



## **PHOTOCATALYTIC DEGRADATION OF CHLOROPHENOL RED IN AQUEOUS SOLUTION BY ZINC OXIDE**

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### **ABSTRACT**

Photocatalytic degradation of chlorophenol red dye by ZnO has been investigated in aqueous solution. The effects of different parameters such as pH, amount of ZnO, dye concentration and light intensity on the rate of degradation of dye solution were also studied. A tentative mechanism has also been proposed for the photocatalytic degradation of dye.

**Key words:** Photocatalytic degradation, ZnO, Chlorophenol red dye.

### **INTRODUCTION**

Textile industries produce large volume of colored dye effluents, which are toxic and non-biodegradable<sup>1</sup>. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the waste water. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents<sup>2-5</sup>. However, these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment<sup>6-8</sup>.

Recently there has been considerable interest in the utilization of advanced oxidation processes (AOP's) for the complete degradation of dyes. AOP's are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants

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quickly and non-selectively<sup>9,10</sup>. AOPs include photocatalytic systems such as combination of semiconductors and light, and semiconductor and oxidants. Semiconductors (such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band<sup>11</sup>. On irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl radical (oxidation potential 2.8 V) or superoxide radicals.<sup>12</sup> Hussein and co-workers<sup>13-17</sup> reported that titanium dioxide and zinc oxide have good photocatalytic properties and both catalysts are nominated to be promising substrates for photodegradation of different organic pollutants under artificial and solar irradiation. Although, TiO<sub>2</sub> in the anatase form has been used for many environmental applications, ZnO (3.2 eV) may be a suitable alternative to TiO<sub>2</sub> so far as band gap energy is concerned. The quantum efficiency of ZnO powder is also significantly larger than that of TiO<sub>2</sub> powder, and higher catalytic efficiencies have been reported for ZnO<sup>18</sup>. Meng and Juan<sup>19</sup> reported that zinc oxide is an excellent photocatalytic oxidant for different types of pollutants in wastewater such as pharmacy wastewater, printing and dyeing wastes and paper making wastewater. Kavitha and Palanisamy<sup>20</sup> found that ZnO is more efficient than TiO<sub>2</sub>- P25 and TiO<sub>2</sub>-UV-100 in photocatalytic degradation of reactive red 120.

More recently work shows successfully photodegradation of *m*-cresol and *p*-cresol by ZnO under visible-light irradiation<sup>21,22</sup>. Mansilla and Villasnov<sup>23</sup> investigated the ZnO-catalyzed photodegradation of Kraft-Black liquor, which is an effluent from pulp and paper industries. Photocatalytic reaction of xylidine ponceau dye by ZnO powder has been reported by Sharma et al.<sup>24</sup> Photocatalytic degradation of azo dyes in water using ZnO as photocatalytic has been investigated by Daneshvar et al.<sup>25</sup> Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins et al.<sup>26</sup>

Chlorophenol red is widely used in textile industries, but it causes great potential of water pollution. As a precaution a proper treatment of waste water is necessary before discharge. Therefore, the aim of the present work is to investigate the potential of ZnO as a photocatalyst under irradiation for the oxidation of Chlorophenol red in aqueous solutions and to evaluate the dependence factors for the color removal rate such as concentration of dye chlorophenol red, photocatalyst semiconductor ZnO, irradiation intensity and pH of the experimental solutions. These are the major variables governing the efficiency of the process.

## EXPERIMENTAL

### Methods and materials

In the present work the commercial dye chlorophenol red and photocatalyst ZnO [(C.D.H.), 99%] were used for photocatalytic degradation. For the photobleaching process,  $1 \times 10^{-3}$  M stock solution of dye chlorophenol red was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

The total volume of the reaction mixture was 50 mL. To carry out the photobleaching, the reaction mixture was irradiated by light source (200W Tungsten lamp). Water filter was used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, Model 335). The progress of the reaction was observed at definite time intervals by measuring optical density using UV-Vis. spectrophotometer (Systronics Model 106) at  $\lambda_{\max}$  570 nm. The rate of dye bleaching with the time was monitored continuously.

## RESULTS AND DISCUSSION

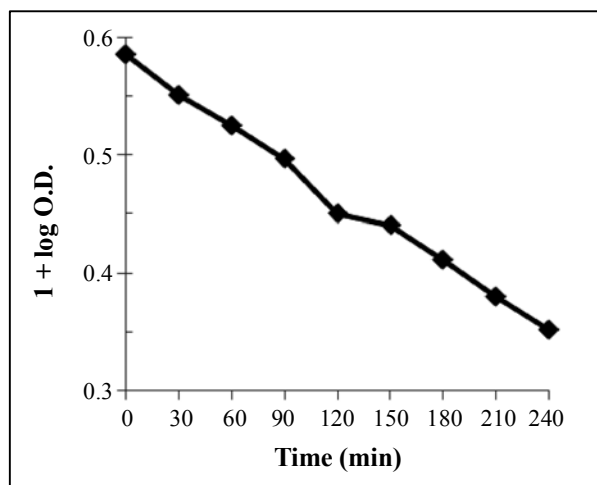
Control experiments (in absence of ZnO, light) confirm the necessity of ZnO and light to follow the photocatalytic path for the photobleaching of dye. The optimum conditions for the photobleaching of dye were  $[\text{Dye}] = 2.0 \times 10^{-5}$  M, ZnO = 0.14 g, and pH = 10.0 at  $\lambda_{\max}$  570 nm. The result of photocatalytic degradation of chlorophenol red is presented in Table 1. It was observed that optical density decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between  $1 + \log \text{O.D.}$  and time was plotted. The linearity of the graph indicates that the photocatalytic degradation of chlorophenol red follows a first order kinetics. The rate constant (k) of this process was  $3.73 \times 10^{-5} \text{ sec}^{-1}$ .

**Table: 1. Typical run of photodegradation of chlorophenol red**

| [Chlorophenol Red] = $2 \times 10^{-5}$ M  |                        | pH = 10.0           |
|--|------------------------|---------------------|
| Light intensity = $80.0 \text{ mWcm}^{-2}$ |                        | Zinc oxide = 0.14 g |
| Time (min.)                                | Optical density (O.D.) | 1+ log O.D.         |
| 0.0  | 0.385                  | 0.5855              |
| 30.0                                       | 0.359                  | 0.5551              |

Cont...

| Time (min.) | Optical density (O.D.) | 1+ log O.D. |
|-------------|------------------------|-------------|
| 60.0        | 0.335                  | 0.5250      |
| 90.0        | 0.314                  | 0.4969      |
| 120         | 0.282                  | 0.4502      |
| 150         | 0.276                  | 0.4409      |
| 180         | 0.258                  | 0.4116      |
| 210         | 0.244                  | 0.3802      |
| 240         | 0.225                  | 0.3522      |



**Fig. 1: Typical run for photocatalytic degradation of chlorophenol red**

### Effect of pH

The effect of pH on the rate of photocatalytic degradation was studied by keeping all the other experimental conditions constant. The results are given in Table 2. It was observed that the rate of photocatalytic bleaching of Chlorophenol red increases on increasing the pH. The increase in the rate of photocatalytic bleaching may be due to more availability of the  $\text{OH}^-$  ions at higher pH values.  $\text{OH}^-$  ions generate more  $\cdot\text{OH}$  radicals by combining with the hole of the semiconductor and these hydroxyl radicals are considered responsible for this photocatalytic bleaching. But after optimum pH (10.0), a further increase in pH of the medium, decreases the rate of photocatalytic bleaching. It may be that Chlorophenol red does not remain in its cationic form due to greater concentration of  $\text{OH}^-$  ions and as such, the force of attraction between dye and negatively charged semiconductor surface decreases. As a consequence, the reaction rate decreases.

**Table: 2. Effect of pH**

[Chlorophenol Red] =  $2.0 \times 10^{-5}$  M      Light intensity =  $80.0 \text{ mWcm}^{-2}$   
 Zinc oxide = 0.14 g

| pH    | $k \times 10^{-5} \text{ sec}^{-1}$ |
|-------|-------------------------------------|
| 4.39  | 1.01                                |
| 5.78  | 1.65                                |
| 7.17  | 1.72                                |
| 8.56  | 1.81                                |
| 10.0  | 3.73                                |
| 11.44 | 2.83                                |

**Effect of concentration of chlorophenol red**

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentration of Chlorophenol red solution. The results are given in Table 3. The rate of photochemical degradation was found to increase with increase in the concentration of Chlorophenol red upto  $2.0 \times 10^{-5}$  M. On further increasing the concentration, a sudden decrease in the rate of degradation was observed. This may be explained on the basis that on increasing the concentration of Chlorophenol red, more molecules of Chlorophenol red, are available for degradation.

**Table: 3. Effect of dye concentration**

pH = 10.0      Zinc oxide = 0.14 g  
 Light intensity =  $80.0 \text{ mWcm}^{-2}$

| [Chlorophenol Red] $\times 10^{-5}$ M | $k \times 10^{-5} \text{ sec}^{-1}$ |
|---------------------------------------|-------------------------------------|
| 0.5                                   | 1.08                                |
| 1.0                                   | 1.91                                |
| 1.5                                   | 2.57                                |
| 2.0                                   | 3.73                                |
| 2.5                                   | 3.13                                |
| 3.0                                   | 2.37                                |

However on increasing the concentration above  $2.0 \times 10^{-5}$  M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of Chlorophenol red is increased, it started acting like a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles, thus, a decrease in the rate of photocatalytic degradation of Chlorophenol red was observed.

#### Effect of amount of semiconductor

The effect of amount of ZnO on the rate of photocatalytic degradation of Chlorophenol red was observed by keeping all other factors constant. The results are given in Table 4. It is clear that the rate of photodegradation increases on increasing amount of ZnO upto 0.14 g, while it becomes almost constant after a 0.14 g. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit (0.14 g) further increase in the amount of ZnO will not increase the exposed surface area of the photocatalyst but it will only increase the thickness of the layer at the bottom of the vessel, once the complete bottom of the reaction vessel is covered by the photocatalyst. It may be considered like a saturation point, above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of Chlorophenol red.

**Table 4: Effect of amount of semiconductor**

[Chlorophenol Red] =  $2.0 \times 10^{-5}$  M      Light intensity =  $80.0 \text{ mWcm}^{-2}$   
pH = 10.0

| Zinc oxide (g) | $k \times 10^{-5} \text{ sec}^{-1}$ |
|----------------|-------------------------------------|
| 0.06           | 1.05                                |
| 0.08           | 1.86                                |
| 0.10           | 2.27                                |
| 0.12           | 2.92                                |
| 0.14           | 3.73                                |
| 0.16           | 3.73                                |

#### Effect of light intensity

The effect of light intensity on the photocatalytic degradation of Chlorophenol red was also observed. The results are given in Table 5. A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity

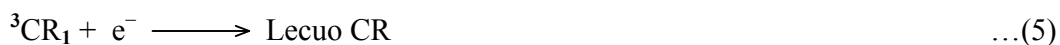
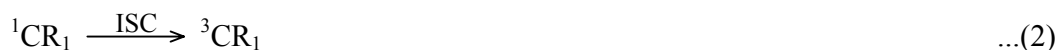
increases the rate of reaction. It may be attributed to the fact an increase in the intensity of light will increase the number of photons striking per unit time per square cm of semiconducting powder.

**Table 5: Effect of light intensity**

| [Chlorophenol Red] = $2.0 \times 10^{-5}$ M |                                      | pH = 10.0 |
|---|--------------------------------------|-----------|
| ZnO = 0.14 g                                |                                      |           |
| Light Intensity (mWcm <sup>-2</sup> )       | $k \times 10^{-5}$ sec <sup>-1</sup> |           |
| 20.0  | 1.12                                 |           |
| 40.0  | 2.53                                 |           |
| 60.0  | 3.27                                 |           |
| 80.0  | 3.73                                 |           |

### Mechanism

On the basis of the experimental observations, a tentative mechanism for photocatalytic degradation of Chlorophenol red may be proposed as-



Chlorophenol red absorbs radiations of suitable wavelength and gives rise to excited singlet state. Then it undergoes inter system crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconductor ZnO also utilizes the radiant energy to excite its electron from valence band to the conduction band, thus leaving behind a hole. This hole abstracts an electron from OH<sup>-</sup> ion to generate  $\cdot\text{OH}$  Free radical, which oxidizes the dye to its leuco form and ultimately degrade it to the end products. The participating of  $\cdot\text{OH}$  radicals as an active oxidizing species was confirmed by using iso-propanol (2-Propanol) as a hydroxyl radical scavenger when the rate of bleaching was drastically reduced.

## CONCLUSION

The experimental data demonstrated that photocatalysis process is promising technique for the degradation of Chlorophenol red dye from aqueous solution. The rate of photocatalytic degradation of Chlorophenol red is enhanced by the production of  $\cdot\text{OH}$  radicals and led to 40% mineralization of the dye in 240 minutes.

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