PHOTOCATALYTIC EFFECTS OF ZINC OXIDE NANOPARTICLES ON DEGRADATION OF ROSE BENGAL DYE

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Abstract

ZnO nanoparticles were synthesized by using the co-precipitation method with the precursors Zn (CH3COO)2, 2H2O, and NaOH. Three different lighting environments-darkness, daylight, and sunlight—were used in this study to examine how ZnO nanoparticles affected the photocatalytic degradation of rose bengal dye solutions. The effects of contact time, dye concentration, and catalytic dosage were studied to better understand the photocatalytic process. The photocatalytic activities of ZnO nanoparticles were investigated at three pH values: 4, 7, and 10. The optimum degradation was found to be 96.483% after 2 h of contact time at a pH of 7 under sunlight. The optimum concentration of the dye solution was determined to be 10 ppm, and the photodegradation percent under sunlight at a pH of 7 was found to be 96.003%. The optimal ZnO nanoparticle dosage was 0.30 g, and the percentage of colour deterioration was calculated to be 98.113% at a pH of 7. The photocatalytic activity of ZnO was highest at a pH of 7, compared to pHs of 4 and 10.

Keywords: ZnO nanoparticles, co-precipitation method, photodegradation, rose bengal dye

Introduction

Zinc oxide (ZnO) nanoparticles (NPs), as a cheap, nontoxic semiconductor with a wide direct band gap (3.37 eV), are a promising material for different applications such as photocatalysts and photodetectors. Zinc oxide is an amphoteric oxide. Zinc oxide is widely used in different areas because of its unique photocatalytic, electrical, dermatological, and antibacterial properties (Becherri et al.,2008). Today, the entire world is facing a major problem of water pollution, which is caused in different ways. Dyes from different textile, dyeing, and printing industries are one type of pollutant, as these industries discharge their influent into nearby natural water resources without any treatment. In recent years, due to industrialization, there has been a rapid increase in the release of pollutants from industries into water bodies. Industries mainly responsible for polluting water bodies are food, textiles, dyeing, chemicals, printing, etc. Out of these industries, the main source of water pollution is the dyeing industry. Discharge from these industries has a deleterious effect on aquatic flora and fauna and renders water toxic and unfit for use. Also, due to their persistent nature, they remain in the environment for a very long period of time (Kaur and Singhal, 2014). Pure zinc oxide is a white powder, but in nature it occurs as the rare mineral zincite (Battez et al., 2008), which usually contains manganese and other impurities that confer a yellow to red colour. It is nearly insoluble in water, but it will dissolve in most acids, such as hydrochloric acid. Nanoparticles have widespread applications in various fields such as science, technology, and medicine due to their unique physicochemical and biological properties (Taghizadeh et al., 2020). Today, nanotechnology is operating in various fields of science via its operation on materials and devices using different techniques at the nanometer scale. Nanoparticles are a part of nanomaterials that are defined as single particles 1-100 nm in diameter (Khan et al., 2022). A nanoparticle is the most fundamental component in the fabrication of a nanostructure and is far smaller than the world of everyday objects that are described by Newton's laws of motion but bigger than an atom or a simple molecule that are governed by quantum mechanics. Nanoparticles are of great interest because of their extremely small size and large surface to volume ratio (Iravani, 2011). Scientists around the world have recently become interested in nanotechnology because of its potential applications in a wide range of fields, including catalysis, gas sensing, renewable energy,

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electronics, medicine, diagnostics, medication delivery, cosmetics, the construction industry, and the food industry.

Materials and Methods

Preparation of ZnO nanoparticles

Zinc oxide (ZnO) nanoparticles (NPs) were synthesized by the co-precipitation method at 300 ˚C. Zinc acetate dihydrate and sodium hydroxide were used as the starting materials for preparing the zinc oxide nanoparticles. In brief, zinc acetate dihydrate and sodium hydroxide were dissolved in deionized water to form two transparent solutions with 0.5 M and 1 M concentrations, respectively. These solutions were poured into a beaker at room temperature. The mixture was stirred for 2 h, during which a white precipitate formed in the solution. The precipitation was then separated after centrifugation. Finally, ZnO nanoparticles were obtained by washing with deionized water and acetone and drying at 300 ˚C.

Preparation of rose bengal dye solution

A stock solution of 100 ppm rose bengal dye was prepared by dissolving 0.1g of rose bengal dye in deionized water in a 1 L volumetric flask and making up to the mark with deionized water. By dilution of rose bengal stock solution, various concentrations of 10, 20, 30, 40, 50, and 60 ppm dye solutions were obtained.

Photocatalytic degradation study on rose bengal dye

The spectrophotometric method was employed for the degradation study of rose bengal dye. Firstly, the wavelength of maximum absorption of the rose bengal dye solution was determined by measuring the absorbance values over the range of 400 to 650 nm. To determine the residual concentration of dye, a calibration curve was constructed by measuring the absorbance values of 10, 20, 30, 40, and 50 ppm dye solutions.

The effect of contact time on degradation was studied by adding 0.05 g of ZnO NPs into each of the beakers containing 50 mL of a 10 ppm rose bengal dye solution (pH 4). The mixture was stirred in darkness for 30 min prior to the experiment to maintain equilibrium between the adsorption and desorption processes between dye molecules and the nanoparticle surface. After 30 min, the dye solutions with ZnO nanoparticles were placed under sunlight irradiation. The residual absorbance of the solution was measured at intervals of 20 min in the range of 20 to 120 min. The above experiment was also carried out in daylight and darkness. To study the effect of the initial concentration of dye solution, concentrations were varied between 10 and 60 ppm while other conditions were kept constant. Similarly, to study the effect of dosage of ZnO NPs on rose bengal dye, dosages of 0.05, 0.10, 0.15, 0.20 ,0.25, and 0.30 g were used. The pH influence on the photodegradation of the dye was studied by doing experiments at pH 7 and 10.

Percentages of rose bengal photodegradation were calculated by the following formula:

$$\%\text{Degradation} = \frac{(C_0 - C)}{C_0} \times 100$$

where (C_0) denotes the initial concentration, while (C) indicates the final concentration.

Results and Discussion

Wavelength of Maximum Absorption and Calibration Curve of Rose Bengal Dye Solution

The wavelength of maximum absorption is typically used for the analysis. The wavelength of maximum absorption (λ_{max}) must be determined before employing UV-visible spectrophotometry to quantify a chemical. The absorption spectra of rose bengal dye solution were obtained at six different concentrations of 0, 10, 20, 30, 40, and 50 ppm in the wavelength region of 400-800 nm. The wavelength of maximum absorption was found to be 510 nm (Figure 1). The calibration curve was constructed by plotting absorbance vs. concentration. A standard calibration curve for rose bengal dye solution was constructed by plotting absorbance vs. six different concentrations of 0, 10, 20, 30, 40, and 50 ppm of rose bengal dye solution at 510 nm (Figure 2 and Table 1). The curve was observed to be linear, and it passed through the origin, so Beer's Law was obeyed (R^2=0.9969).

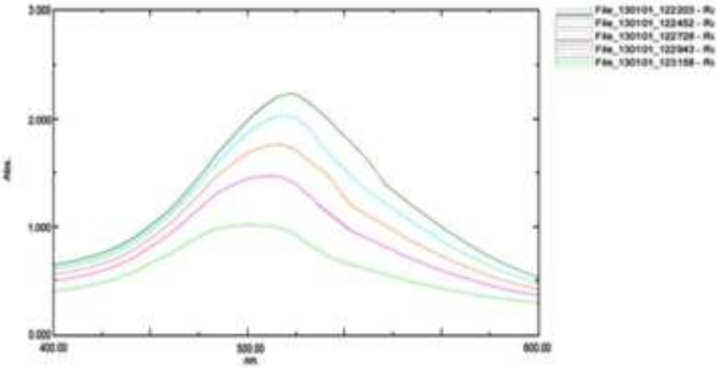

Figure 1. The wavelength of maximum absorption spectra of rose bengal dye

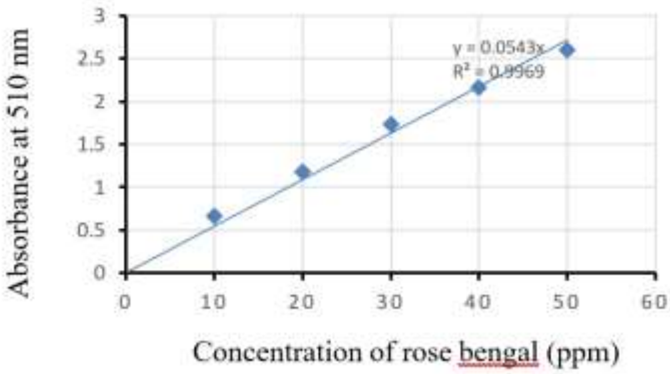

Figure 2. Calibration curve of rose bengal dye

Table 1. Relationship Between Absorbance and Concentration of Rose Bengal Dye Solution

No.	Concentration (ppm)	Absorbance at 510 nm
1	0	0.000
2	10	0.668
3	20	1.179
4	30	1.734
5	40	2.165
6	50	2.595

Photocatalytic Activity of ZnO NPs

Effect of contact time

The effect of contact time on the degradation of rose bengal dye solutions was investigated at different contact times (20–120 min) at pH 4. The presence of ZnO photocatalyst was tested in the dark, as shown in Table 2 and Figure 3. ZnO NPs had just a little effect on dye degradation in the dark, i.e., 10.703% of rose bengal dye decomposed photochemically within 2 h. Under daylight and sunlight conditions, a time-dependent decrease in the absorbance occurred with an increase in the degradation percentages of rose bengal dye. In daylight, 35.183% of rose bengal was degraded after 2 h of contact time. Furthermore, the rose bengal dye had almost completely degraded (95.044%) under sunlight in just 2 h. In the absence of a ZnO NPs catalyst, rose bengal degradation under three conditions exhibited little degradation.

Table 2. Degradation of Rose Bengal Dye using ZnO Nanoparticles with Different Contact Times at pH 4

No.	Contact time (min)	Degradation (%)		
		In dark	Daylight	Sunlight
1	0	0	0	0
2	20	1.387	19.425	64.915
3	40	2.576	21.407	71.645
4	60	4.955	27.849	83.349
5	80	7.234	29.335	88.701
6	100	8.225	31.615	92.460
7	120	10.703	35.183	95.044

Concentration of rose bengal dye = 10 ppm,
Dosage = 0.05 g,
Volume of dye solutions = 50 mL, pH 4

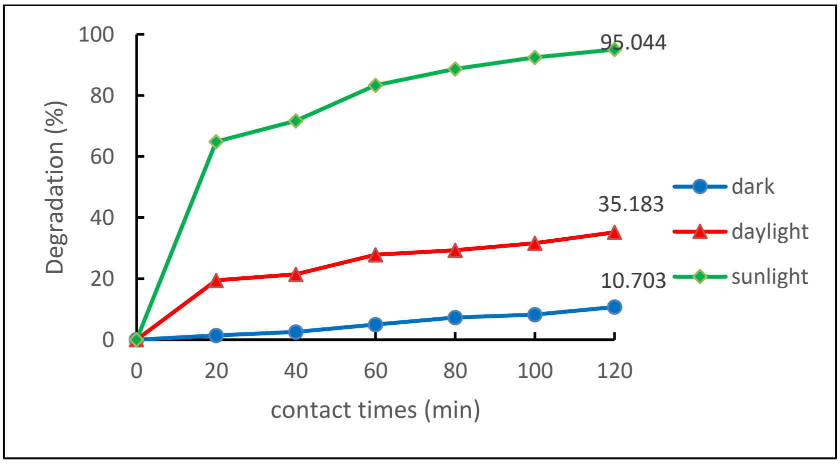

Figure 3. A plot of contact times vs. degradation (%) of ZnO nanoparticles on rose bengal dye at pH 4

The effects of contact time on the degradation of rose bengal dye solutions were also investigated at pH 7 and pH 10. The resulting data and the corresponding graphs are depicted in Table 3 and Figure 4 for pH 7 and in Table 4 and Figure 5 for pH 10. At these pH values, similar degradation patterns like pH 4 were observed. After 2 h of contact time, the degradation percent of rose bengal at pH 7 was found to be 96.483%, compared to 95.044 and 95.253% at pH 4 and 10 under sunlight, respectively. Moreover, the degradation percentages of rose bengal in daylight were 35.183, 41.743, and 40.261% for 2 h of contact time at pH 4, 7, and 10, respectively. In dark conditions, the degradation percentages of rose bengal were 22.344% and 18.003% at pH 7 and pH 10, respectively, during 2 h of contact time. In all three conditions, the highest degradation percentage of rose bengal was found at pH 7, compared to the other two pH values.

Table 3. Degradation of ZnO Nanoparticles on Rose Bengal Dye with Contact Times at a pH of 7

No.	Contact Time (min)	Degradation (%)		
		In dark	Daylight	Sunlight
1	0	0.000	0.000	0.000
2	20	2.140	6.116	77.675
3	40	5.045	12.385	81.192
4	60	9.021	19.418	84.097
5	80	10.856	28.593	88.837
6	100	19.418	37.155	94.189
7	120	22.344	41.743	96.483

Concentration of rose bengal dye = 10 ppm,
Dosage = 0.05 g,
Volume of dye solutions = 50 mL, pH 7

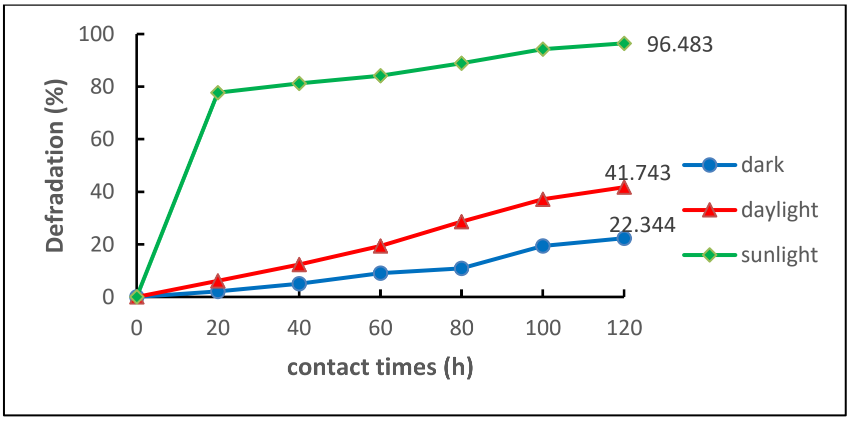

Figure 4. A plot of contact times (h) vs. degradation (%) of ZnO on rose Bengal dye at a pH of 7

Table 4. Degradation of ZnO Nanoparticles on Rose Bengal Dye with Different Contact Times at a pH of 10

No.	Contact time (min)	Degradation(%)		
		In dark	Daylight	Sunlight
1	0	0.000	0.000	0.000
2	20	2.945	10.149	71.849
3	40	6.873	14.729	73.813
4	60	8.674	20.621	79.541
5	80	12.929	28.150	84.779
6	100	14.402	34.369	92.144
7	120	18.003	40.261	95.253

Concentration of rose bengal dye = 10 ppm,
Dosage = 0.05 g,
Volume of dye solutions = 50 mL, pH 10

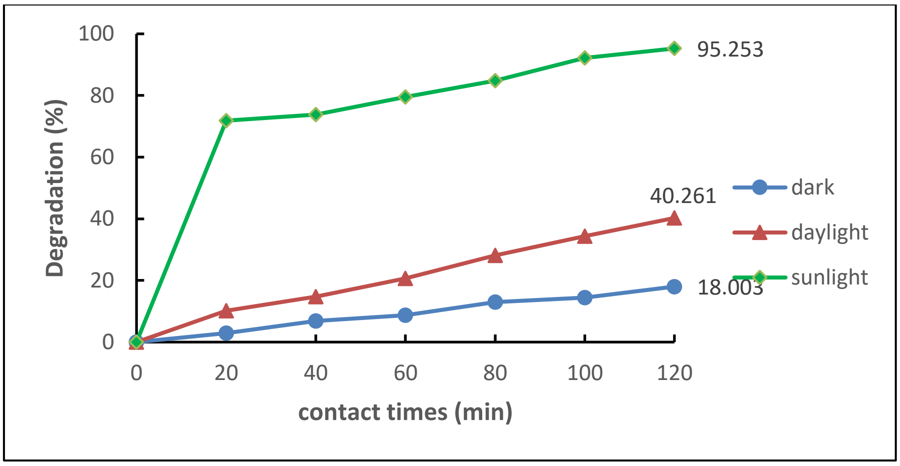

Figure 5. A plot of contact times (min) vs. degradation (%) of ZnO nanoparticles on rose Bengal dye at a pH of 10

Effect of the concentration of dye solution

The effect of the concentration of dye solution on photocatalytic degradation was also investigated at pH 4. It was found that in all three conditions, the degradation percent decreased as the concentration of dye solution increased (Table 5 and Figure 6). In daylight and in sunlight, as the concentration of dye increases, keeping the photocatalyst constant, the catalyst surface gets saturated. The intense colour of the dyes does not permit light to reach the ZnO photocatalyst. The dye molecules covered the active sites of ZnO NPs, and the degradation percent of the dye decreased. Using zinc oxide nanoparticles, the lower the concentration of rose bengal dye, the higher the degradation percentage of rose bengal dye.

Table 5. Effect of ZnO Nanoparticles on Degradation of Different Concentrations of Rose Bengal Dye at a pH of 4

No.	Concentration (ppm)	Degradation (%)		
		In Dark	Daylight	Sunlight
	0	0	0	0
1	10	7.366	19.153	94.860
2	20	7.331	17.640	91.408
3	30	6.673	16.102	83.558
4	40	5.727	14.411	80.046
5	50	5.258	12.284	79.555
6	60	2.665	9.684	77.765

Dosages = 0.05 g,
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH= 4

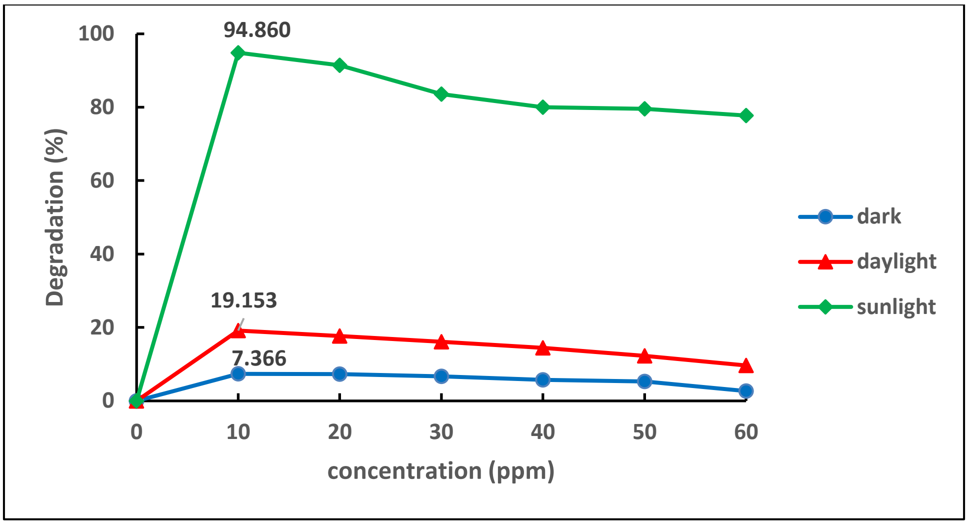

Figure 6. A plot of concentration (ppm) vs. degradation (%) of ZnO nanoparticles on rose bengal dye at a pH of 4

The effects of the concentration of rose bengal dye on the photocatalytic degradation were also studied at pH values of 7 (Table 6 and Figure 7) and 10 (Table 7 and Figure 8). As expected, the increased initial concentration of the dye solution has a negative impact on percent degradation. The same number of reactive radicals were generated on the surface of ZnO, but more and more dye molecules were adsorbed on its surface. Thus, the number of reactive radicals available for attack decreases, and photodegradation decreases. Among three different pH values, the degradation of dye was highest at pH 7 under sunlight (84.451%).

Table 6. Degradation of ZnO Nanoparticles on Rose Bengal Dye with Concentrations at a pH of 7

No.	Concentration (ppm)	Degradation (%)		
		In dark	Daylight	Sunlight
1	0	0	0	0
2	**10**	9.769	16.607	96.003
3	20	7.784	14.517	94.890
4	30	7.427	13.984	93.580
5	40	6.927	12.955	90.958
6	50	3.938	11.371	87.262
7	60	1.776	10.484	84.451

Dosages = 0.05 g,
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH= 7

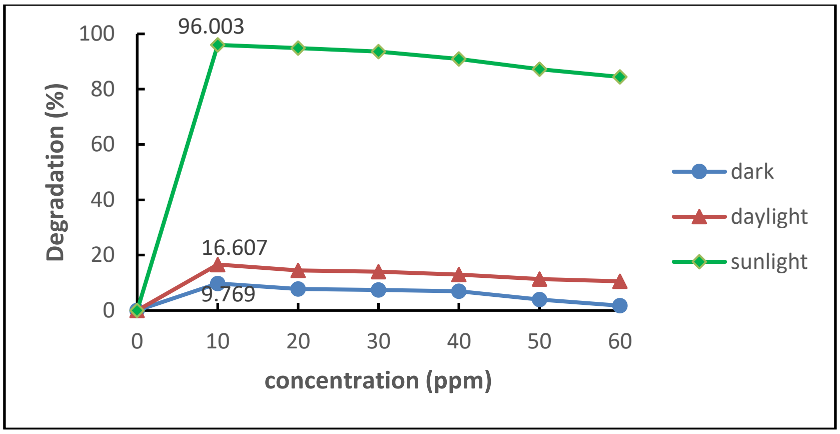

Figure 7. A plot of concentration (ppm) vs. degradation (%) of ZnO nanoparticles on rose Bengal dye at a pH of 7

Table 7. Degradation of Rose Bengal Dye using ZnO Nanoparticles with Different Concentrations pH 10

Sr No.	Concentration (ppm)	Degradation (%)		
		In Dark	Daylight	Sunlight
1	**0**	0	0	0
2	**10**	15.898	30.365	95.389
3	20	14.340	26.200	94.323
4	30	12.692	20.476	92.847
5	40	10.398	19.064	88.561
6	50	8.769	15.384	85.692
7	60	5.286	12.124	84.044

Dosages = 0.05 g,
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH= 7

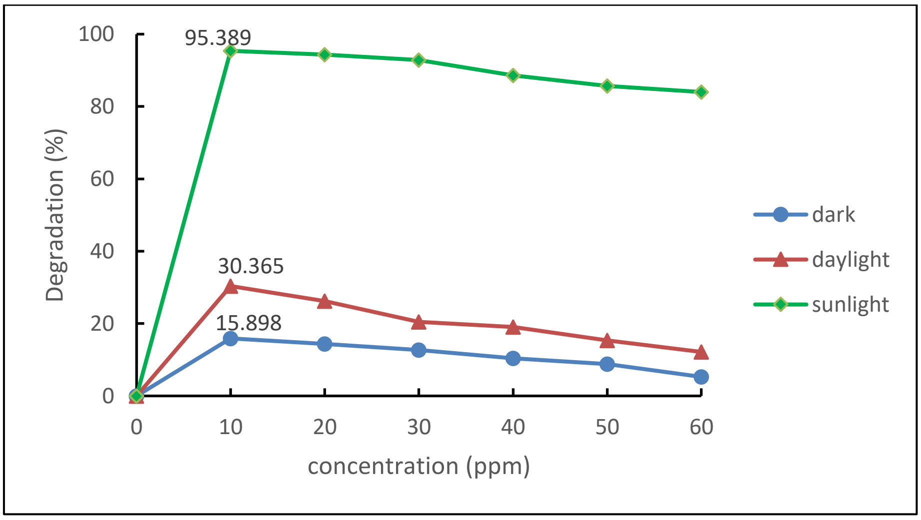

Figure 8. A plot of concentration vs. degradation (%) of ZnO nanoparticles on rose Bengal dye at a pH of 10

Effect of the dosage of ZnO nanoparticles

The effect of the dosage of ZnO on the degradation of 10 ppm of rose bengal dye solutions was investigated at pH 4. In this study, as the catalyst dosage was increased from 0.05 to 0.30 g, the percentage degradation of the dye was found to increase. Table 8 and Figure 9 show that the higher the dosage of zinc oxide nanoparticles, the higher the degradation of rose bengal dye in all three conditions. The increase in the dosage of ZnO increased the number of active sites on the photocatalytic surface, thus increasing the number of hydroxyl radicals (Wang *et al.*, 2007). The highest degradation of rose bengal was found to be 97.348% under sunlight, compared to 37.315 % in darkness and 64.454 % in daylight.

Table 8. Degradation of Rose Bengal Dye using ZnO Nanoparticles with Different Dosages Condition (pH4)

No.	Weight of ZnO (g)	Degradation percent(%)		
		Daylight	In dark	Sunlight
1	0.05	5.014	52.064	83.775
2	0.10	9.734	58.259	85.103
3	0.15	16.799	58.849	88.348
4	0.20	21.091	61.061	91.592
5	0.25	30.383	62.094	95.280
6	0.30	37.315	64.454	97.348

Concentration of rose bengal dye = 10 ppm
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH 4

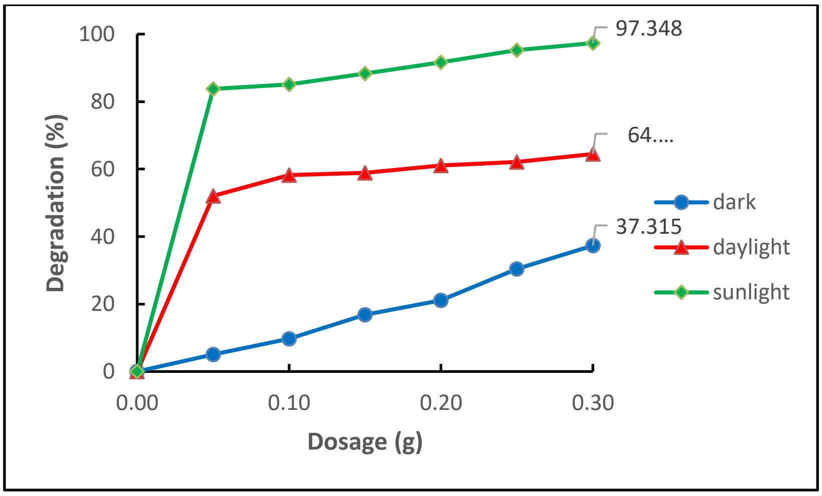

Figure 9. A plot of dosage (g) vs. degradation (%) of ZnO nanoparticles on rose bengal dye at a pH of 4

Table 9 and Figure 10 depict the degradation of rose bengal at pH 7, and Table 10 and Figure 11 show the degradation of rose bengal at pH 10 by ZnO. As the amount of ZnO increases, the surface area of the catalyst increases; hence, the adsorption of dye molecules over the surface of ZnO increases, which increases the percent degradation. The highest degradation percentage of rose bengal was found to be 98.113% at pH 7 under sunlight when compared to 97.348% at pH 4 and 95.505 % at pH 10.

Among three pH values, the photocatalytic activity of ZnO on the degradation of rose bengal was highest at pH 7 under sunlight. It may be explained as follows: at low pH, the anionic dye molecules remain in their protonated form, and the ZnO surface also possesses a positive charge due to the adsorption of H^+ ions. Hence, the dye molecules and ZnO repel each other. This results in low degradation efficiency. As pH increases to 7, the repulsion between ZnO and dye molecules decreases and the degradation efficiency increases. At pH 10, the surface of ZnO is negatively charged and again repels dye molecules. So, degradation efficiency decreases (Kumawat *et al*., 2012).

Table 9. Degradation of ZnO Nanoparticles on Rose Bengal Dye with Dosages at a pH of 7

No.	Weight of ZnO (g)	Degradation (%)		
		In dark	Daylight	Sunlight
1	0	0	0	0
2	0.05	5.525	19.137	90.431
3	0.10	8.490	20.350	91.239
4	0.15	11.590	21.832	93.126
5	0.20	12.803	23.450	94.878
6	0.25	15.363	27.892	97.574
7	0.30	20.889	34.905	98.113

Concentration of rose bengal dye = 10 ppm
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH 7

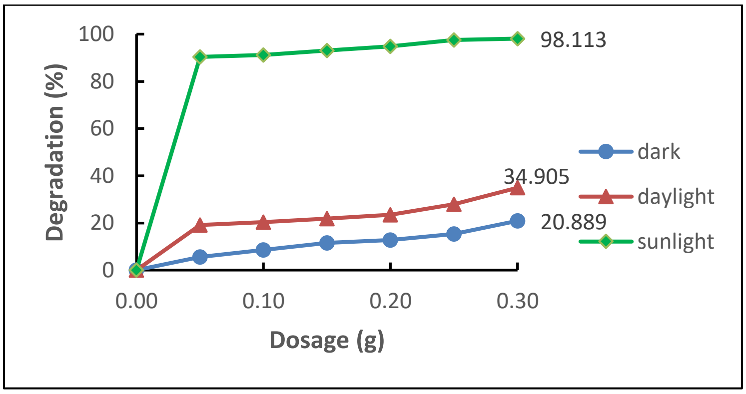

Figure 10. A plot of dosage (g) vs. degradation (%) of ZnO nanoparticles on rose Bengal dye at a pH of 7

Table 10. Degradation of Rose Bengal Dye using ZnO Nanoparticles with Different Dosages pH 10

No.	Weight of ZnO (g)	Degradation (%)		
		In dark	Daylight	Sunlight
1	0	0	0	0
2	0.05	3.720	13.643	87.131
3	0.10	8.837	19.224	91.472
4	0.15	13.646	27.906	93.333
5	0.20	17.984	31.937	94.108
6	0.25	21.05	35.193	95.193
7	0.30	23.255	39.222	95.505

Concentration of rose bengal dye = 10 ppm,
Volume of dye solutions = 50 mL,
Contact time = 2 h, pH 10

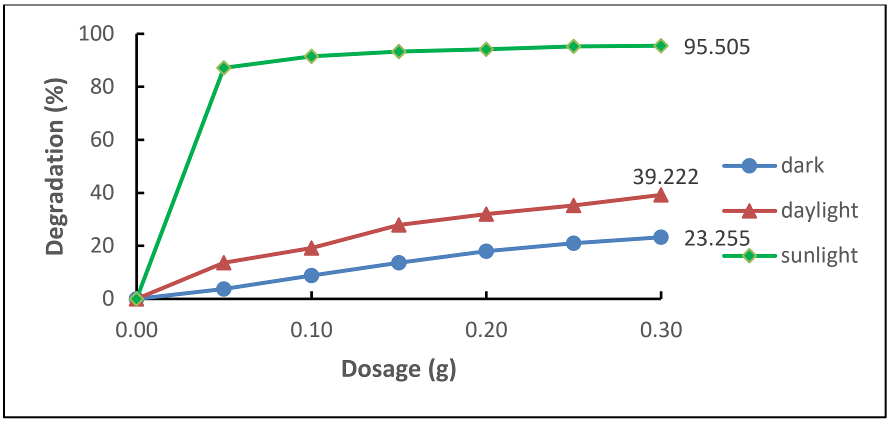

Figure 11. A plot of dosage (g) vs. degradation (%) of ZnO nanoparticles on rose bengal dye at a pH of 10

Conclusion

This study used a rose Bengal dye solution at various pH levels (4, 7, and 10) to examine the colour degradation efficiency of synthesized ZnO nanoparticles in the dark, in daylight, and in sunlight. The variable parameters (contact times, concentrations, and dosages) of synthesized ZnO nanoparticles were used in those conditions. In sunlight at a pH of 7, the colour degradation efficiencies of the produced ZnO nanoparticles on solutions of rose bengal dye were found to be more than 90%, indicating their high photocatalytic activity. At pH 7, ZnO nanoparticles exhibit the best photocatalytic behaviour (as compared to pH 4 and 10). ZnO was found to be an efficient photocatalyst for the degradation of rose bengal dye. From this study, ZnO nanoparticles can be utilized to treat wastewater from industrial zones as an effective colour degradation agent.

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