_2$  at different doses of  $H_2O_2$  (i.e. 2.5%, 0.5% of total sample respectively), pH = 3, Concentration of OG = 50 ppm].

It was also observed that maximum degradation occurred at pH 3 and with an increase or decrease that resulted in less degradation of the dye (Fig. 11). The lowering of degradation efficiency at higher pH range is due to reduction of hydroxyl radical concentration. Under these conditions, H<sub>2</sub>O<sub>2</sub> undergoes photodecomposition to water and oxygen and does not form hydroxyl radical [Eq.(6)] (Murugandham and Swaminathan, 2004).



Optimum dose of H<sub>2</sub>O<sub>2</sub> as observed was 0.5% of the sample solution but above it there was decrease in the degradation efficiency. This is because hydrogen peroxide inhibits the electron-hole recombination and could act as an alternative electron acceptor to oxygen at its low concentration, according to the Eq. (7).



But at high concentration of hydrogen peroxide, the  $\cdot OH$  radical could be consumed by H<sub>2</sub>O<sub>2</sub> and generates less reactive  $\cdot OOH$  radical (Eq. (8)) (Sun et al., 2006):



Similar results have also been reported in the literature (Cho and Zho, 2007; Murugandham and Swaminathan, 2004; Chen et al., 2001). From the present experiments we observed that 0.5% H<sub>2</sub>O<sub>2</sub> was an optimum dose. In case of 0.5% H<sub>2</sub>O<sub>2</sub> dose the degradation efficiency was 18% higher than that corresponding to 2.5% H<sub>2</sub>O<sub>2</sub> (Fig.12).

### Conclusion

It has been found that Orange G dye can be effectively treated by UV/H<sub>2</sub>O<sub>2</sub> combination in acidic medium, with small amount of H<sub>2</sub>O<sub>2</sub> and the degradation was maximum in the pH range 1-3. Nearly complete degradation of Orange G dye was observed with UV/ H<sub>2</sub>O<sub>2</sub> combination even without using TiO<sub>2</sub>.

It is also observed that the reflective surface reaction chamber was more effective for degradation of OG azo dye in comparison to ordinary black painted surface. The high intensity light sources increase the degradation efficiency. The dye degradation was fast for dilute effluent in comparison to the concentrate one. The rate of degradation of OG increased with increase in H<sub>2</sub>O<sub>2</sub>

concentration up to 0.5% of sample solution, but above it, there was a decrease in the degradation efficiency.

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