

Treatment of Textile Wastewater Containing Rhodamine B Using Advance Oxidation Processes

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ABSTRACT: Photochemical and Photocatalytic degradation of Rhodamine B (Rh B) dye has been studied in presence of catalyst TiO₂ (Kronos 7050). The degradation study was carried out by using 3 UV lights of different wattage 11watt, 15 watt, and 26watt. The effects of several parameters such as catalyst loading, dye concentration, pH, addition of oxidant H₂O₂ and intensity of UV light were observed for the degradation of Rh B. It was observed that 98% maximum degradation was attained by using TiO₂ (Kronos 7050) at pH 3. Kinetic study showed that first order rate of degradation of Rh B was achieved. It was also observed that intensity of light plays a main role in case of photochemical and photocatalytic degradation of RhB dye.

KEYWORDS: H₂O₂, TiO₂, Photocatalytic, Photochemical, Rhodamine B, UV light source

1. INTRODUCTION

Paper / Textile industry is the major consumer and polluter of water in the manufacturing sector as large quantity of dyes are possible to be out into waste watercourses. The textile/paper industry is growing and subsequently the volumes of wastewater from it have been exponentially increasing with the constantly growing demands [1]. Due to high stability of dyes in temperature and light they can stay in the surroundings for a long time period. The presence of even very small concentrations of dyes in the effluent stream can be very toxic. Depending on the dye concentration and exposure time, dyes or organic material can have severe or long-lasting effects on bare animals. The occurrence of dyes in natural water bodies intimidating the photosynthetic action of aquatic plant and algae and reduces oxygen solubility due to its effect on the absorption of sunlight. Decrease in the level of oxygen hinders the bacterial growth and consequently they become incompetent for the biological degradation of impurities present in the waste water effluent. These reasons make it imperative to eliminate these dyes effectively from the effluents of paper/textile industries before they are thrown into the surroundings [1-3].

For this, generally chemical agent coagulation, adsorption on activated charcoal or reverse osmosis has been used [4]. Though, these systems are non-destructive, and simply transfer pollutants from water to sludge [5]. In addition, such contaminants are often highly toxic, which means that biological treatments cannot be used, although they would be preferable in terms of the financial cost and energy consumption [6].

The elimination of textile dyes from waste water effluent has received a lot of consideration in the last few periods of time by way of accepting different and effective old-style techniques. These include biological, chemical and physical treatment and also some solar and UV light based techniques [7-9]. However, these techniques help to avoid secondary pollution because they are non-destructive and they convert an organic compound into another phase which requires further treatment. In order to overwhelm these drawbacks, because of non-toxicity, high photocatalytic activity, high stability of the TiO₂ photocatalyst, heterogeneous photo catalysis techniques can be efficiently used for the dyes degradation. [10-15].

When energy of UV light with TiO₂ greater than or equal to the band gap energy [16], electrons get transmitted from the valence band to the conduction band of TiO₂ to give electron (e⁻)hole pairs. Generation of hydroxyl radicals at the surface takes place due to positive valence band hole (h⁺). Also, another series of hydroxyl radical is generated due to negatively charged conduction band electron (e⁻) to decrease the no. of oxygen particles existing in the solution[17], [18] as shown in Fig1:

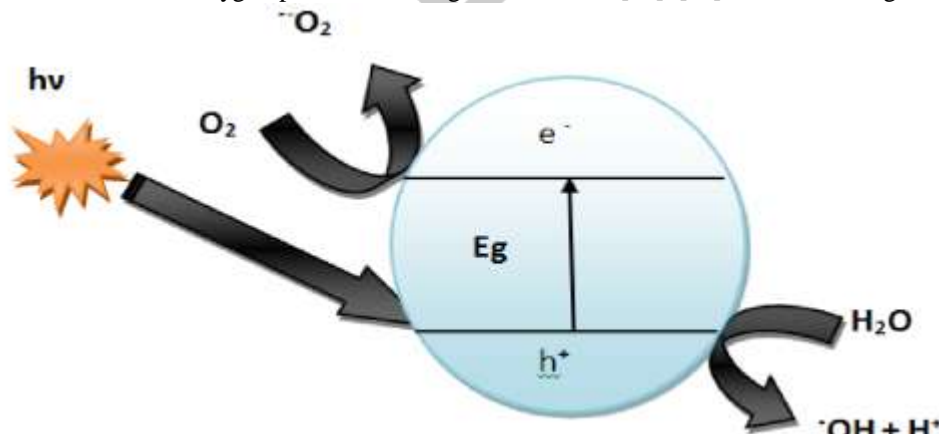


Fig.1: Common photocatalysis mechanism on TiO₂ molecule

In this work the degradation study of Rh B is carried out using photochemical and photocatalytic route. The effects of several parameters such as Rh B dye concentration, catalyst TiO_2 loading, H_2O_2 as external oxidant and pH had been studied on the photocatalytic degradation of Rh B in the existence of TiO_2 (Kronos) under irradiation of different intensity UV lights.

2. EXPERIMENTAL PROCEDURE:-

2.1 Materials

85% pure Rh B dye (Rh B, CAS number: 81-88-9) AR (M.S.) was gained from Thomas baker, Mumbai. Hydrogen peroxide (30% W/V H_2O_2) was acquired from Thomas baker, Mumbai and TiO_2 Kronos was purchased from LobaChemie, Mumbai. Other reagents namely, hydrochloric acid and sodium hydroxide were of A.R. grade (from Merck).

To prepare the dye solutions as per required concentrations demineralized water was used. The molecular weight of Rh B is 479.02 gm/mole and formula of Rh B is $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$. The structure of Rh B [19] is shown in Fig.2

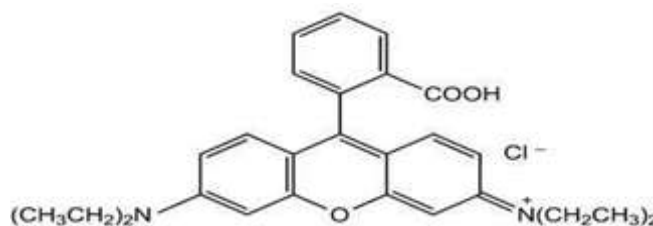


Fig 2: Molecular Structure of Rh B dye

1000 mg/ L stock solution of Rh B was obtained by diluting the Rh B mass in demineralized water and kept in dark. This standard stock solution was used to prepare different initial concentration of Rh B. UV light absorbance reading of spectrophotometer was used for analysis of treated solution

2.2. Photocatalytic Reactor:-

Evaluation of photocatalytic activity of commercial TiO_2 (Kronos 7050) was studied by the degradation of solution of Rh B dye in a cylindrical Quartz glass photocatalytic reactor. The reactor consists of 500 mL quartz glass reactor and three UV lights (11 watt, 15 watt, 26 watt) attached on top of the reactor.

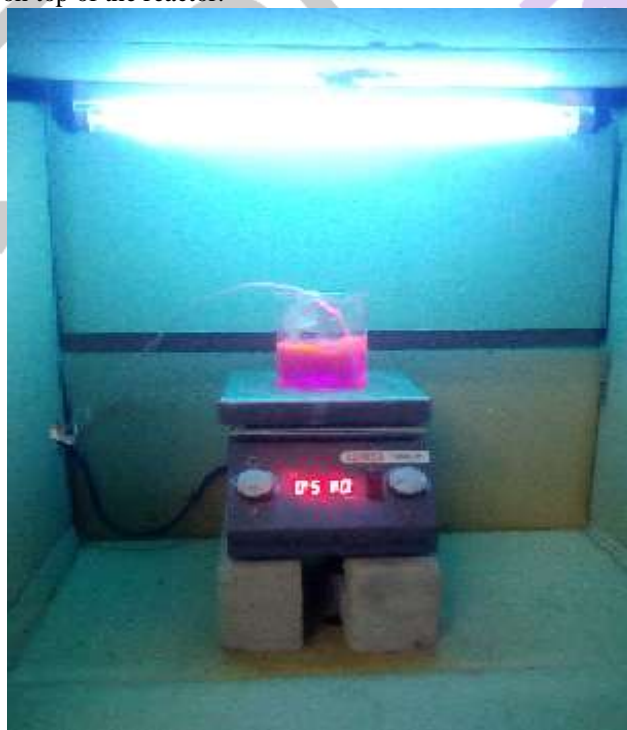


Fig 3. Photocatalytic Reactor Setup

2.3 Experimental Methods

The photochemical degradation of Rh B dye was studied taking 250 ml of 5 mg/L of dye, 0.4ml H_2O_2 and irradiated with UV light. During the photochemical reaction Rh B dye degradation was studied using the H_2O_2 oxidant. The dye concentration was

remaining constant at optimum 5 mg/L and constant pH of 6.5. The photocatalytic degradation was studied using TiO₂ (Kronos 7050) catalyst at optimum dye concentration 5 mg/L. During both the degradation processes the effect of parameters like Rh B concentration, H₂O₂ concentration, pH and TiO₂ (Kronos 7050) were studied. The concentration of dye was varied from 5 mg/L to 50 mg/L. The effect of pH on both processes was studied by varying the pH of the solution from 2 to 10. To reach the desired value of pH of the solution 0.1M HCl or 0.1 M NaOH solutions were added. The photochemical degradation was carried out by adding oxidant like H₂O₂. The effect of oxidant was studied with different concentration. It was 0.1 mL to 1 mL. In photocatalytic processes, Rh B solution was added in the quartz glass reactor with different amount of TiO₂ (Kronos 7050) catalyst. The catalyst amount was varied between 0.4 to 2.4g/L. At the time of experimental work the setup was evacuated for 15 min in dark atmosphere with constant stirring to assure the uniform mixing of Rh B with catalyst. All the experiments were performed for the duration of 150 min. The UV irradiation was carried out with the varying intensity of light using three Phillips 11W, 15W and 26W UV sources. After all the irradiation cycles all the treated samples were cooled. All the initial and final concentrations were measured using the UV- VIS spectrophotometer (SHIMADZU 3200, Japan). To separate the TiO₂ particles from treated samples of photocatalytic process, the samples centrifuged for 10 min. The TiO₂ free samples were used for UV measurement.

After some intervals of time, UV irradiated samples were immediately withdrawn for spectrophotometric analysis. Spectrophotometer was used to record the absorption spectra of samples taken. The % decolorization were measured with spectro-photometric technique by keeping track of the absorbance change at (λ_{max} : - 554nm) of maximum peaks for dye.

3. RESULT AND DISCUSSIONS

Degradation of Rh B dye exhibits first order kinetics w. r. t dye concentration. According to reaction kinetics, a graph of the log of reactant concentration verses time, result in a line whose slope shows the rate of degradation.

$$\ln C_{A0} = k \times T \quad (1)$$

So, % degradation was carried out according to the following relation:

$$\% \text{ Degradation} = (C_{A0} - C_A / C_{A0}) \times 100 \quad (2)$$

Where, C_{A0}: Initial dye concentration (mg/L), C_A: Dye concentration after treatment (mg/L), T: Time of reaction (min). k: Reaction rate constant (min⁻¹),

3.1 Rh B Dye Concentration effect on the %Degradation

The effect of initial Rh B dye concentration on the % degradation was studied at diverse dye concentration (05-25 mg/L), operating temperature of 20 ± 3 °C at 6.65 pH for 60 minutes. The source of UV irradiation is 15 watt UV light.

Fig. 4 shows the results of Rh B dye concentration on % degradation of Rh B using UV light source. It was observed that with increase in Rh B dye concentration, % degradation declines.

It has been observed that with increase in concentration of Rh B dye from 5 to 25 mg/L, the extent of degradation of Rh B dye decreased from 28.8 % to 10.68 %. It is found in many photochemical experiments that rate of degradation were not altered by the initial concentration of compound. The % degradation was maximum at 5 mg/L. The further decrease in rate of degradation above a certain substrate concentration could be due to the combination direct and reverse reactions. Hence further studies were performed at the optimal initial concentration of Rh B i.e. 5 mg/L.

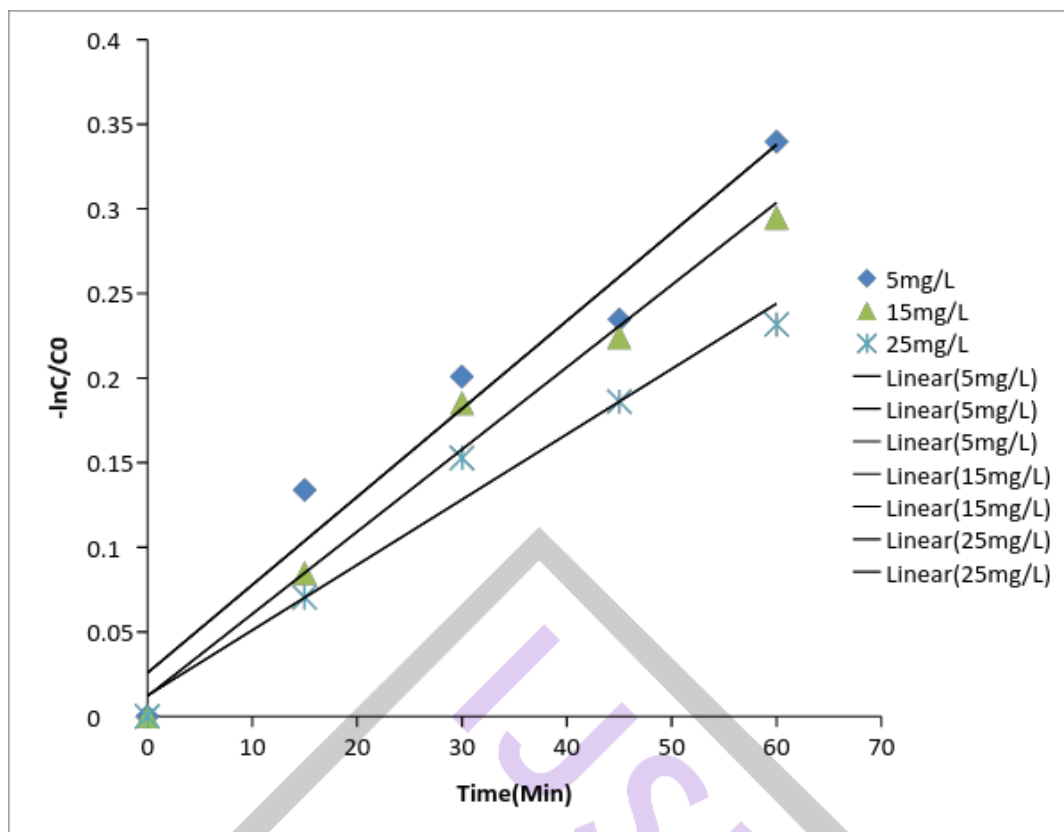


Fig. 4 Graph of First order kinetic showing the effect of Rh B concentration on % degradation of Rh B dye using UV light source (UV light-15 Watt, pH- 6.65 and time - 60 min)

3.2 Effect of Oxidant H₂O₂ on % degradation of Rh B

The Rh B dye degradation was studied with of H₂O₂ ranging from 0.1ml to 1ml under 15 Watt low-pressure mercury UV light source (Philips). The OH[•] radical generation depends on the UV light absorption by H₂O₂ [20]. Hydrogen peroxide readily decomposes into hydroxyl radicals in the presence of UV lights given in below reaction,

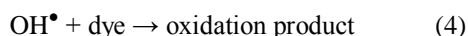
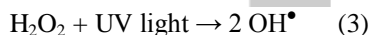


Fig 5 shows the effect of H₂O₂ on % degradation of Rh B using photochemical process. It has been observed that Rh B dye degradation rate increases with increase in concentration of H₂O₂ from 0.1 ml to 0.4ml and decreases after concentration of 0.5 to 1ml.

It was observed that the extent of degradation of Rh B increases from 81.62 % to 94.46 % with increase in the H₂O₂ concentration from 0.1ml to 0.4ml, and formerly decreases up to 54.38 % at 1ml H₂O₂ concentration. This can be explained by the fact that H₂O₂ itself acts as an active OH[•] radical scavenger. At some H₂O₂ concentration, the competition between scavenging of radicals by H₂O₂ and degradation of dye reaches a point with optimal dye degradation. H₂O₂ in presence of UV forms OH[•] radical. With increase in concentration of H₂O₂ the rate of OH[•] radical also increases. But after a certain limits the excess H₂O₂ remains. This excess H₂O₂ recombines with hydroxyl radical and forms H₂O and O₂H[•] radical which has very less oxidation potential compared to that of OH[•] radical. This results in reduction in the time taken for degradation. This optimal concentration of H₂O₂ depends on chemical structure (reactivity and photosensitivity) of the dye [21].

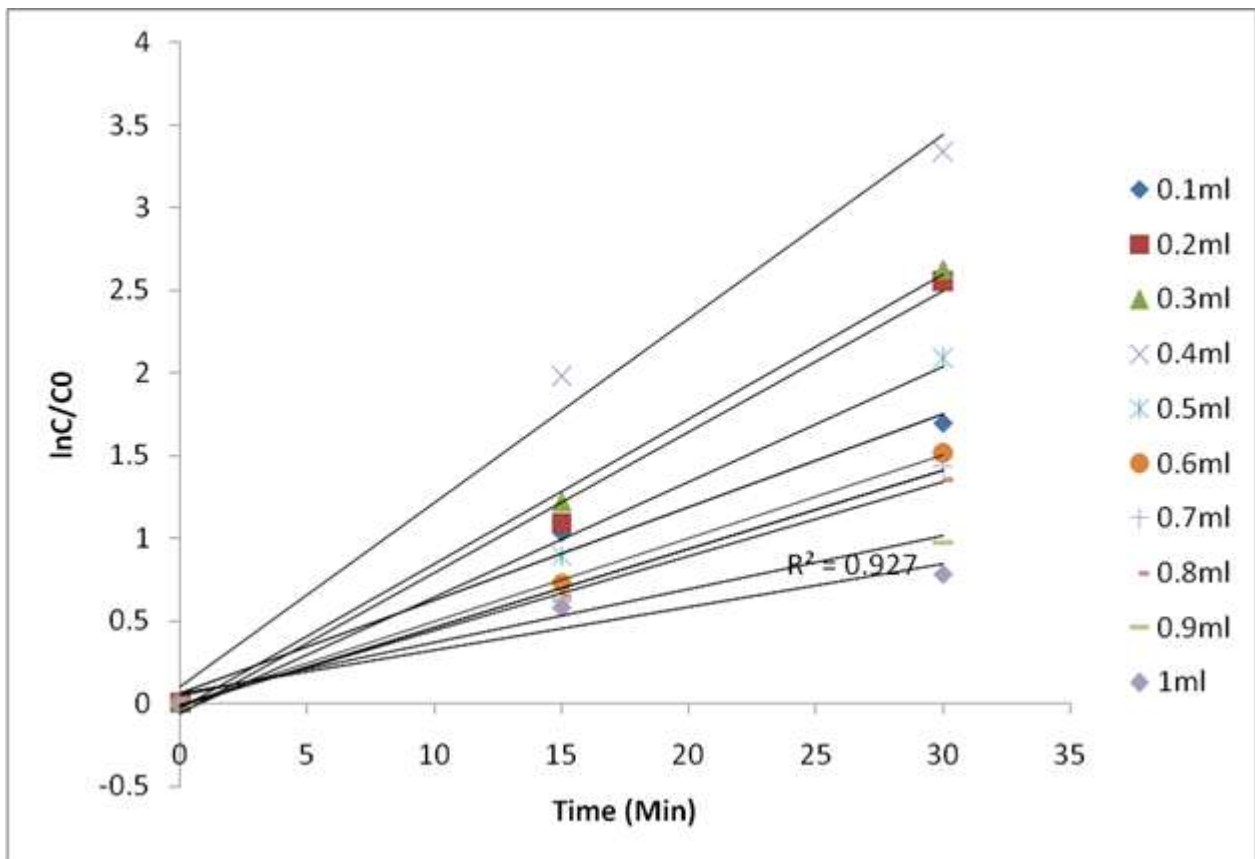


Fig. 5 Graph of First order kinetic showing the effect of H_2O_2 on % degradation of Rh-B dye using photochemical process (Rh B dye concentration – 5mg/L, pH – 2 and total treatment time - 30 min)

3.3 Effect of Initial pH on % Degradation of Rh B Dye

In order to study the effects of pH on UV degradation of Rh B dye wastewater, experiments were performed at various pH values 2, 4, 6.65, 8 and 10. These experiments were conducted at optimal dye concentration (5 mg/L), temperature of $28 \pm 3 \text{ }^\circ\text{C}$ and for 60 minutes. Fig. 6 shows the effect of initial pH on % degradation of Rh B dye using UV light. Initial pH influenced the degradation and the maximum degradation 43.5% was observed at 2 pH. On the other side, at basic pH values lower degradation efficiency was achieved may be due to oxidation potentials of OH^\bullet radicals are less in basic medium as compared to that in the acidic medium and similar things was observed by many authors [22], [23],[24].

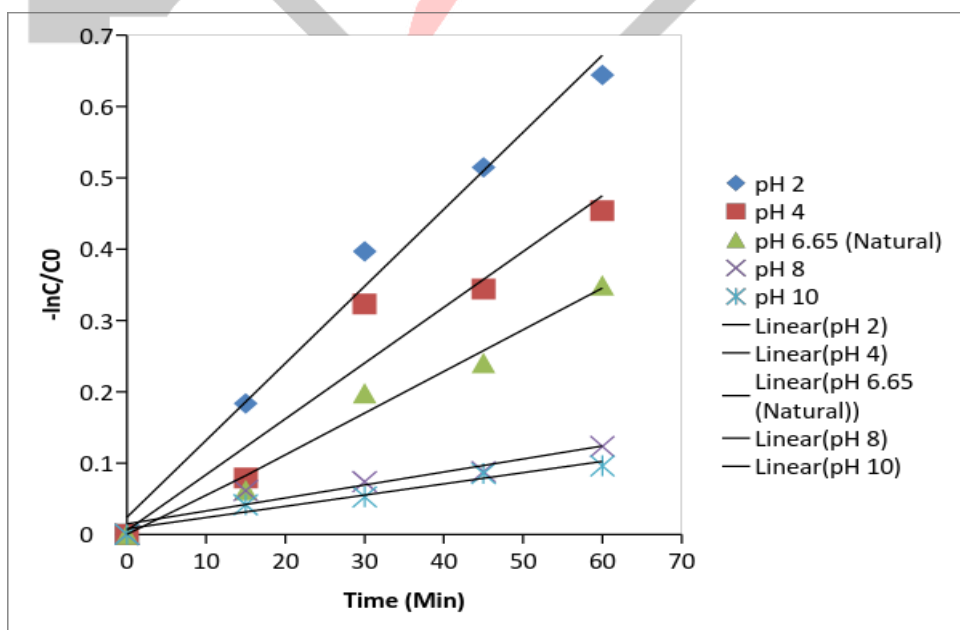


Fig. 6 Graph of First order kinetic showing the effect of pH on % degradation of Rh B dye in presence of UV (initial dye concentration – 5 mg/L, UV light-15watt and UV irradiation time – 60mins)

3.4 Effect of H₂O₂ on Various Concentration of Rh B Dye by Using UV+H₂O₂

The degradation of Rh B dye ranging from 5mg/L to 50 mg/L was investigated in presence of optimal concentration of hydrogen peroxide using UV irradiations of 15 Watt low-pressure mercury UV tube lights (Philips).

Fig.7 projects the effect of oxidant H₂O₂ on the rate of degradation of Rh B using photochemical process.

It has been examined that as we increased concentration of Rh B dye from 5 to 50 mg/L the extent of degradation decreased from 96.46 % to 10.18 %. The degradation was max. at 5 mg/L. The further decrease on rate of degradation above a certain substrate concentration could be due to combination direct and reverse reactions.

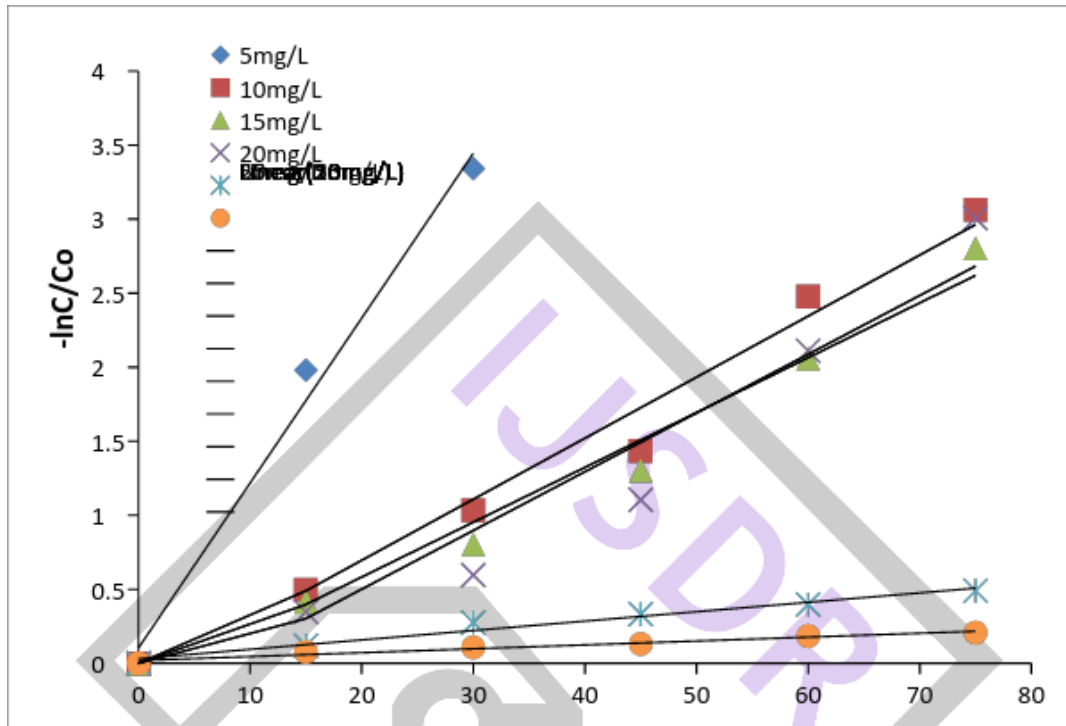


Fig. 7 Graph of First order kinetic showing the effect of oxidant H₂O₂ on % degradation of Rh B dye in presence of UV light (15 watt) (subjected to concentration Rh B dye - 5mg/L, 10mg/L, 15mg/L, 20mg/L, 25 mg/L, pH-2, H₂O₂ loading- 0.4ml (UV irradiation time-75min)

3.5 Effect of Oxidant H₂O₂ % degradation of Rh B Dye in Absence of UV

The % degradation of Rh B dye ranging from 5mg/L to 50 mg/L was studied at optimal concentration of H₂O₂ in absence of UV light. Fig.8 shows the effect of H₂O₂ on the rate of degradation of Rh B in absence of UV light source. It has been observed that with increased in concentration of Rhodamine- B dye from 5 to 50mg/L rate of degradation decreased. It has been perceived that with the increase in concentration of Rh B dye from 5 to 50mg/L the extent of degradation decreases from 24.3 % to 9.57 %. The degradation was max. at 5 mg/L. The further decrease in rate of degradation above a certain substrate concentration could be due to the combination direct and reverse reactions.

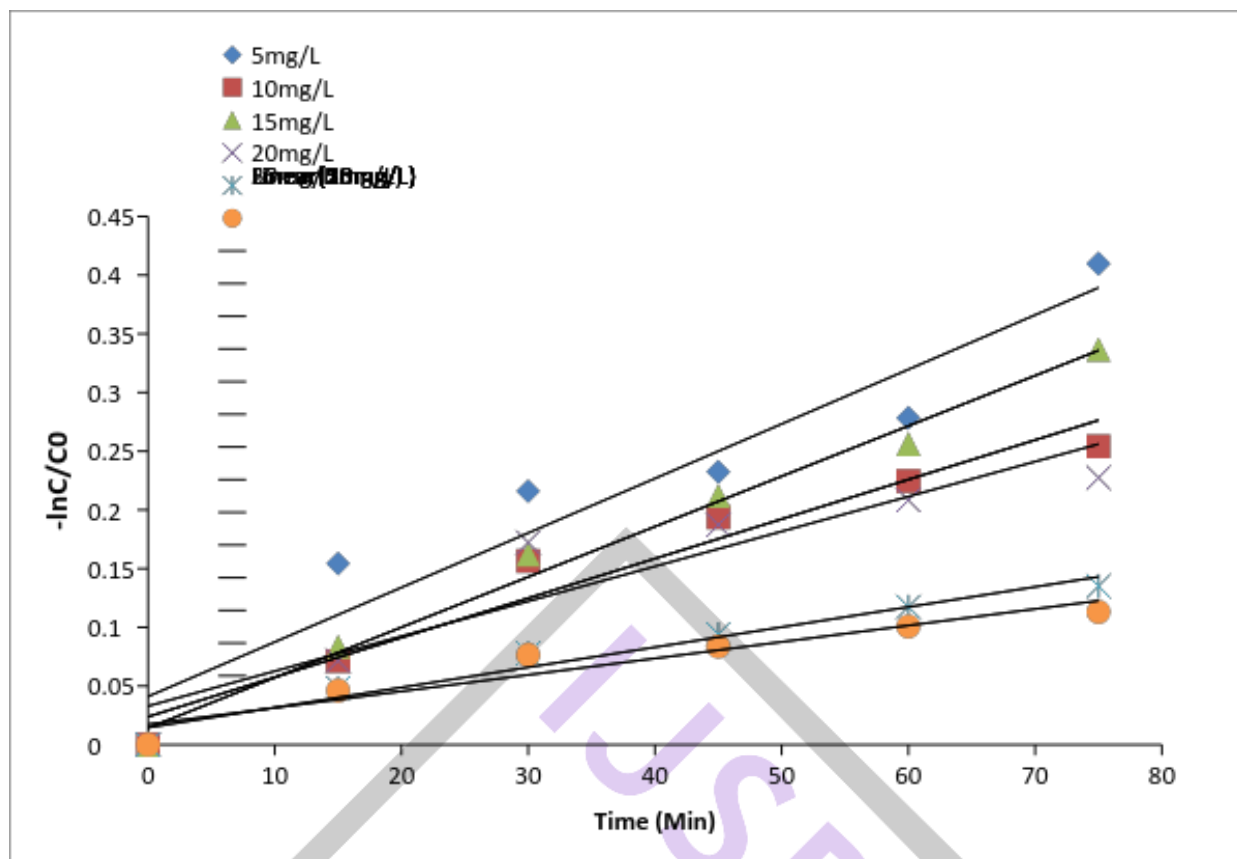


Fig.8 Graph of First order kinetic showing the effect of oxidant H₂O₂ on % degradation of Rh B dye in absence of UV light (subjected to concentration Rh B dye - 5mg/L, 10mg/L,15mg/L,20mg/L,25 mg/L, pH-2, H₂O₂ loading- 0.4ml (time-75min)

3.6 Effect of Intensity of UV Light on % degradation of Rh B Dye

The % degradation of 5mg/L Rh B dye was studied in presence of different intensity UV light (11 watt, 15 watt and 26 watt) at 2pH for 15minutes. Fig.9 (a) and (b) shows the effect of Intensity of UV light on % degradation of Rh B using photochemical process. It has been noticed that the rate of degradation of Rh B dye increases with increasing Intensity of light. The results indicate that as light intensity increases, the photocatalytic degradation of Rh B increases achieving a maximum value at 26watt. Table 1 shows the effects of intensity of UV light on degradation % and first order reaction rate constant of Rh B dye. Study shows that increase in the Intensity of UV light from 11watt to 26Watt the extent of degradation of Rh B increases from 41.6% to 99.1%

Table 1 Effect of Intensity of light on the First order reaction rate constant Rh B dye by using UV light (Total treatment time – 15 min)

Intensity of UV light	First order reaction rate constant ($k \times 10^{-3}, \text{min}^{-1}$)
11 Watt	35.85
15 Watt	232.88
26 Watt	314.03

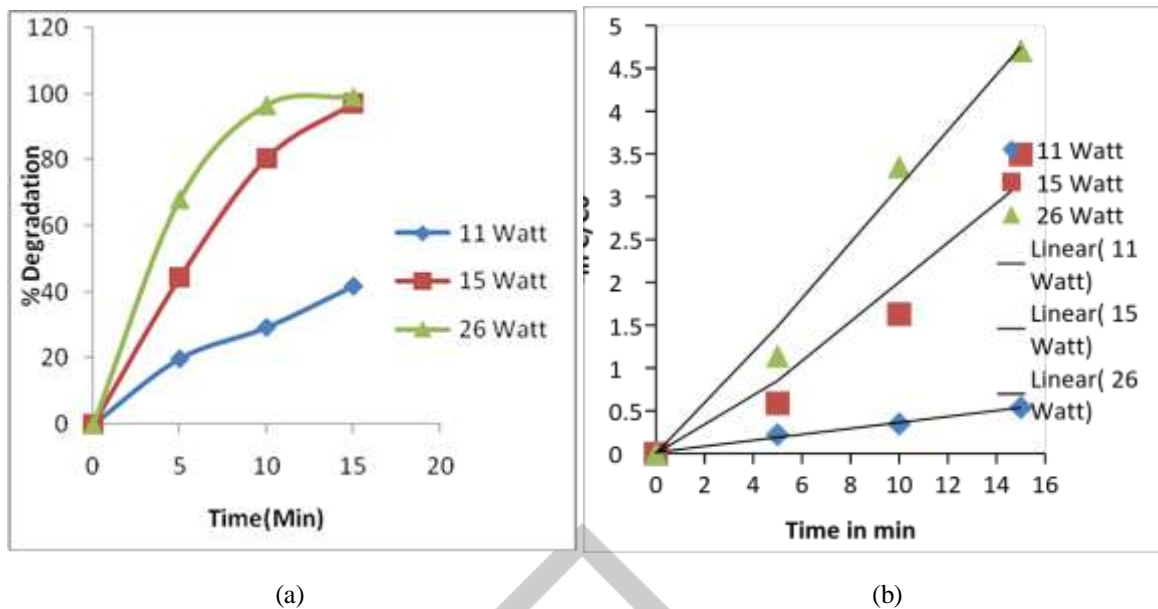


Fig.9(a)First order kinetic and (b) % Degradation plot showing the effect of Intensity of light on degradation rate of Rh B dye by using UV light (subjected to concentration Rh B dye - 5mg/L, pH-2, H₂O₂ loading- 0.4ml (time-15min)

3.7. Photocatalytic Degradation of Rh B

The photocatalytic reaction result of TiO₂ (Kronos 7050) was studied for the degradation of Rh B (5mg/L) dye irradiated with UV light. To study the photo degradation of dye, following experiments were carried: (a) UV light irradiation on Rh B dye solution without contact of photocatalyst; (ii) UV light irradiation on Rh B dye aqueous solution and TiO₂ (Kronos 7050) photocatalyst (1.6 g/L) Table 2 shows the effects UV light on extent of degradation and first order reaction rate constant of Rh B dye with and without catalyst. It was observed that % degradation of RhB dye was 28.8% in the absence of photocatalyst whereas, 75.06% degradation was obtained in presence of photocatalyst TiO₂ (Kronos 7050) and UV light source at the end of 150 min as shown in Fig. 10.

Table 2 Extent of Degradation of Rh B dye with and without TiO₂ (Kronos 7050) catalyst in the existence of UV light source (Total treatment time – 150 min)

System	Extent of degradation (%)	First order reaction rate constant (k×10 ⁻³ , min ⁻¹)	R ² Value
Only UV	28.8	2.44	0.9598
UV+Catalyst	75.06	18.2	0.9732

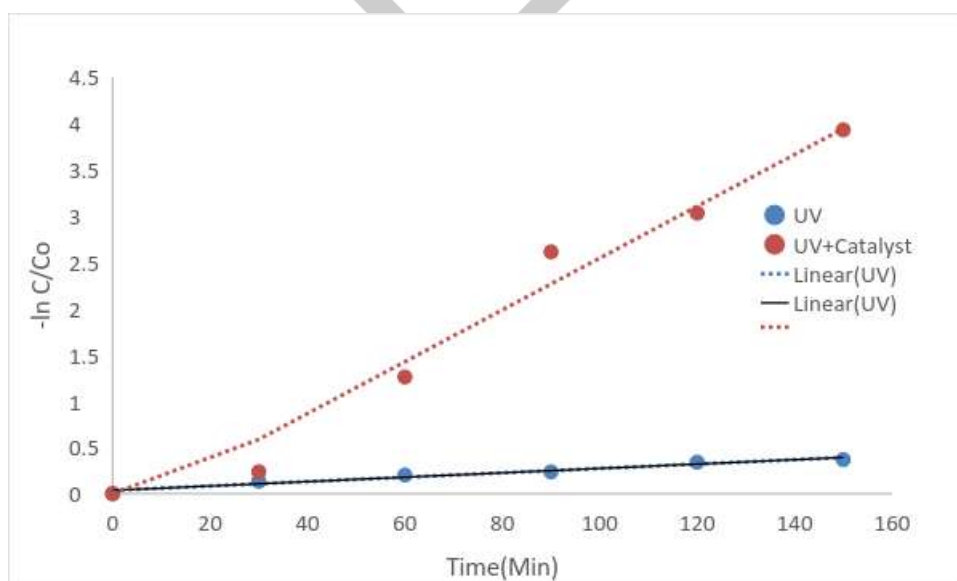


Fig. 10 Graph of First order kinetic showing the effect of catalyst on the rate of degradation of Rh B dye by using UV.

3.8 Effect of catalyst concentration on % degradation of Rh B dye:-

To find out optimum amount of catalyst is necessary for higher photocatalytic degradation for that in experiments, catalyst concentration was varied from 0.4 to 2.4 g/L. Optimum concentration of Rh B (5mg/L) was taken for all experiments. The effect of catalyst concentration on % degradation of Rh B dye by using UV light irradiation shown in Fig 11. The reaction was carried out for 150 minute from the study it was observed that % degradation of Rh B dye increased from 41.04 to 75.06% with increase of amount of catalyst till 1.6 g/L. But % degradation of Rh B dye was reduced from 75.06 to 52.4% as increased in catalyst concentration from 1.6 to 2.4 g/L. This may be found because of with increase in turbidity of solution by catalyst loading results into UV light penetration [25, 26] or due to scattering of light. From the results, it was observed that 1.6 g/L optimum amount of TiO₂ required to achieve higher degradation rate optimal amount of catalyst (1.6g/L) required.

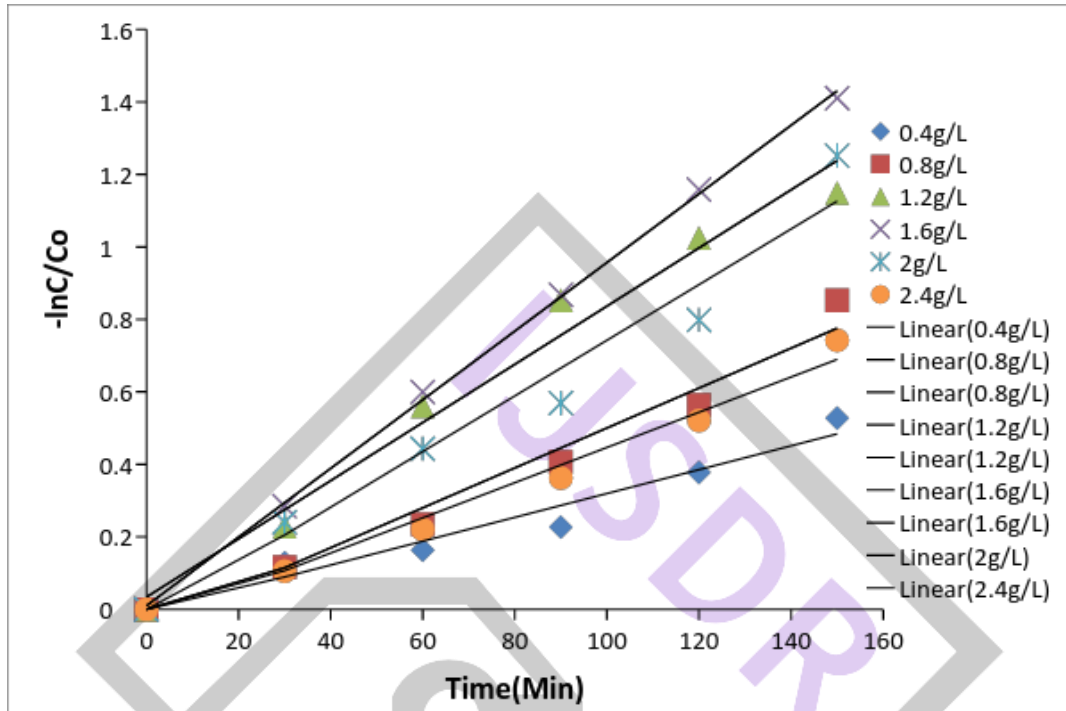
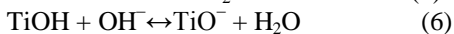
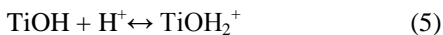


Fig.11 Graph of First order kinetic showing the effect of catalyst concentration on the rate of degradation of Rh B dye by using UV.

3.9 Effect of pH on Degradation of Rh B

Wastewater effluent of different industries is acidic or basic in nature. [27,28] So, for effective degradation of different dyes optimum pH value should be find out., but pH value id dependent upon ionization state of reactant and catalyst surface. The states of ionization of TiO₂ surface are as follows (i) positive(+) charge in alkali medium (ii) negative (-) charge in alkaline medium.



Experiment were carried out at optimal Rh B dye concentration (5mg/L) and optimal catalyst concentration (1.6g/L) by varying pH of mixture from 2 to 11. By adding appropriate amounts of HCL or NaOH solution pH was adjusted. The natural pH of the Rh B dye solution was 6.65. Table 3 shows the effects pH on extent of degradation and first order reaction rate constant of Rh B dye in presence of catalyst. Fig. 12 shows that % degradation of Rh B increased from 75.6 to 80.4% as decreased in pH value from 6.65 to 4 and decreased in % degradation of Rh B dye from 80.4 to 60.54% at 2 pH. Similarly, the % degradation was decreased from 75.6 to 43.4% with increase in pH from 6.65 to 11. Under alkali condition the surface of TiO₂ catalyst becomes positively charged. Dye adsorption on catalyst surface and % degradation (max. 80.4%) of dye is increased because of carboxylic (CO⁻) groups of Rh B were ionized and form a negatively charged atom [29]. At lower pH value Rh B get highly adsorbed because of that TiO₂ catalyst withdrawn the light penetration.

Table 3 Effect of pH on first order reaction rate constant of Rh B dye with catalyst TiO₂ in the presence of UV light irradiation (Total treatment time – 150 min)

pH	First order reaction rate constant (k×10 ⁻³ , min ⁻¹)
2	6.19
4	10.86
6.65	9.4
8	5.72
10	3.794

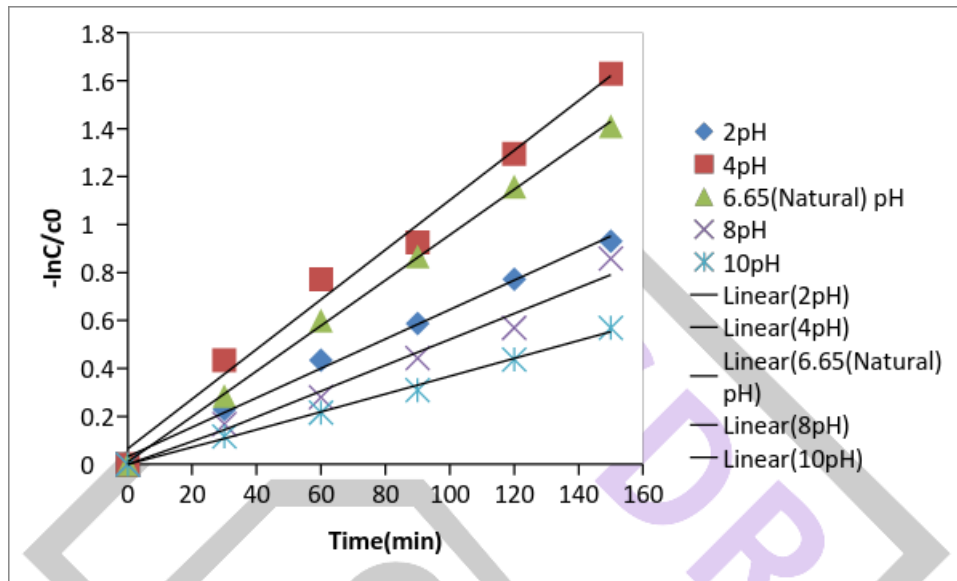
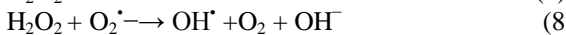
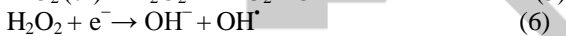
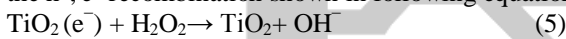


Figure 12 Graph of First order kinetic shows the effect of % degradation of Rh B dye by using UV + TiO₂.

10. Effect of Intensity on % Degradation of Rh B using H₂O₂ and TiO₂ (Kronos 7050)

Hydroxyl radical concentration helps to increase rate of degradation of dye. OH[•] radical act as an substitute electron acceptor to oxygen. For that to increase hydroxyl radical concentration for increase in degradation of Rh B dye degradation hydrogen peroxide was added to the reaction mixture. Likewise H₂O₂ also produces OH[•] radicals through photo degradation and it prevents the h⁺, e⁻ recombination shown in following equations [30, 31].



To study the effect of H₂O₂ on % degradation of Rh B dye, the addition of H₂O₂ was done at optimum 0.4ml by keeping Rh B dye concentration(5mg/L) and amount of catalyst (1.6 g/L) fix for all experiments. Table 4 shows % Degradation of Rh B dye in presence of catalyst TiO₂ with varying intensity of UV light (Total treatment time – 150 min)

The results shown in Fig. 13 (a) and (b) demonstrated that the percentage degradation and first order kinetics of RhB was increased due to H₂O₂ addition. Rh B dye degradation without addition of H₂O₂ was 80.4% at optimum pH 4 and after addition optimum 0.4ml of H₂O₂, it was reached to 99.8% at maximum intensity of light 26 watt. For the same optimum condition but at lower intensity of UV light 11watt, 15 watt the percentage degradation was 53.6% and 75.8% respectively after 150 min irradiation of UV tube light [32].

Table 4 First order reaction rate constant of Rh B dye in presence of catalyst TiO_2 with varying Intensity of UV light from 11 watt to 26 watt under of UV light irradiation (Total treatment time – 150 min)

Intensity of light(Watt)	First order reaction rate constant ($k \times 10^{-3}, \text{min}^{-1}$)
11	5.12
15	9.45
26	26.08

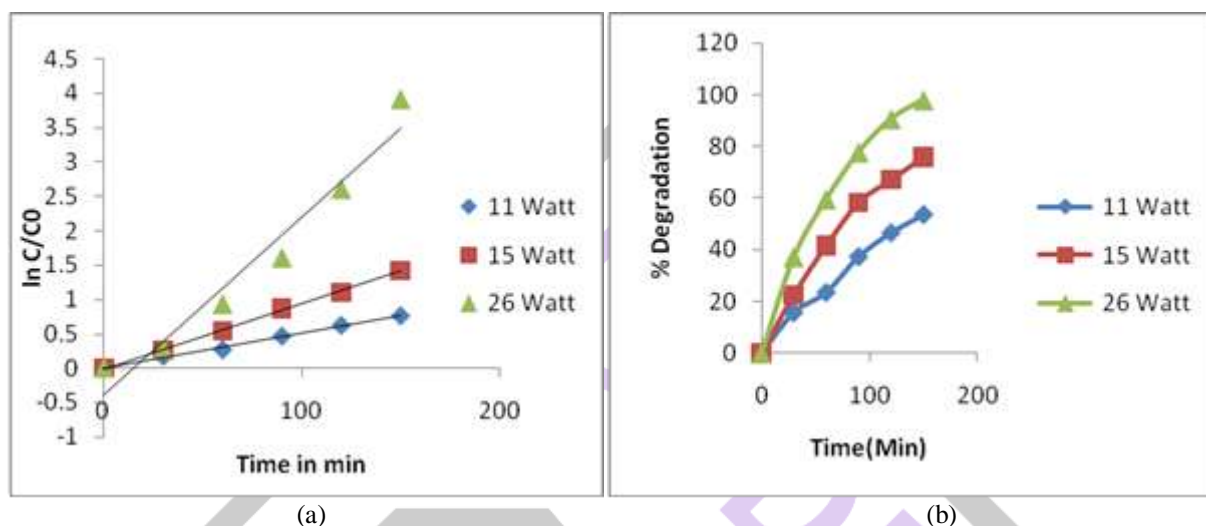


Fig. 13(a) First order kinetic plot and (b) % Degradation plot showing the effect of H_2O_2 and intensity of UV tube lights on the rate of degradation of Rh B dye by using UV + TiO_2

CONCLUSION

We have studied the novel photochemical and photocatalytic degradation of Rh B dye using H_2O_2 and TiO_2 (Kronos 7050) respectively. The percent degradation and degradation rate were influenced by the initial concentration of Rh B, pH of solution, amount of H_2O_2 for photochemical, amount of TiO_2 for photocatalytic and intensity of UV light. The optimum conditions for the degradation of Rh B in photochemical processes were observed at pH 2, 0.4ml of H_2O_2 with 5 mg/L Rh B dye concentration at 26 W UV light. The optimal amounts of pH, dye concentration and catalyst concentration for higher degradation in photocatalytic process were 3, 5mg/L and 1.6 g/L respectively at 26 watt UV light. It has been observed in photochemical process that increase in the intensity of UV light From 11 W to 26W, the extent of degradation of Rh B increases from 41.6 % to 99.1 % for 15 min reaction time and 53.6% to 99.8% for 150 min reaction time for photocatalytic process. This increase in reaction time was described due to increase in turbidity of the solution due to light scattering and screening which results decrease in UV light penetration and photo activated volume. We recommend that photochemical process can be utilized for the photo degradation of other dyes also. This method is cheap, rapid degradation and simple handling method.

ACKNOWLEDGEMENT

We would like to gratefully acknowledge Bharati Vidyapeeth Deemed University College of Engineering, Pune and K. K. Wagh Polytechnic, Nashik for providing the necessary infrastructural facilities during my research.

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