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## VISIBLE LIGHT IRRADIATED PHOTOCATALYTIC DEGRADATION OF ORANGE II DYE IN PRESENCE OF ZnO NANOPARTICLES

Veer Singh Barde <sup>\*1</sup>, Brijesh Pare <sup>2</sup>, Shivpriya Pare <sup>3</sup>, Satish Piplode <sup>4</sup>

<sup>\*1, 2, 3, 4</sup> Laboratory of Photocatalysis, Department of Chemistry, Government Madhav Science P G College, (af. Vikram University), Ujjain, MP 456 010, India



### Abstract:

*Zinc oxide nanoparticles were obtained by chemical precipitation method using zinc nitrate and aqueous solution of sodium hydroxide as precursors. The ZnO nanoparticles exhibited excellent photocatalytic activity for Orange-II dye degradation under visible light irradiation. ZnO nanoparticles are easy to recover and can be used upto three times without loss of degradation activity. We observed that Fenton reagent showed good activity for Orange II dye decolourization and degradation. Photocatalytic degradation of Orange II dye using  $H_2O_2/Fe^{3+}$  has also been studied and optimum conditions for the decolourization and degradation of dye has been established.*

**Keywords:** ZnO Nanoparticles; Orange-II Dye; Photo-catalytic Degradation; Visible Light.

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### 1. Introduction

In the textile industries, during manufacturing and processing operations large amount of dyes are lost to the effluents and these colored dye effluents create severe environmental pollution issues by discharging toxic and potential carcinogenic substances into the aquatic sources.<sup>1</sup> Therefore, some new treatment methods are required for the removal of persistent dye molecules into converting them in harmless compounds in water.<sup>2-5</sup> These effluents generated from these industries when contains considerable amounts of dyes causes coloration of water and poses a threat to aquatic life as well.<sup>6</sup> Moreover, their existence in drinking water constitutes a potential human health hazard. Hence, it is crucial to eliminate these dyes from water.<sup>7-8</sup>

Advanced oxidation processes (AOPs) have been popular for degradation of organic pollutants in recent years, due to its effectiveness and environmentally safe nature. These processes are based on the production of  $\cdot OH$  radicals and for degradation they attacks on most of the organic molecules without any specific selectively.<sup>9-10</sup>

Photo-catalysis using semiconductor has been widely studied for its potential application in environmental protection and solar energy transformation. In the past few years many catalysts

like ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, CdS and ZnS have been studied for photocatalytic oxidation of dyes.<sup>11</sup> In present work ZnO NPs were used for degradation of Orange II (OII), in presence of visible light.<sup>12-13</sup>

Several parameters like concentrations of H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, NaCl, and Na<sub>2</sub>CO<sub>3</sub> in the degradation of Orange-II dye have been studied. The effects of some other parameters like initial dye concentration, amount of ZnO NPs, solution pH, temperature and light intensity were also studied. The destruction of aromatic ring and mineralization of dye was confirmed by the estimation of COD, CO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> ion and UV-Visible spectral analysis.<sup>14-15</sup>

## 2. Materials and Methods

### 2.1. Reagents

Zn (NO<sub>3</sub>)<sub>2</sub>, LOBA Chemie, NaOH, Merck and Orange-II dye (ALDRICH) were used. All other chemicals used were of analytical grade. Double distilled water was used throughout the study to prepare the solution. The catalyst and dyes were used without further purification.

### 2.2. Photo Reactor and Light Source

A 500-W halogen lamp was used as the light source. The photocatalytic reaction was carried out in a batch reactor with dimension of 7.5 x 6.0 cm (height x diameter) provided with an external water flow jacket connected to a thermostatic bath and able to maintain the temperature in the range of 30±0.5°C.

### 2.3. Procedure

For irradiation experiment 100ml aqueous solution of the Orange II dye of desired concentration was taken in the photoreactor and the solution was stirred and bubbled with air for at least 10 min in the dark to establish the adsorption equilibrium. The solution was then analyzed spectrometrically. Aliquots were taken at 10 min time intervals and centrifuged to separate the catalyst from the solution. A visible spectrophotometer (Systronic model no. 166) was used for measuring the absorbance of the reaction mixture. The intensity of light was measured by digital lux meter (Lutron LX-101). The pH of the solution was measured using a digital pH meter. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution.

## 3. Results and Discussion

### 3.1. Effect of Catalyst

The photodegradation of the Orange II has been found at different amount of ZnO NPs. With the increase in amount of photocatalyst the rate got improved from 60 mg to 90 mg/100mL and then the degradation rate decreased upto 120 mg/100mL. The increase in the reaction rate was due to the increase in active sites for the production of •OH radicals. The degradation reached maximum at optimal concentration of ZnO NPs. Moreover increase in the photocatalyst amount resulted in

the decrease in the degradation rate due to turbidity, which reduce the light transition through the solution, while below this optimum level it is assumed that the catalyst surface and adsorption of light by the catalyst are limited.<sup>16</sup>

### 3.2. Effect of pH

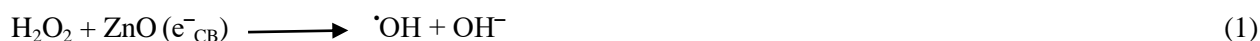
The photocatalytic degradation efficiency got greatly influenced by pH changes. The effect of pH on the photocatalytic reaction could be mainly explained by the surface charge of ZnO NPs. Experiments were conducted at different initial pH values varying from 4 to 10. The current degradation of dye was increased up to 7.5 and further increase in pH got resulted into decreased in the degradation rate. The increase in rate of photocatalytic mineralization might be due to the further availability OH<sup>-</sup> ions in basic medium which would generate more <sup>•</sup>OH radicals by combining with holes, which are formed due to the electronic excitation. At higher pH the rate of degradation decreased due to competition between OH<sup>-</sup> groups to attach to active site of catalyst.<sup>17</sup> At lower pH positively charged active sites on catalyst surface caused low concentration of positively charged dyes molecule on catalyst surface.<sup>18</sup>

### 3.3. Effect of Orange II (OII) Concentration

The effect of different initial dye concentration was investigated in suspensions containing 90 mg / 100 mL ZnO NPs at constant pH 7.5 and varying the initial dye concentration from 1x10<sup>-5</sup> mol dm<sup>-3</sup>. The rate of degradation increased up to a concentration 5x10<sup>-5</sup> mol dm<sup>-3</sup>. This was due to the fact that more dye molecules were available in photoactive volume for the degradation processes. The possible reason for this decrease is, as the initial concentration of the dye got increased, more dye molecules got adsorbed onto the surface of ZnO NPs. The rate of degradation was decreased with further increase in dye concentration.<sup>19</sup>

### 3.4. Effect of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

The photocatalytic degradation of Orange II (OII) dye was conducted at different concentration of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The degradation rate increased with increasing H<sub>2</sub>O<sub>2</sub> concentrations from 2.0 x 10<sup>-6</sup> mol dm<sup>-3</sup> to 8.0 x 10<sup>-6</sup> mol dm<sup>-3</sup>. The reaction rate increased for H<sub>2</sub>O<sub>2</sub> from 5.25 x 10<sup>-4</sup> s<sup>-1</sup> to 6.77 x 10<sup>-4</sup> s<sup>-1</sup>. This was because H<sub>2</sub>O<sub>2</sub> inhabited the electron-hole recombination and hence, quickens the reaction by producing an extremely strong and non-selective oxidant hydroxyl radical from scavenging the electrons and absorption of visible light by the following reactions:<sup>20</sup>



Moreover increase in concentration of H<sub>2</sub>O<sub>2</sub> beyond optimal concentration, resulted into the decrease in rate constant because at an excess H<sub>2</sub>O<sub>2</sub> concentration, it might start acting as hydroxyl radical and hole scavenger.





With increase in  $\text{K}_2\text{S}_2\text{O}_8$  concentration from  $2.0 \times 10^{-6} \text{ mol dm}^{-3}$  to  $8.0 \times 10^{-6} \text{ mol dm}^{-3}$ , rate constant increased from  $5.32 \times 10^{-4} \text{ s}^{-1}$  to  $6.93 \times 10^{-4} \text{ s}^{-1}$ . At optimal amount of  $\text{K}_2\text{S}_2\text{O}_8$ , the rate of degradation has been found to be  $6.93 \times 10^{-4} \text{ s}^{-1}$ .  $\text{K}_2\text{S}_2\text{O}_8$  has always been found to be a beneficial oxidizing agent in photocatalytic decontamination due to generation of  $\text{SO}_4^{\cdot-}$  radicals.<sup>21</sup>



### 3.5. Effect of NaCl and $\text{Na}_2\text{CO}_3$

NaCl often comes out in the effluent along with wastewater. Consequently rate of degradation in presence of  $\text{Cl}^-$  ions has been studied by change in concentration of  $\text{Cl}^-$  ions from  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  to  $12.0 \times 10^{-5} \text{ mol dm}^{-3}$  that resulted into decrease of rate constant from  $4.03 \times 10^{-4} \text{ s}^{-1}$  to  $1.61 \times 10^{-4} \text{ s}^{-1}$ . The decrease in the degradation of dye in the presence of chloride ion might be due to the hole scavenging properties of chloride ion.

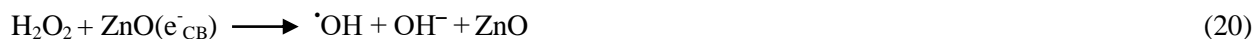


Similarly  $\text{Na}_2\text{CO}_3$  is mostly used in the dyeing bath in order to adjust the pH of the bath as it plays an important role in fixing of dye on the stuffs and in the fastness of color. Consequently the wastewater from the dyeing operation will contain considerable amount of carbonate ion.<sup>22</sup> With an increase in the amount of carbonate ion from  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  to  $12.0 \times 10^{-5} \text{ mol dm}^{-3}$  resulted into reduction of rate constant from  $4.42 \times 10^{-4} \text{ s}^{-1}$  to  $2.07 \times 10^{-4} \text{ s}^{-1}$ . The inhibition in the degradation of dye is due to the hydroxyl scavenging property of carbonate ions, which can be accounted from the following equation.



### 3.6. Mechanism of Orange II (OII) Dye Degradation

The mechanism of photosensitization approach for degradation of dye molecules on ZnO NPs surface is shown as under:



The (OH $\cdot$ ) radical being very strong oxidizing agent can oxidize most of organic pollutants to end product. The role of reductive pathways in heterogeneous photocatalysis has been found to be in minor extent as compared to oxidation.

As the degradation process precedes with illumination of many unstable intermediate species which finally mineralized into CO $_2$ , H $_2$ O and NO $_3^-$ . Significant amount of NO $_3^-$  released during the mineralization of dye. Complete disappearance of peaks in UV-Vis region indicates the absence of any organic moiety.<sup>23-24</sup>

#### 4. Conclusion

This detailed study confirmed that ZnO NPs is efficient for photocatalytic mineralization of Orange-II dye. The present method depends on solution pH. The result clearly indicated that Orange-II dye underwent massive degradation in pH more than 7.5 and addition of H $_2$ O $_2$  and S $_2$ O $_8^{2-}$  oxidants significantly increased the photocatalytic activity of ZnO NPs but, the presence of NaCl and Na $_2$ CO $_3$  inhibited the photodegradation process. UV-Visible spectral data and evolution of CO $_2$  and formation of NO $_3^-$  ions confirmed the mineralization of dyes during photocatalytic degradation.

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\*Corresponding author.

E-mail address: barde.veeru90@ gmail.com/brijeshpare2009@ hotmail.com