Optimized photocatalytic parameters for the degradation of Rhodamine-B dye with ZnO under artificial light illumination

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*Abstract:*Present work summarized fast, efficient, solvent free and green synthesis of Zinc Oxide (ZnO) by thermal disintegration of zinc oxalate precursor for photocatalytic degradation of Rhodamine-B dye. Synthesized ZnO catalyst was primarily characterized by UV- Visible Spectroscopy, FT-IR Spectroscopy, XRD techniques. Optimization of photocatalytic parameters were investigated with dye initial concentration (50-150ppm), ZnO loading quantity (50-150mg/100ml), Initial pH of the suspension (6-11), Illumination time (0-6 hrs) under sufficiently constant light intensity irradiation source (400W-MH-TBT-E40) providing 52000-53000 Lux radiation intensity at 15cm distance. Degradation efficiency was estimated from colorimetric absorbance measurement. The optimum photocatalytic parameters were found to be 50 ppm of Rhodamine-B and 100 mg ZnO /100 ml of dye solution at pH=10 for illumination time of 6hrs and for 100% degradation efficiency. Present work is important for understanding the effect of various photocatalytic parameters for the degradation of Rhodamine-B dye with ZnO under artificial light illumination.

*Keywords:*ZnO; Rhodamine-B; photocatalytic parameters;

I. INTRODUCTION

Global climate change and water scarcity are two tenacious present issues. During present days every continent in the world are fighting against problem of water scarcity and drought situations [1-3]. Increased demands of clean intake water and water for sterile purposes are two burning problems of our society [4]. To tackle not only with water scarcity and drought situations but also to meet the demand of society, rain water harvesting and water treatment or detoxification are best initiatives needs to be implemented.

Dyes are colored organic substances mainly used in textile, leather, paper and plastics industries as coloring agents [5]. Inappropriate release of effluents by these industries generally contains dyes and pigments at non acceptable levels, hence severely contributes to the soil, water and environmental contamination [6-8].   A total of 10–15% of the world production of dyes is lost during the dyeing process and is released in textile effluents [9, 10]. This huge discharge of untreated organic chemicals into the water reservoirs leads to severe effect on aquatic life such as enhanced eutrophication, reduction of the local biodiversity[9, 11] and promoting environmental danger due to the chemicals refractory carcinogenic nature [9, 12]. The degradation of these dyes from effluents is necessary prior to their release into water to stop the soil and water pollution. Due to toxic and nonbiodegradable nature, majority of dyes cannot be subjected to use biological treatment processes [6, 13-15]. Traditional methods like adsorption, flocculation, coagulation, ultrafiltration, reverse osmosis and activated sludge process are not capable for complete destruction of dye pollutants [5, 16].Thus development of novel technologies for the remediation of water contaminated with dyes are necessary.

The implementation of solar light driven advanced oxidation process (AOPs) has been a promising alternative for the detoxification of industrial effluents [9, 17-20], and hence for the environmental protection [20]. Among AOPs, the photocatalysis is one of the most efficient and economical methods employed for the total mineralization of organic contaminants to CO_2, H_2O and inorganic salts[6, 21-24]. Several metal oxides like TiO_2, ZnO, SnO_2, NiO, Cu_2O, Fe_3O_4, etc. have been utilized as photocatalyst for dye degradation; these are stable, nontoxic, highly photosensitive, wide band gap materials[5]. An activated metal oxide usually promotes the photodegradation of dyes under solar light[5].

Lack of sufficiently intensity solar lights during cloudy days and its absence during night time limits the extent of photocatalysis for some instance. Also there are few countries in the world which are far away from the reach of solar light for sufficient period of time. Now a days variety of artificial irradiation sources having several thousand hours of lifetimes are economically available providing desirable flux light intensity. Photocatalysis using artificial light illumination needs to be developed, which will be beneficial for water remediation and waste water treatments.

Present work is on the optimization of photocatalytic parameters for the degradation of Rhodamine-B dye with ZnO under artificial light illumination. Rhodamine B, which belongs to the dyes family known as fluorides, is an organic molecule considered to be very stable that does not suffer degradation with visible light [6]. The chemical structure of the dye molecule is shown in Figure 1.
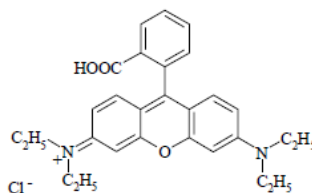
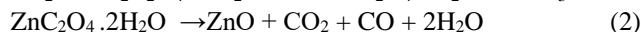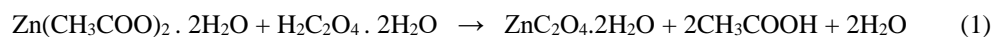**Figure 1: Chemical structure of the Rhodamine-B dye molecule**

II.EXPERIMENTAL

2.1. Materials

Zinc acetate dihydrate (99.0%), oxalic acid dihydrate (99.5%), Rhodamine-B (99.0%) and all other chemicals used during this work were of A.R.grade, obtained from S.D. Fine Chemicals, India and were used without further purification. Distilled water was used to prepare all solutions. The desired pH of the solutions was attuned with NaOH (0.1N) and HCl (0.1N).

2.2. Synthesis of photocatalyst

Zinc oxide (ZnO) powder was prepared by fast, efficient, solvent free and green synthesis by thermal disintegration of zinc oxalate dihydrate precursor obtained with simple mechanical hand grinding of a mixture of 1.0mol of zinc acetate dihydrate and 1.1mol of oxalic acid dihydrate in agate mortar for 20-30 minutes at room temperature. Thermal disintegration of zinc oxalate precursor by calcination at 450^0C leads to the formation of ZnO[25-27].

$$Zn(CH_3COO)_2 . 2H_2O + H_2C_2O_4 . 2H_2O \rightarrow ZnC_2O_4.2H_2O + 2CH_3COOH + 2H_2O \quad (1)$$
$$ZnC_2O_4 .2H_2O \rightarrow ZnO + CO_2 + CO + 2H_2O \quad (2)$$

2.3. Equipments

The synthesized ZnO powder was preliminarily studied by UV-Visible Spectrophotometer (*PerkinElmer* Lambda 365) and FT-IR (*PerkinElmer* UATR Spectra Two) spectrometer. The X-ray diffraction (XRD) pattern of the ZnO crystallite was obtained on X-ray Diffractometer (*Miniflex*-600) with Cu Kα radiation (λα = 1.5418Å) and the average crystalline size (D) of the particles was determined from the Debye-Scherer equation: $D = 0.90\lambda / \beta cos\theta$ where, λ is the wavelength (Cu Kα), β is the full width at the half maximum (FWHM) of ZnO and θ is the diffraction angle **[28]**. The photocatalytic reactions were carried out at room temperature in batch reactor under sufficiently constant intensityartificial light irradiation source (400W MH-TBT-E40) providing 52000-53000 Lux radiation luminous intensity at 15cm distance. Degradation efficiency was estimated from colorimetric absorbance measurement with digital colorimeter (EQUIP-TRONICS EQ-353). The initial pH of suspension was adjusted with the help of pH meter (LABTRONICS LT-11). Intensity of light was checked by Lux meter (HTC LX-100).

2.4. Photocatalytic degradation experiments

For photocatalytic degradation and photocatalytic parameters optimization studies, Rhodamine-B dye solutions with different initial concentration were prepared using distilled water. In all experiments in a batch photoreactor, 100 mL of Rhodamine-B dye solution with known initial concentration at appropriate pH and at room temperature was taken with known amount of zinc oxide powder in a glass container with 5 cm inner diameter and mixture was then agitated by means of sonication for 5 minutes to obtain uniform suspension[26]. Container was then mounted on magnetic stirrer kept under artificial light irradiation sourceat a distance of 15 cm. At specific intervals the 5 ml sample from supernatant solution was collected, centrifuged to separate ZnO powder and the absorbance was recorded with digital colorimeter at 500-530nm. The degradation efficiency was estimated as % Degradation: $\%D = 100[A_0 - A_t] / [A_0]$ where %D – Percent Degradation, A_0-Initial absorbance, A_t -Absorbance at time t.

III. RESULT AND DISCUSSION

3.1. Characterization of Zinc oxide

Primary characterization of the synthesized zinc oxide powder was done by various techniques viz. FT-IR Spectroscopy, XRD technique and UV- Visible Spectroscopy.

3.1.1. FT-IR Study

Zinc oxalate precursor shows well defined bands at 493, 588, 723, 822, 1122, 1245, 1319, 1364, 1626, 1888 & 3390 cm^{-1} frequencies corresponding to various stretching and bending vibrations. When zinc oxalate precursor is subjected to calcination at 450^{0}C all other bands other than those for Zn-O bond stretchingat 450cm^{-1} were disappeared, which confirms the formation of spherical shape ZnO and same also confirmed by XRD study.

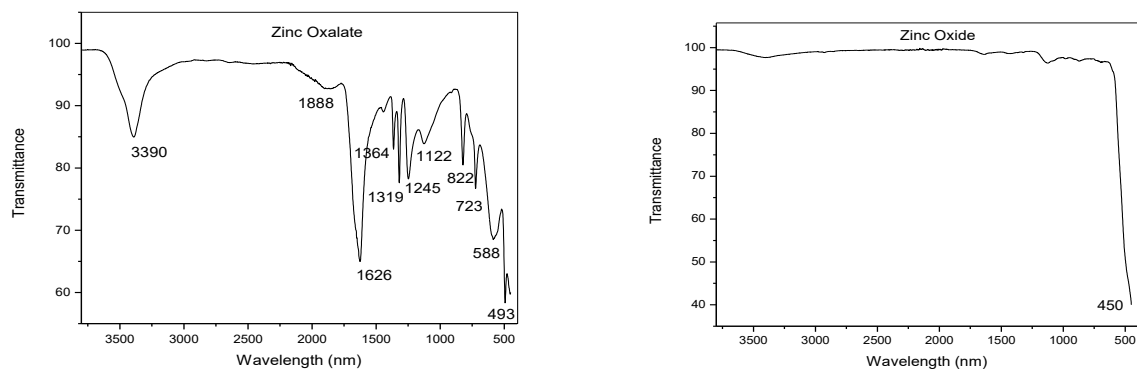**Figure 2: FT- IR spectra of zinc oxalate dihydrate and zinc oxide**

3.2.2. XRD Analysis

The XRD intensity data for ZnOwere collected over a 2θ range of 20-80°using Cu Kα radiation (λ=1.5418 A^{o}) representing a series of peaks centered at 2θ = 31.86°, 34.52°, 36.36°, 47.64°, 56.68°, 62.96°, 66.44°, 68.04°, 69.18°, 72.62°, 77.04° belonging to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes respectively (Figure 3). This data were in good agreement with the JCPDS card for the standard wurzite structure of pure ZnO[29]. The average crystallite size of ZnO was found to be 44.34nm with FWHM = 0.2287^{0} for most intense peak corresponding to (101) plane and as estimated by Debye Scherer's formula [28].
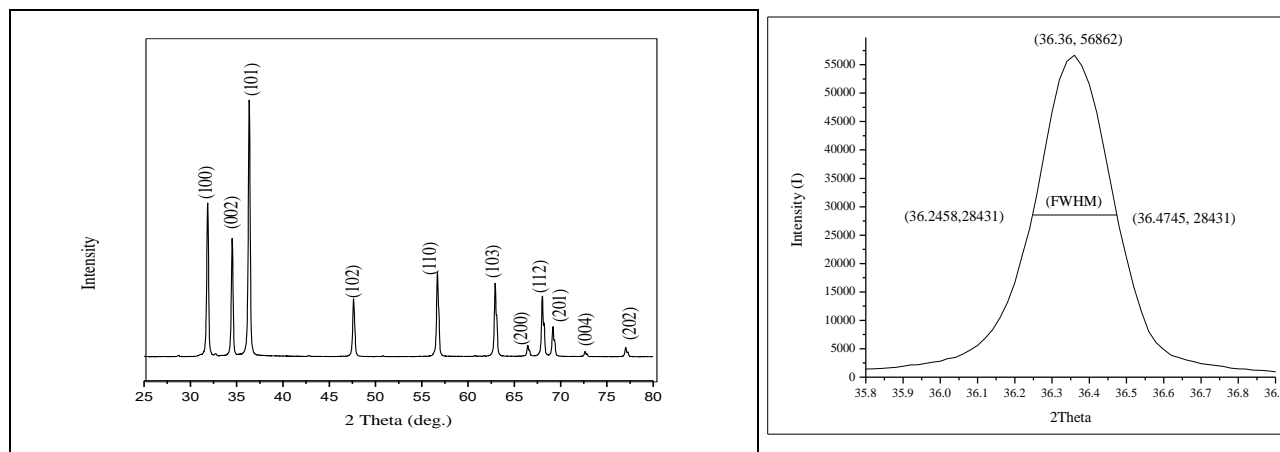

Figure 3: XRD pattern of ZnO

3.2.3. UV-Visible Spectra

UV-visible Spectra of ZnO is shown in the Figure 4 which shows markedly situated optical extinction bands in the range of 385 nm to 410 nm. The band gap energy of ZnO was calculated with cutoff wavelength ($\lambda_{cutoff} = 396.36nm$) using well known relation $E_{bandgap}$ (in eV) = (1240/ λ_{cutoff}) which is found to be 3.128eV.
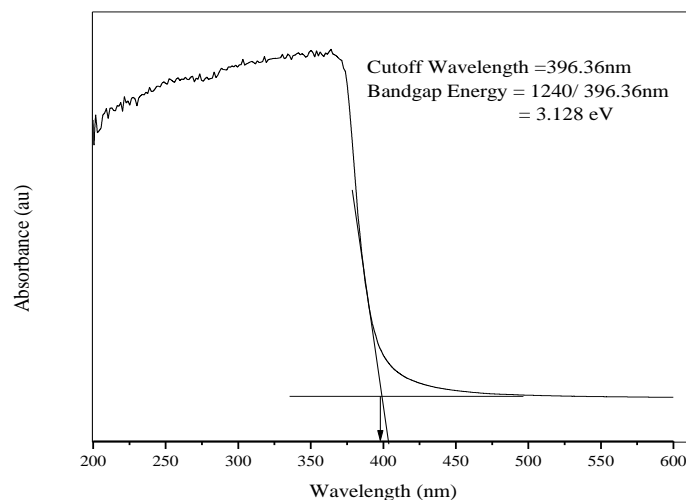

Figure 4: UV-visible Spectra of ZnO

3.3. Optimization of photocatalytic parameters for degradation of Rhodamine-B over ZnO catalyst

Optimization of photocatalytic parameters for the degradation of Rhodamine-B over ZnO surface were investigated with dye initial concentration (50-150ppm), ZnO loading quantity (50-150mg / 100ml), Initial pH of the suspension (6-11), Illumination time (0-6 hrs) under sufficiently constant intensity irradiation source. Degradation efficiency was estimated from colorimetric absorbance measurement and the results are encountered as follows

3.3.1. Effect of the photocatalyst amount

Rhodamine-B does not showed photolysis in absence of ZnOas found in blank experiment. The optimum amount of ZnO photocatalyst required for complete mineralization of Rhodamine- B dye to CO_2 and H_2O and inorganic ions was examined by varying the amount of ZnO from 50 to 150 mg/100 ml. It was observed that, the percent degradation increases with the increased amount of ZnO loading. The results obtained are summarized in Table 1 and Figure 5. 100ml 50ppm Rhodamine-B dye solution at natural pH (7.42 - 8.04) was almost completely mineralized on 7 hours irradiation under artificial light source to an extent of 91.13% with 100mg ZnO, 100% with 125mg ZnO and 100% with 150mg ZnO. That is there is very small change in the percent degradation of Rhodamine-B dye for the increase of ZnO loading by 25mg from 100mg to 125mg to 150mg of ZnO, analogous results were also illustrated for the degradation of 100ml 25ppm Rhodamine-B dye solution at natural pH (7.42 - 8.04) on 4 hours of irradiation. Hence 100mg ZnO / 100ml of dye solution was selected as the optimum quantity of ZnO for the optimization studies of rest of the parameters. Also less quantity of ZnO was selected as optimum quantity because as the amount of ZnO increases the turbidity of solutions also increases which produces shadowing and screening effect for the light photons due to scattering of light **[30, 31]** and hence contributes to negative impact on photocatalytic degradation.

Table 1 : Variation of % degradation with catalyst quantity for 100ml 50ppm Rhodamine-B dye solution at natural pH (7.42 - 8.04)

| [ZnO] (mg/100ml)	Irradiation time (hrs)								
	1	2	3	4	5	6	7	8	9
50mg	0.00	2.42	4.84	10.48	22.58	33.06	45.16	69.35	89.52
75 mg	0.00	3.23	5.65	13.71	25.00	36.29	50.81	74.19	93.55
100 mg	0.81	4.84	6.45	24.19	47.58	69.35	91.13	100.00	100.00
125 mg	2.42	5.65	17.74	37.10	67.74	87.10	100.00	100.00	100.00
150 mg	3.23	11.29	28.23	50.00	72.58	92.74	100.00	100.00	100.00
100ml 50ppm Rhodamine-B dye solution at natural pH (7.42 - 8.04)									
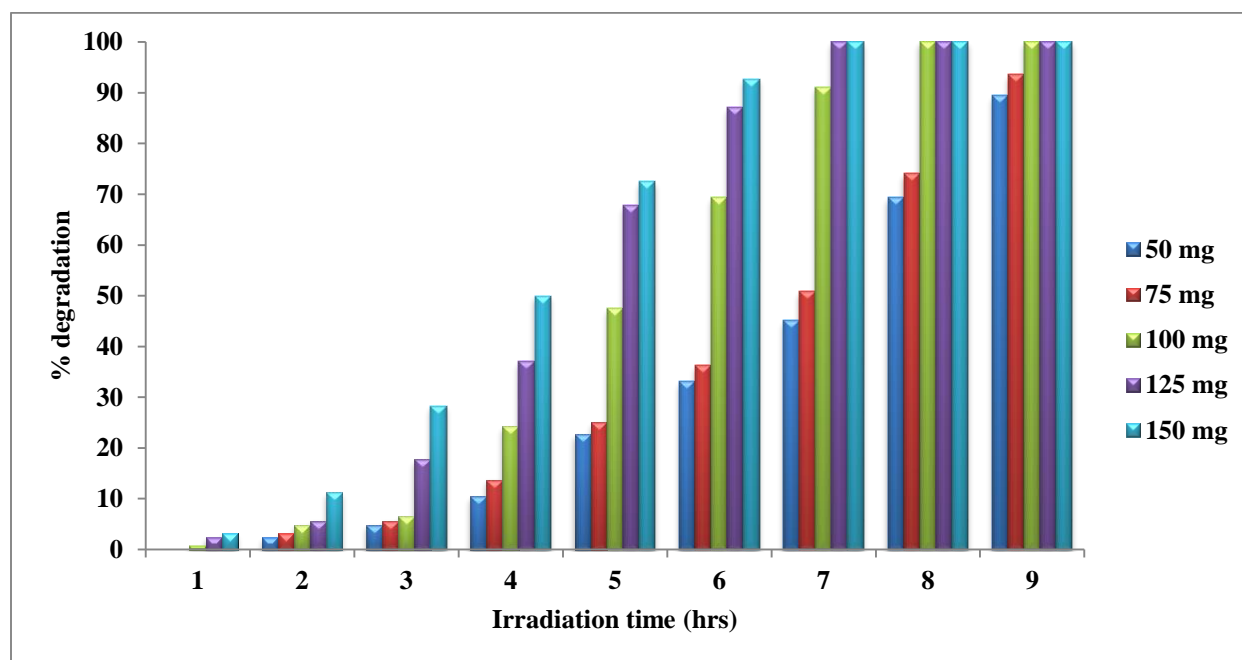
Figure 5 : Variation of % degradation with catalyst quantity for 100ml 50ppm Rhodamine-B dye solution at natural pH (7.42 - 8.04)

3.3.2. Effect of the pH of dye solution

The effect of initial pH of the Rhodamine-B dye solution on its photocatalytic degradation was studied from 6 to 11 with 25ppm and 50ppm dye solution and 100mg ZnO /100ml loading in each case. The pH of the dye solutions was adjusted only before irradiation and it was not at all controlled during the course of reaction[26]. Rest of the parameters was kept constant. The results obtained are summarized in Table 2 and Figure 6. Slight dissolution of ZnO at low pH 6 may be responsible for the less percent degradation of Rhodamine-B in acidic medium[32]. The percent degradation was found to increase linearly with increase in initial pH of the solution exhibiting maximum (100%) degradation within small irradiation time at pH 10 which is also selected as optimum pH for the present study. Excess of hydroxyl anions in an alkaline medium facilitate photogeneration of •OH radicals[26] which are primary oxidants for the photocatalytic degradation [31, 33, 34] hence increases degradation efficiency. For higher pH 11 than optimum the solutions becomes more turbid showing shadowing effect and screening effect wherein decreasing the penetration depth of light photons so extent of photocatalytic degradation declined [26, 31] as observed for the degradation of 25ppm Rhodamine-B dye solution with 100mg ZnO / 100ml loading giving 87.13% degradation in 4 hours.

Table 2 : Variation of % degradation with initial pH of dye solution for 100ml 50ppm Rhodamine-B dye solution with 100mg ZnO catalyst

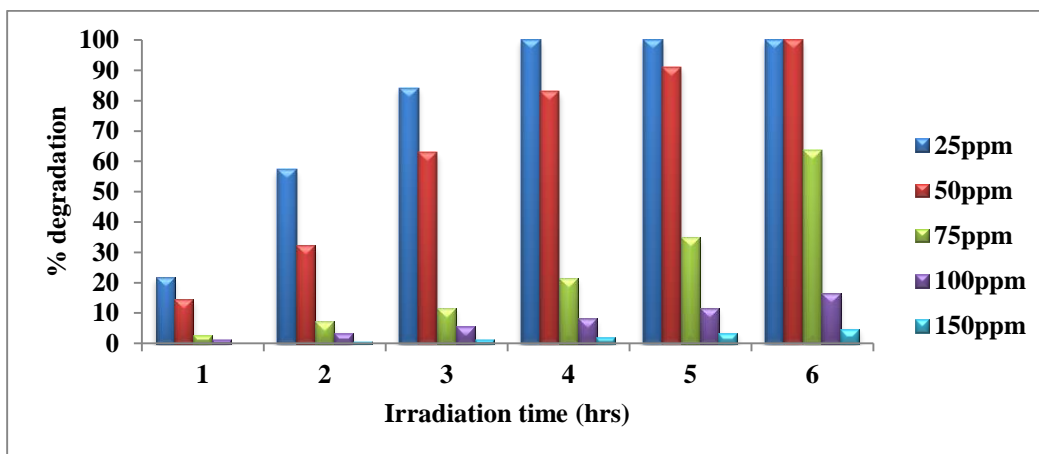| pH of dye solution	Irradiation time (hrs)								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
pH = 6	0.00	0.81	15.32	36.29	62.10	78.23	88.71	94.35	100.00
pH = 7	0.81	4.03	16.94	38.71	65.32	80.65	95.16	100.00	100.00
pH = 8	0.81	4.84	17.74	37.10	67.74	87.10	99.19	100.00	100.00
pH = 9	2.42	8.06	23.39	50.81	74.19	93.55	100.00	100.00	100.00
pH = 10	6.45	21.77	50.81	75.81	92.74	100.00	100.00	100.00	100.00
100ml 50ppm Rhodamine-B dye solution with100mg ZnO									
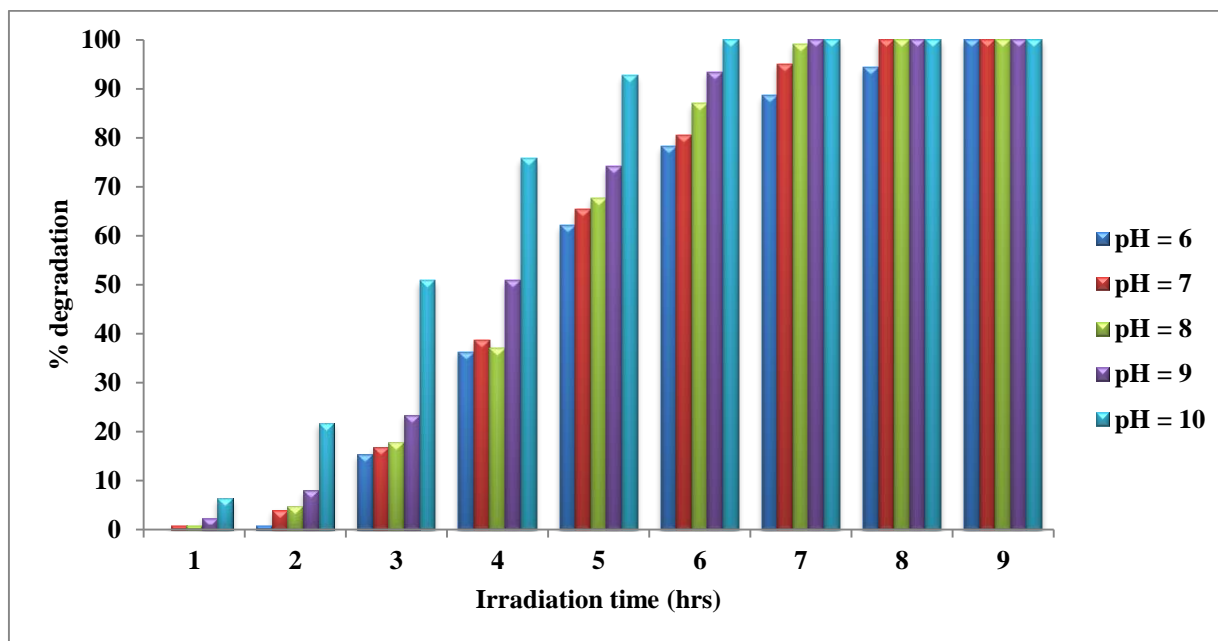
Figure 6: Variation of % degradation with initial pH of dye solution for 100ml 50ppm Rhodamine-B dye solution with 100mg ZnO catalyst

3.3.3. Effect of the initial concentration of dye solution

The degradation of Rhodamine-B at different initial concentrations in the range 25 to 150 ppm was investigated as a function of illumination time at the optimum pH 10 and with optimum catalytic amount of 100mg ZnO / 100ml of dye solution. The results obtained are summarized in Table 3 and Figure 7. As expected the increased initial concentration of the dye solution inversely affect the percent degradation. This is due to the fact that the same number of reactive radicals was generated on the surface of ZnO as its amount and the irradiation time were constant but more and more dye molecules were adsorbed on the surface of ZnO with increased initial concentration of the dye solution[31]. Therefore relative number of reactive radicals available for attacking the substrate becomes less in comparison to dye molecules. Hence photo-degradation decreases[26, 31, 35]. Also, with increased concentration of dye solution, the photons got interrupted before reaching to the ZnO surface hence absorption of photons by the photocatalyst decreases and consequently the photodegradation reduces[31]. Hence 100ml 50ppm Rhodamine-B dye solution was completely degraded by 100mg of ZnO at pH 10 on 6 hours of illumination under the aforesaid light source.

Table 3: Variation of % degradation with initial concentration of dye solution for 100ml Rhodamine-B dye solution at pH = 10 and with 100mg ZnO catalyst

| Initial concentration of dye solution	Irradiation time (hrs)					
	1	2	3	4	5	6
25ppm	21.78	57.43	84.16	100.00	100.00	100.00
50ppm	14.52	32.26	62.90	83.06	91.13	100.00
75ppm	2.86	7.14	11.43	21.43	35.00	63.57
100ppm	1.38	3.45	5.52	8.28	11.72	16.55
150ppm	0.00	0.68	1.35	2.03	3.38	4.73
100ml Rhodamine-B dye solution at pH =10 & with100mg ZnO						

Figure 7: Variation of % degradation with initial concentration of dye solution for 100ml Rhodamine-B dye solution at pH = 10 and with 100mg ZnO catalyst

3.3.4. Effect of the Irradiation time

The degradation of Rhodamine-B at different initial concentrations of 25, 50 and 75ppm was investigated as a function of illumination time at the optimum pH 10 and with optimum catalytic amount (100mg ZnO / 100ml of dye solution). The results obtained are illustrated in Table 4 and Figure 8. Under given set of experimental parameters 25, 50 and 75ppm of Rhodamine-B dye solutions were completely mineralized over ZnO on 4, 6 and 9 hours of continuous illumination respectively under aforesaid artificial visible light irradiation source. Thus ZnO was proven to be an efficient photocatalyst for artificial visible light driven photodegradations.

Table 4: Variation of % degradation with irradiation time for 100ml Rhodamine-B dye solution at pH = 10 and with 100mg ZnO catalyst

Initial concentration of dye solution	Irradiation time (hrs)								
	1	2	3	4	5	6	7	8	9
25ppm	21.78	57.43	84.16	100.00	100.00	100.00	100.00	100.00	100.00
50ppm	14.52	32.26	62.90	83.06	91.13	100.00	100.00	100.00	100.00
75ppm	2.86	7.14	11.43	21.43	35.00	63.57	83.57	92.86	100.00
100ml Rhodamine-B dye solution at pH =10 with100mg ZnO									
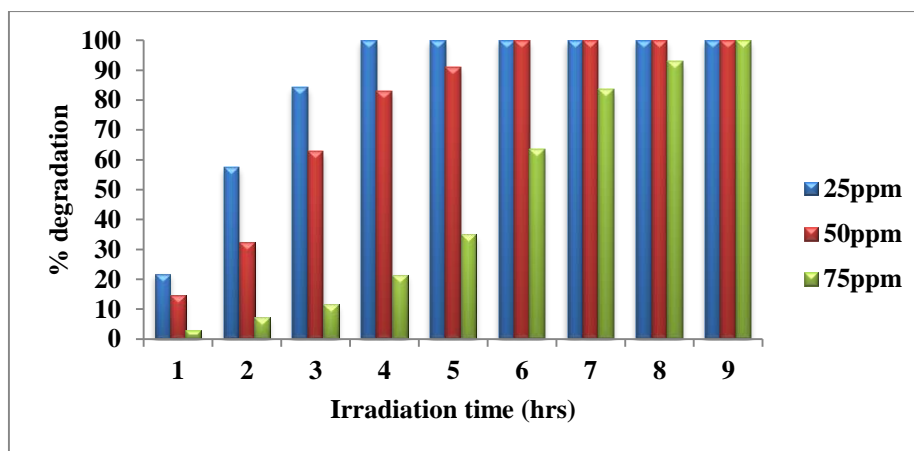
Figure 8: Variation of % degradation with irradiation time for 100ml Rhodamine-B dye solution at pH = 10 and with 100mg ZnO catalyst

IV. CONCLUSIONS

In the present research work,

1. Photocatalytic parameters for the degradation of Rhodamine-B dye with ZnO under artificial light illumination were satisfactorily optimized.
2. ZnO was found to be a better photocatalyst under artificial light illumination for degradation of Rhodamine-B dye.
3. In dark condition ZnO is found to be inactive.
4. Rhodamine-B solutions of lower concentration were completely mineralized by photo-degradation on the surface of ZnO under artificial light illumination.
5. The photodegradation of Rhodamine-B was more favorable in alkaline medium.
6. Waste water containing higher concentrations of contaminants may be completely degraded by modified ZnO, which is the interest of our current research.

V. ACKNOWLEDGEMENTS

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