



Nanocatalytic Degradation of Azo Dye with ZnO Nps in Presence of Sunlight

M. Akram and A.S. Meena*

Research Scholar and Assistant Professor*

*Solar Energy Laboratory, Department of Chemistry, University of Rajasthan, Jaipur-3002004, INDIA

Abstract: The nanocatalytic degradation of azo dye (Direct Red 5B) in photochemical reactor is carried out with ZnO Nps under the sunlight. The effect of variables including dye content, pH, light intensity, and Nps dosage on degradation efficiency is investigated. The rate constant is best at 30°C, pH 7.5-9.0, 200 mg/l ZnO Nps, 200 watt mercury lamp light intensity, and 40 mg/l dye concentration. The degradation of azo dyes by nanocatalysis follows pseudo first order kinetics.

Index Terms: Nanocatalyst, DR5B, photodegradation, photochemical reactor.

I. INTRODUCTION

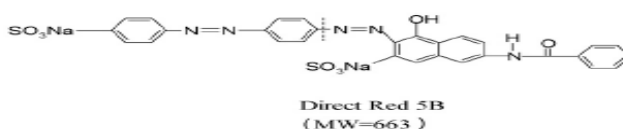
Textile azo dyes, such as Reactive dyes, Direct dyes, and other industrial dye stuffs, are one of the most significant classes of organic compounds that are contributing to rising environmental pollution. Textile dyeing and finishing is one of the most polluting industries in terms of volume and chemical constituents of discharged effluents¹⁻². According to studies, dye stuffs are added in significant volumes during manufacturing and processing processes, and the resulting colour is released into the environment via effluents from industrial wastewater treatment plants. Adsorption and chemical coagulation are two prominent treatment methods for this type of wastewater. However, these technologies transfer dyes from the liquid to the solid phase, resulting in secondary contamination that requires additional treatment. Textile wastewater treatment procedures that use coagulation, flocculation, ultra filtration, and dye adsorption to remove the colour of the wastewater.³⁻⁵ Another wastewater treatment approach, Advance Oxidation Processes (AOPs), has been proposed⁶. AOPs can oxidize a wide spectrum of substances that are difficult to degrade using existing physicochemical and biological methods⁷. In recent years, Photocatalytic oxidation methods have received increased attention among AOPs for decomposing various organic molecules and contaminants in water.⁸⁻¹¹

Maria et al¹² use TiO₂ as a photocatalyst to explore the total mineralization of acid orange 7 dye into simple organic compounds. Wang et al. demonstrated improved photocatalytic performance of a nanosized linked SnO₂ photocatalyst.¹³ In the presence of surfactants, Ameta et al¹⁴ investigated the photo bleaching of Basic Blue-24 and Orange-G over TiO₂ powder. For the degradation of methylene blue dye, Yaun et al¹⁶ used a combination of TiO₂ and activated fiber. Purification using TiO₂-mediated photocatalysis under UV light has been found to be potentially beneficial, as it can result in complete mineralization of pollution to CO₂, water, and mineral acids.¹⁷⁻¹⁸ Although TiO₂ is the most extensively used catalyst, owing to its photo stability, low cost, lack of toxicity, and inability to dissolve in water under most environmental circumstances, it is also the most expensive.¹⁹ However, issues with the separation of TiO₂ particles from suspension have prevented this technique from being successfully industrialized in the past. Supported nanophotocatalysts (ZnO Nps) have been developed to overcome this problem²⁰⁻²¹. The manufacture of ZnO Nps for the degradation of azo dyes was investigated to see if it might operate as a nanocatalyst in the photosensitized induced process. As the nanophotocatalyst becomes more sensitive, electrons migrate from VB to CB and undergo inter system crossing (ISC), resulting in electronic transitions between Nps, water molecules, DR5B molecules, and dissolved oxygen, as well as highly oxidizing

II. MATERIAL AND METHODS

2.1 Dye

The Dye Direct Red 5B (a sulfonated azo dye) mol.wt, 663; λ_{\max} 510nm was collected from the nearby textile industry and used as such.



2.2 Nanophotocatalyst

In this study, we used the sol-gel method to make ZnO NPs utilizing a variety of solvents (distilled water, ethanol or isopropanol). To commence, add 2.2 g (0.1M) Zn(CH₃COO)₂·2H₂O to 100 ml distilled water and mix constantly at room temperature. When the Zn(CH₃COO)₂·2H₂O is completely dissolved, add the 0.2M NaOH solution (0.4 g in 50 ml deionized water) drop by drop at room temperature using a dropping funnel. At room temperature, the solution mixture is stirred for 1 hour. The temperature of the reaction mixture is raised to 90°C, and it is stirred for 4 hours. The resultant solution is then

allowed to sit overnight. To eliminate contaminants and side products, ZnO Nps are washed twice in ethanol and then once in distilled water. After washing, ZnO Nps are dried in a hot air oven at 90°C. During the drying phase, ZnO will be completely converted. In ethanol and isopropanol solvents, a similar approach is also used to synthesize ZnO Nps.

2.3 Stability of The Catalyst

The catalyst is recycled five times by using dye solution at optimum conditions, after each experiment the nanocatalyst is separated from solution by filtration, washed with deionized water for several times, derived at 35°C for overnight, and then used for the next run, as observed after cycles of the experimentation, the degradation efficiency of the nanocatalyst is still higher than 98%, and the catalytic performance is still higher than 98%. As a result, the produced nanocatalyst has the same catalytic effect as a conventional catalyst.

2.4 Analytical Methods

Making an aqueous solution of the desired concentration from the standard solutions indicates the nanocatalytic degradation of DR5B. A mercury lamp of 200 watts is used to irradiate the area. A spectrophotometer is used to calculate the optical density of a solution (Systronic model 106). Using a standardised 1N NaOH and 1N H₂SO₄ solution, the pH conditions of the desired solution are adjusted. A digital pH meter is used to check the solution's pH. (Fisher Scientific Accumet 50). All of the experiments are carried out at room temperature with the help of photochemical reactor (figure-1).

2.5 Procedure

To accomplish the photochemical reaction, 50ml of the dye solution (DR5B dye) with the optimal concentration (40 mg/l) is taken and 200 mg/l of ZnO nanocatalyst is added to it. A mercury lamp is used to irradiate the mixture with visible light. After a certain time interval, a 3 ml volume of the dye solution is extracted and the absorbance is measured at 510 nm with a spectrophotometer (Systronic model 106) After a set amount of time, the rate of colour loss is measured.

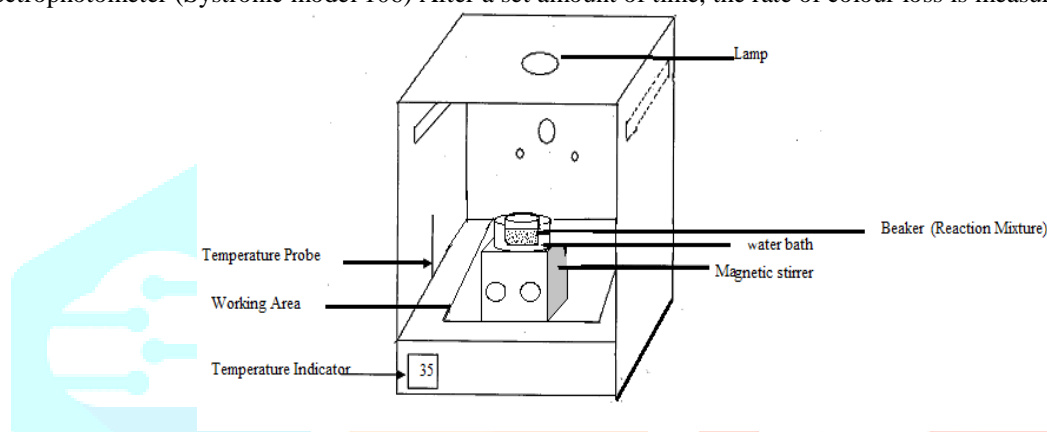


Figure-1: Photochemical Reactor

III. RESULT AND DISCUSSION

At a wavelength of 510 nm, direct dye (DR5B) undergoes nanocatalytic degradation. Dye concentration of 40 mg/l, pH of 7.5-9.0, catalyst loading of 200 mg/l, and light intensity of 200 watt mercury lamp are the best conditions for dye removal. The reaction rate (k) is calculated using the formula: rate (k) = 2.303 × slope. The 1+log O.D. vs exposure time semi logarithmic plot is shown to be a straight line, indicating that the dye bleaching follows pseudo first order kinetics. Figure-2 shows the results graphically.

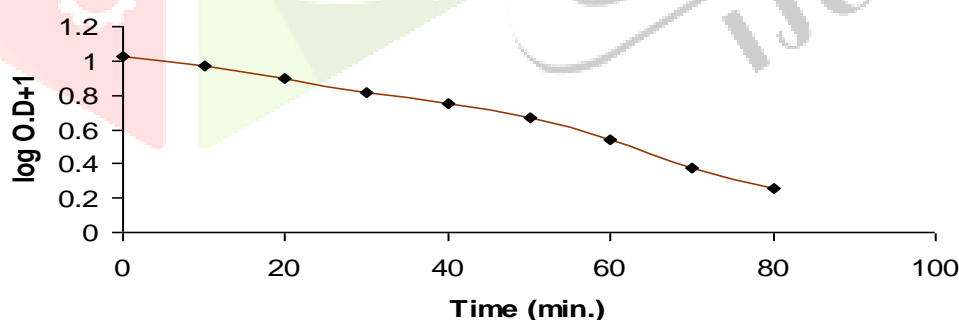


Figure-2: Nanocatalytic degradation of DR5B (λ_{max} 510 nm) under optimum conditions.

3.1 Effect of pH

Nanocatalytic degradation of azo dye is investigated at pH levels ranging from 3.5 to 11.5. In the acidic pH range, the dye degrades at a relatively slow rate. The rate of degradation increases as the pH range increases. Bleaching is quite good in the pH range of 7.5-9.0. Figure-3 illustrates the results graphically. As the pH rises, the rate of degradation begins to slow. Increased availability of OH⁻ ions by interacting with holes generated owing to electronic excitation in the catalyst may explain the increased rate of photocatalytic degradation in the neutral to alkali range (pH 7.5-9.0). The nanocatalytic bleaching is thought to be caused by these hydroxyl radicals.

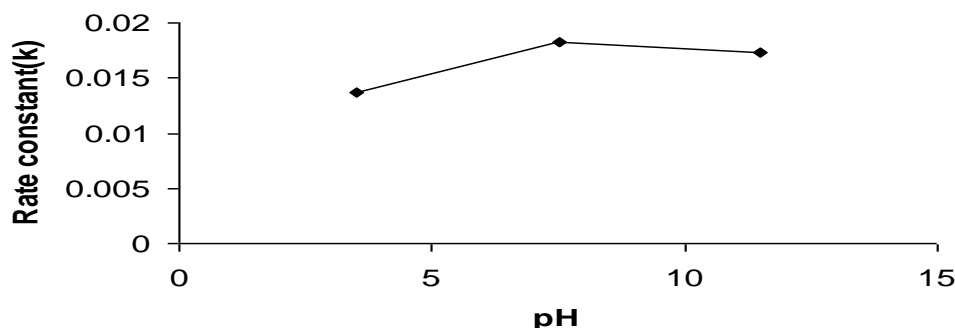


Figure-3: Effect of pH on nanocatalytic bleaching of the dye

3.2 Effect of Nanocatalyst Dosage:

By keeping other parameters constant, the rate constant increases from 100 mg/l to 300 mg/l as nanocatalyst dosing increases. This could be attributed to an increase in the amount of holes, hydroxyl radicals, and supra oxide ions (o^-) as a result of greater catalyst surface area for absorption of quanta and interaction of molecules of the reaction mixture with nanocatalyst. The rate of degradation increases since they are the main oxidizing intermediates in AOP Figure-4 illustrates this graphically.

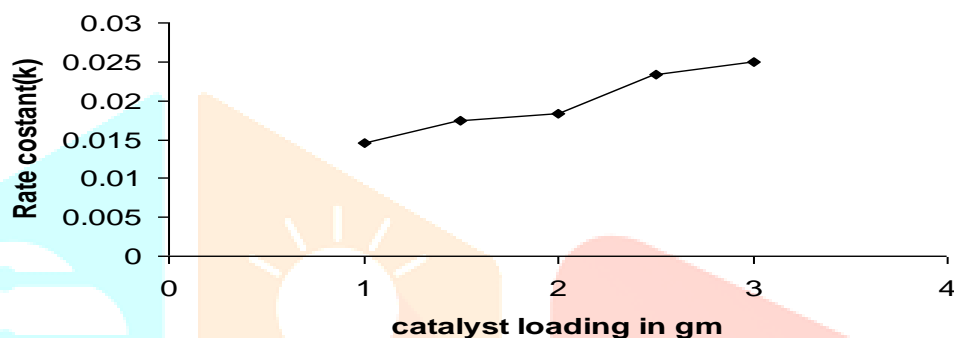


Figure-4: Effect of nanocatalyst loading on nanocatalytic bleaching of the dye

3.3 Effect of Dye

The rate of dye degradation efficiency decreases as the dye concentration rises from 10 mg/l to 70 mg/l Figure-5 illustrates this. The highest degradation was found at low dye concentrations, according to the rate constant. As concentration rises, the rate constant decreases below the ideal level. The decrease in degradation phenomenon at high concentrations can be explained by the dye concentration increasing. However, because the irradiation time and catalyst amount are kept constant, the formation of OH radicals and supra oxide ions are controlled.

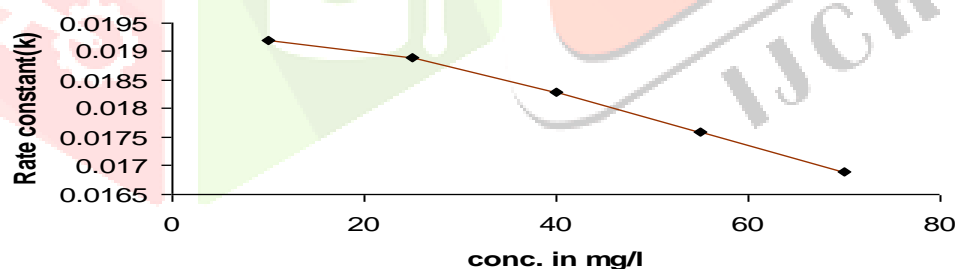


Figure-5: Effect of concentration on nanocatalytic bleaching of the dye

3.4 Effect of Light Intensity

An essentially linear plot between the rate constant and light intensity is obtained in the region of 60 watt to 500 watt, indicating that an increase in light intensity will enhance the rate of reaction. As demonstrated in Figure-6. This could be due to an increase in the amount of photons reaching the catalytic surface area, resulting in an increase in the number of holes, hydroxyl radicals, and supra oxide ions (o^-). As a result, the rate of dye molecule breakdown appears to be increasing in general.

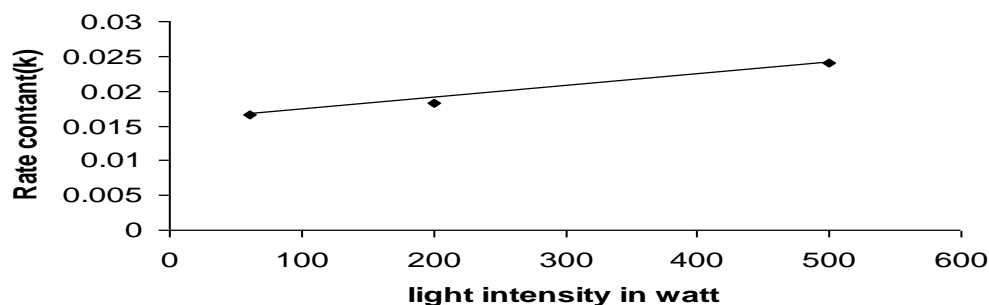


Figure-6: Effect of light intensity on nanocatalytic bleaching of the dye

IV. MECHANISM

On the basis of the previous experiment results, a catalytic degradation mechanism is proposed. When dye molecules are exposed to light, they absorb photons and become excited, causing electrons to move to the singlet state. Intersystem crossing converts these excited singlet state molecules into triplet state molecules. The photocatalyst may accept an electron from the triplet dye, which causes the dye to become positively charged. The solution's dissolved oxygen will extract an electron from the nanocatalyst's conduction band. The dye's positively charged molecules will react with the hydroxyl ion instantly to create hydroxyl radicals, which will oxidize the dye molecule into the product.

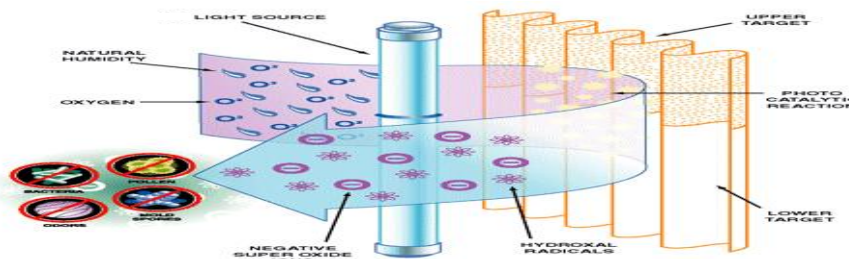


Figure-7: Nanophotocatalysis Action

V. CONCLUSIONS

Finally, it was demonstrated that Nps of ZnO is an effective nanocatalyst for the degradation of DR5B dye in the presence of solar radiation in this work. 30°C, pH 7.5-9.0, 200 mg/l catalyst dose, 40 mg/l dye concentration, and 90 minute solar irradiation period were shown to be the best conditions for the nanocatalytic degradation of DR5B Dye. With respect to the concentration of DR5B dye, the degradation of DR5B by Nanophotocatalyst (Nps of ZnO) followed the Pseudo-first order Kinetics. After 5 cycles, there is no discernible decrease in nanocatalyst efficiency, demonstrating the nanocatalyst's stability and recyclability.

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