



## Degradation of Azo Dyes of Textile Industries Through Green Approach: Solar Nps (ZnS)

M.L. Meena<sup>1</sup>, J. Meena<sup>1</sup>, D. Meena<sup>2</sup> and A.S.Meena<sup>2\*</sup>

Assistant Professor, Assistant Professor, Research Scholar and Assistant Professor

<sup>1</sup>Department of Chemistry, Govt. PG College, Karauli ( Rajasthan)-322255, INDIA

<sup>2\*</sup>Solar Energy Laboratory, Department of Chemistry, University of Rajasthan, Jaipur (Rajasthan)-302004, INDIA

**Abstract:** Dye degradation attempts that are not biodegradable and last for years in aquatic bodies have been made. For researchers and environmentalists, the remediation of azo dye-polluted water from textile industry wastewater is a challenge. Water contaminated with dye or azo dye is dangerous (cancer-causing, reduces soil fertility). A great replacement for expensive industrial treatment methods is the newly discovered solar NPS (ZnS), which efficiently degrades these dyes and azo dyes (water treatment). Solar Nps has the ability to break down all dye molecules, and we can extract 99-99.9% transparent water from dark-colored textile wastewater in a matter of hours using ZnS Nps and Solar Nps. We study how many variables, including pH, light intensity, dye concentration, and Nps quantity, affect the rate of deterioration.

**Index Terms:** Solar Nps; Green approach; Degradation; Sirius light yellow R.

### I. INTRODUCTION

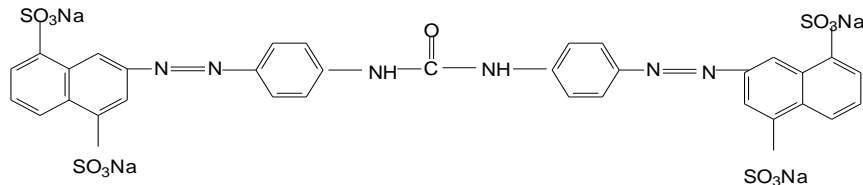
Remaining dye molecules from the treatment of dye-polluted wastewater from the textile, paper, food, and chemical sectors are not biodegradable. Typical treatment methods include chemical coagulation and adsorption. However, by transferring colours from the liquid to the solid phase, these processes cause secondary contamination and need for additional treatment. Recent advances in photochemistry have led to the development of the advance oxidation process (AOP), which is the best method for treating wastewater from the textile industry (wastewater). For the degradation of dye pollutants, we utilize zinc sulphide nanoparticles (ZnS). This newly created solar NPS has enormous promise for azo dye degradation. Numerous research on the sun catalytic degradation of Azo dyes have been published. We need a catalyst that can totally remove all types of dye contaminants because photocatalyst materials are so scarce and the present catalysts cannot entirely decolorize wastewater from the textile industry. In such a background, in this study a new solar nanocatalysts with high activity have recently been developed and nanocatalyst such as: ZnS Nps prove to be a better solar nanocatalyst. In 1977, Frank and Bard<sup>1-2</sup> first investigated the potential of using TiO<sub>2</sub> to break down cyanide in water. Since then, interest in environmental applications has grown. A new group of photo catalyst materials have emerged for the splitting of water into H<sub>2</sub> & O<sub>2</sub> and organic molecular degradation under ultraviolet/visible light irradiation. These new photo catalysts include Alkali and alkaline earth tantalates, TiO<sub>2</sub>, and other photo catalyst in different applications with new techniques. The development of photocatalysis method is considerably aided by the extensive knowledge that was gathered during the 1970s and 1980s while working to create semiconductor photo electrochemistry, according to Heller<sup>3</sup>. Many researchers agree that transition metal oxides, including TiO<sub>2</sub>, ZnO, CdS, and WO<sub>3</sub>, are good photocatalysts for degrading organic pollutants<sup>4-10</sup>. Bhatkhande and co. identified the chemicals that different researchers' photocatalytic degradation of by reviewing recent works in this field. Recent years have seen some study on the degradation of azo dyes in textile wastewater and photocatalyst published.<sup>12-17</sup> In 1993, Legrini et al.<sup>18</sup> proposed that purification using a TiO<sub>2</sub> photocatalyst in the presence of UV radiation has various benefits, including efficient removal of organic molecules dissolved or dispersed in water and low cost. Styliadi<sup>19</sup> and co. proposed a TiO<sub>2</sub>-mediated photodegradation mechanism for Acid Orange 7, which caused the organic molecule to completely mineralize into rings of the naphthalene and benzene types, rings of carbon, nitrogen, and sulphur, and ions of carbon, nitrogen, and sulphur. Under UV Light (300 nm) illumination, Methyl Orange was degraded by Chin Cheng Hsu and N.L. Wu<sup>20</sup> utilising ZnO/ZnO<sub>2</sub> as a photocatalyst<sup>13</sup>. Using SO<sub>4</sub><sup>2-</sup>/ZnO/TiO<sub>2</sub> and ZnO as photo catalysts, respectively, Wang et al.<sup>21</sup> observed increased photocatalytic activity for the degradation of methyl orange. Anaerobic treatment of the azo dye Acid Orange 7 was conducted by Gubury<sup>22,29</sup>, Sudha et al.<sup>23</sup> Mendez-Pazet et al.<sup>24</sup> in fed batch and continuous conditions. When some glucose is added to the reaction mixture, the removal rate of dye pollution increases significantly. ZnO exposed to sunlight was used by Sakthivel et al.<sup>25</sup> to study the degradation of Acid Green 17. Here, the initial dye concentration-dependent photo degradation efficiency decreased. The 250 mg in 100 ml catalyst loading that was determined to be ideal. Work on the photocatalytic degradation of dyes from various sectors was done by Akyol et al.<sup>26</sup> in 2018. Reactive Black 5 was investigated for photocatalytic degradation by Poullos and Tsachpinis<sup>27</sup> using a variety of semi-conducting oxides, including TiO<sub>2</sub>, UV-100 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>/WO<sub>3</sub>. As the UV light source, four parallel black light blue fluorescent tubes were used. The total mineralization of environmental contaminants attracted a lot of interest. Work on improved photocatalytic activity of supported TiO<sub>2</sub>: SiO<sub>2</sub>'s dispersion effect has been done by Yiming Xu et al.<sup>28</sup>. Our goal in the current effort is to use solar energy to degrade dye contaminants using Solar ZnS Nps and discover new solar nanocatalyst for various uses. This catalyst is more useful and cheaper than solar catalyst. The ZnS Nps nanocatalyst has a stronger potential for

degrading the dyes (Sirius bright yellow R, the model compound for the experiment), and it also works well in low light. We find out how various parameters affect the pace of degradation. Examples include (1) changes in the catalyst loading, (2) changes in the dye concentration, (3) changes in pH, (4) changes in light intensity, and (5) changes in the action of dissolving oxygen.

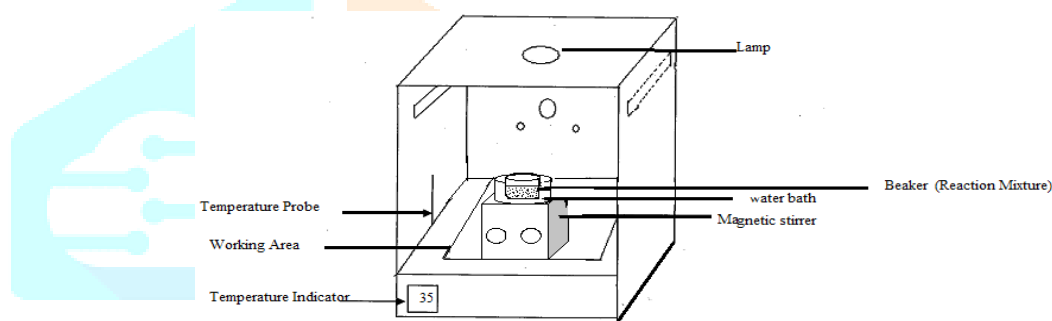
## II. MATERIALS AND METHODS:

### 1. Materials and Experimental Method

As a model compound, Sirius Light Yellow-R (Direct Yellow 50), an azo dye, was used. Textile wastewater contains the refractory azo dye Sirius Light Yellow-R. An exact amount of the dye was dissolved in distilled water to create the solution. The dye absorbs at its peak at 390 nm.



We prepare approximately M/1000 concentration solution of Methylene Blue in Double distilled water and add Dowex-11 resin in this solution and shake well. The Shimadzu-160 UV/Visible spectrophotometer is used to easily measure the change in dye concentration. At intervals of 15 minutes, we pipette out 10 ml of the solution to observe changes in the dye solution's percentage transparency. A mixture of Dyes (Sirius light yellow R) and a photocatalyst are used in a glass reactor to conduct the photo process. Throughout the experiment, a magnetic stirrer is continuously stirring the reactor's solution. Above the reactor, a 500/1000 W halogen lamp illuminates the solution. Figure 2 shows a schematic representation of the experimental setup.



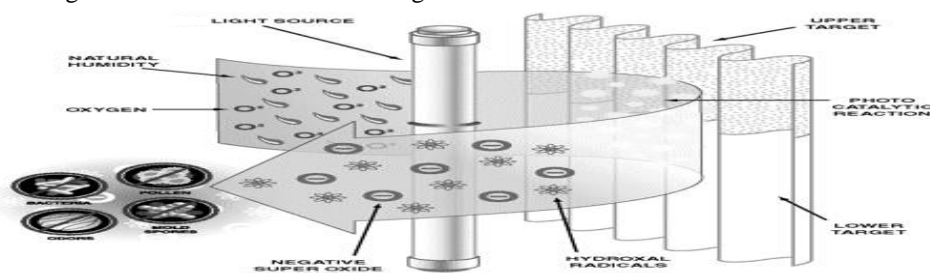
**Fig. 2. Schematic Diagram of The Experimental Set-up**

10 ml of the solution are removed from the reaction mixture at fixed times, filters catalyst particles and uses a spectrophotometer (160 UV/Visible spectrophotometer) to measure changes in the transparency of colored water.

## III. RESULT AND DISCUSSION

### 1. Chemical Reaction of Degradation:

Nps of ZnS, This photocatalyst is brand-new. The resin's pores allow the colour molecules to become immobile. Due to its photosensitivity, methylene blue undergoes an electronic transition from its valence band (VB) to its conduction band (CB), and an intersystem crossover (ISC) allows an electron to enter the methylene blue triplet state. After the intermolecular electronic transition between the resin, Methylene blue, pollutant dye molecules, water molecules, and dissolved oxygen begins, holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ), all of which are highly oxidizing in nature, are produced as a byproduct through a chain reaction. By acting on the azo dyes, holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ) transform them into simple organic compounds like  $CO_2$ ,  $H_2O$ ,  $SO_2$ . The main factors influencing the nanocatalytic degradation of Azo dyes is variation in nanocatalyst amount, concentration of dye, variation in pH of the solution, variation in light intensity, variation in dissolve oxygen. The proposed figure can be used to explain the formation of holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ). The activity of the photocatalyst and the process of producing oxidative intermediates are depicted in this proposed diagram. Proposed Mechanism of Degradation Process is shown in Figures 3 and 4.



**Figure-3: Photocatalysis Action**

## MACHANISM OF PHOTOCHEMICAL REACTION ( SIRIUS LIGHT YELLOW-R)

Photocatalytical degradation of azo bonds in Dye

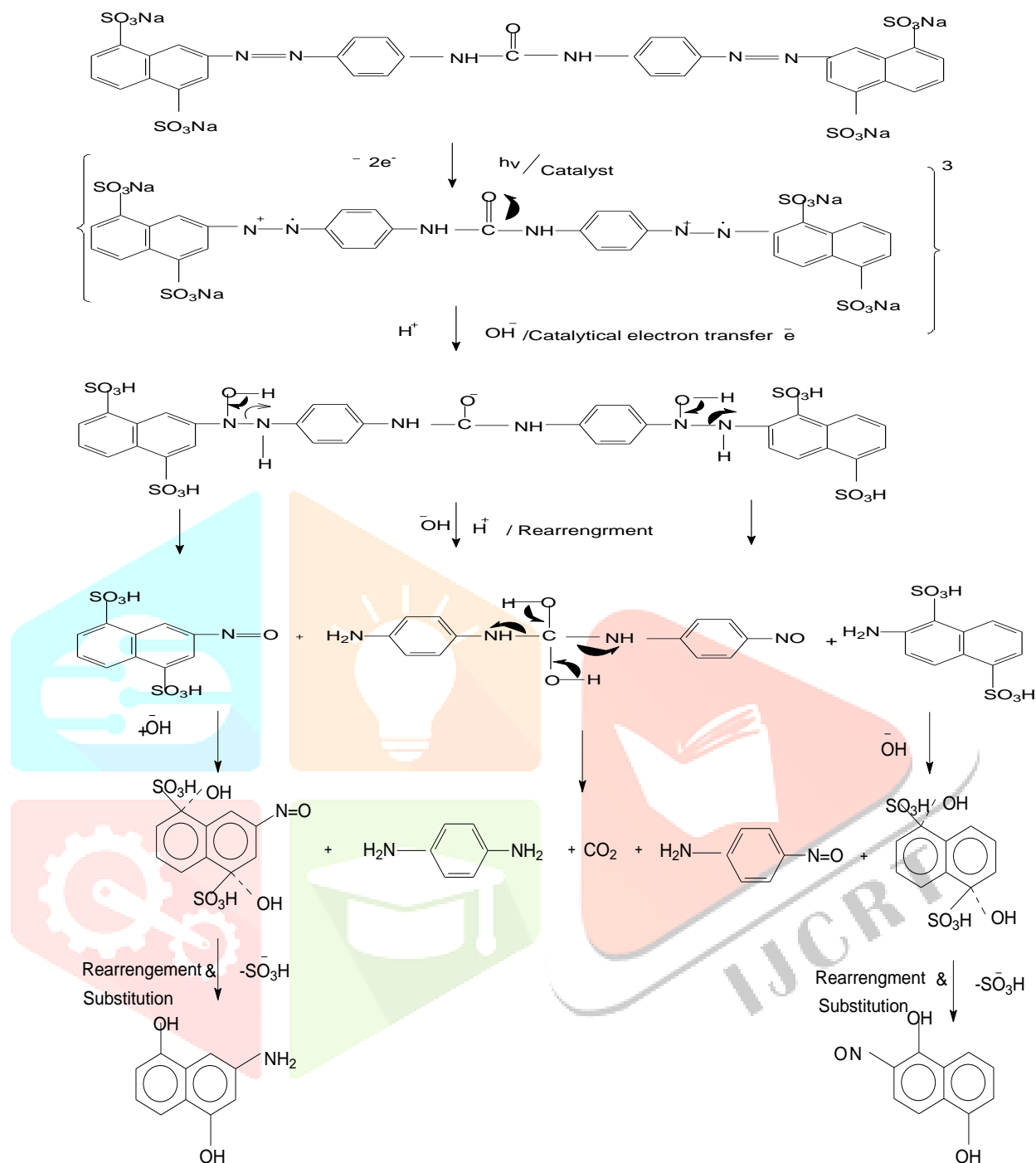


Figure-4: Mechanism of Photocatalytic Degradation of Dye (SLY-R).

## 2. Effect of nanocatalyst.

We determine how variations in nanocatalyst concentration affect the rate of degradation at a fixed pH of 8. The rate of deterioration likewise increases as catalyst concentration does.

The availability of more surface area for the absorption of quanta and interaction of molecules of the reaction mixture with the catalyst is what causes the rate of degradation to increase with an increase in the amount of catalyst; the end result is an increase in the number of holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ). These are the primary oxidizing intermediates in the early stages of oxidation, which accelerates the rate of deterioration. Figure 5 shows the impact of catalyst loading on deterioration rate graphically.

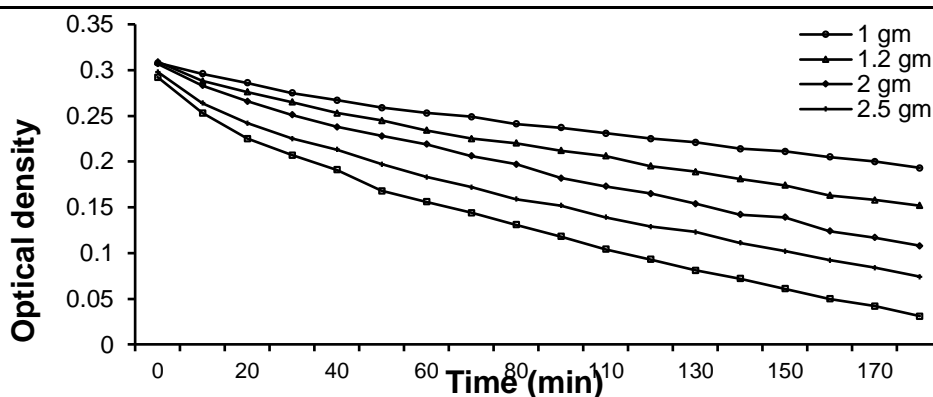


Figure-5: Effect of Catalyst Loading on Photocatalytic Degradation

### 3. Effect of Initial Dye Concentration.

We observe the effect of change in dye concentration on nanocatalytic degradation and find out that as concentration of dye increases the rate of degradation decreases. This effect may be caused due to following reason:

1. Important factor: As dye concentration rises, fewer photons reach the catalyst surface, which results in fewer catalyst molecules being excited. As a result, the rate of formation of holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ) is slowed down, which in turn slows down the rate of degradation.
2. There is a fixed amount of surface area on the catalyst, which causes the rate of degradation to decrease as the concentration of dye increases. This is because only a small number of dye molecules can attach to the catalyst's active site, and the remaining dye molecules can remain in solution until the degradation of earlier attached molecules. Less photons are available to excite the molecules of the catalyst, which results in a decrease in the number of active sites.
3. Dye molecule competition for the active site has an impact on the rate of degradation as well. Since there will be more competition for attachment to the catalyst's active site when the concentration of dye molecules is larger, the rate of degradation will slow down as a result. Figure 6 shows the impact of a change in dye concentration graphically.

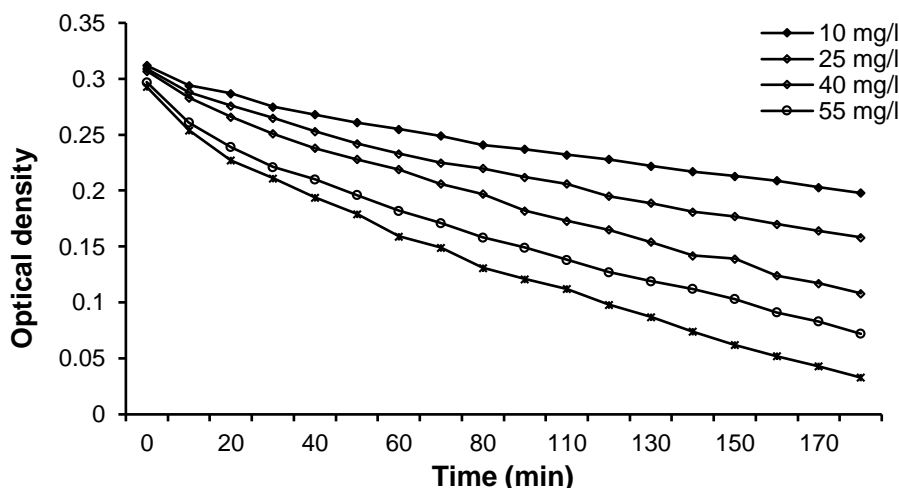


Fig.-6: Effect of Initial Dye Concentration on Degradation

### 4. Effect of pH.

It's fascinating to note how pH affects how quickly colour molecules degrade. The results show that the rate of degradation is very low in the acidic pH range; if pH is lower than 3.5, the rate of degradation is very low. The rate of degradation also increases as pH increases; however, it increases quickly when pH reaches the basic range; the pH range of 8 to 9 has a very good rate of degradation. After pH range 10 or above, the rate of deterioration is reduced and reduces as pH increases. This is followed by further increasing pH. Therefore, we draw the conclusion that basic media degrade at a faster pace than acidic media. The more readily available  $-OH$  ions in the pH range of 8 to 9 will likely generate more, which may be the cause of the increased rate of photo catalytic degradation.  $OH$  radicals by joining with the holes created in the catalyst as a result of electrical excitation. More hydroxyl radicals than supraoxide are produced during photocatalytic degradation ( $\cdot O$ ).

The rate of deterioration slows down at higher pH levels. This impact results from rivalry amongst  $-OH$  groups to attach to the catalyst's active site, which lowers the rate of  $-OH$  group attachment. Result is that formation of hydroxyl radicals ( $\cdot OH$ ) decreases and due to this reason rate of degradation also decreases. Graphical representation of pH effect is shown in figure-7.

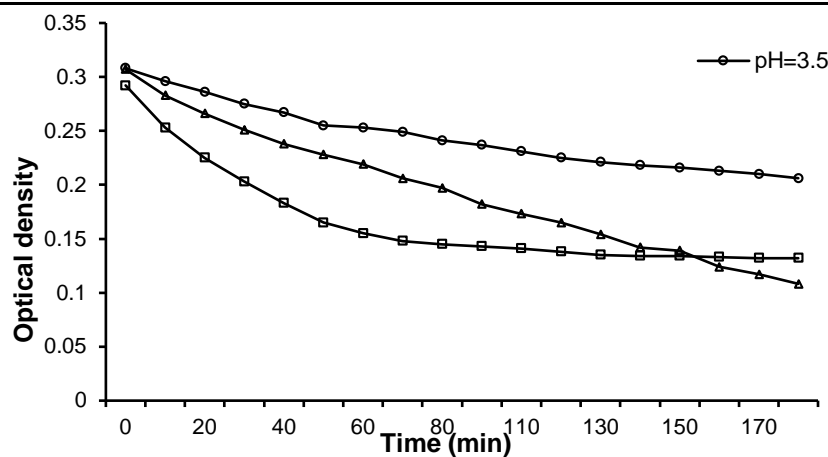


Fig.-7: Effect of pH on Degradation

#### 5. Effect of light intensity

We observe a direct correlation between light intensity and rate degradation. Up until a certain point, the rate of degradation of dye molecules also increases, but after that point, no changes in the rate of degradation are seen. These variations in the rate of dye molecule degradation caused by variations in light intensity are caused by the fact that as light intensity rises, more photons will reach the catalyst surface. This will lead to more catalyst molecules exiting the reaction, which will increase the amount of holes, hydroxyl radicals, and supra oxide ions ( $O^{\cdot-}$ ), as well as the rate at which dye molecules degrade.

It has been noted that after a certain point, increasing light intensity has no further impact on the rate of degradation. The reason for this is because the maximum number of photons needed for excitation is present in a fixed range of light intensity, and that at this point, no appreciable changes in the rate of degradation are seen since no additional photons are needed for excitation. If we raise light intensity to any range after it, all catalyst molecules become active in a fixed light intensity range, hence the rate of degradation does not change. Figure 8 illustrates the variation in light intensity graphically.

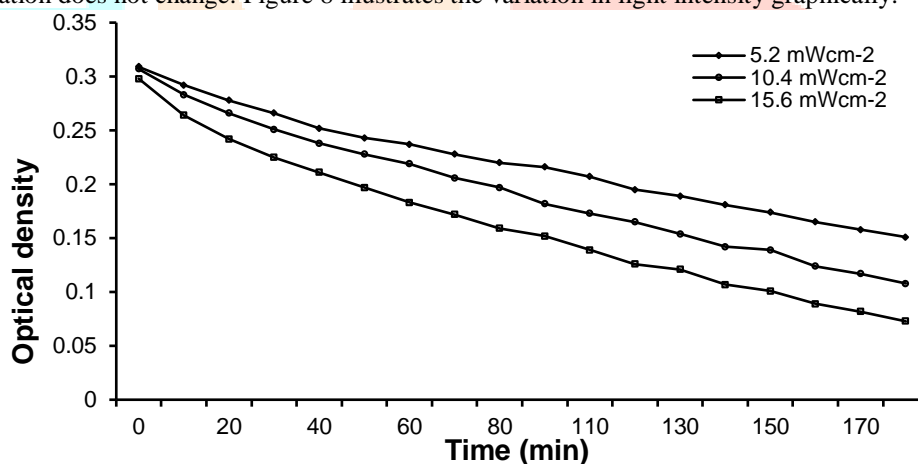


Fig.8: Effect of Variation of Light Intensity on Degradation

#### 6. Effect of Dissolved Oxygen on Rate of Degradation

The rate of dye degradation increases as dissolved oxygen levels in the solution rise. We found that passing oxygen through a reaction mixture causes the pace of degradation to rise, whereas passing nitrogen or any other non-reacting gas through the solution has no impact on the rate of degradation. The increased oxygen available for the production of supraoxide ( $O^{\cdot-}$ ) and hydroxyl radicals may be the cause of this impact. These have a strong oxidative character and speed up the degradation of color molecules.

### IV. CONCLUSION

Following extensive experimental investigation, we have come to the conclusion that this nanocatalyst (Nps of ZnS) has excellent potential for degrading Azo colours and dyes from textile effluent (wastewater), which contain significant amounts of non-fixed dyes, primarily Azo dyes. These azo dyes cannot be degraded biologically. We observe the effect of different parameters given in order

1. Variation in dye concentration: The rate of degradation is inversely proportional to dye concentration i.e. Rate of degradation =  $1/\text{Dye concentration}$ .
2. Amount of nanocatalyst: The concentration of catalyst increases the rate of degradation of dye molecules also increases i.e. Rate of degradation = concentration of nanocatalyst
3. Variation in pH: Between pH ranges 8 to 9 rate of degradation is faster on further increase in pH the rate of degradation decreases.



4. Light intensity: On increasing light intensity the rate of degradation of dye molecules increases up to certain limit after it there is no further changes in the rate of degradation.
5. Dissolved oxygen: Rate of degradation increases up to some extent on increasing the dissolved oxygen in dye solution.

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