

## Photocatalytic Degradation of Health Hazardous Dye Alizarin Red by Zinc Oxide in Aqueous Solution

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**Abstract :** *Photocatalytic degradation of Alizarin Red by ZnO has been investigated under different conditions. The effects of some parameters such as pH, amount of ZnO, dye concentration and irradiation time on the degradation rate of dye solution were also examined. A tentative mechanism has also been proposed for this photocatalytic degradation.*

**Keywords:** Photocatalysis, Degradation, ZnO, Alizarin 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 aqueous phase. 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 (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively<sup>9,10</sup>. AOPs include photocatalysis 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>. Upon 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 (oxidation potential 2.8 V) or super oxide radicals<sup>12</sup>. Although, TiO<sub>2</sub> in the anatase form has been used for many environmental applications, ZnO (3.2 eV) is 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>13</sup>.

The hydroxyl radical ( $\bullet$ OH) is a powerful oxidant for degrading non selective organic compounds<sup>14</sup>. The most frequently used photocatalysts are TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, CdS, and SnO<sub>2</sub><sup>15</sup>. Among these ZnO removed several environmental contaminants under UV irradiation<sup>16</sup>. While the great advantage of ZnO is its ability to absorb larger fractions of the solar spectrum than the other photocatalysts<sup>17</sup> and removed many organic contaminants in aqueous solution under visible irradiation<sup>18,19</sup>. More recently our previous work shows

successfully photodegradation of *m*-cresol by ZnO under visible-light irradiation<sup>20</sup>. Sharma *et al.*<sup>21</sup> observed the photocatalytic bleaching of Crystal violet in aqueous suspensions of zinc oxides. Mansilla and Villasnov<sup>22</sup> investigated the ZnO-catalysed photodegradation of Kraft-Black liquor, which is an effluent from pulp and paper industries. Lizama *et al.*<sup>23</sup> reported that ZnO is a more efficient catalyst than TiO<sub>2</sub> for degradation of reactive blue 19.

Alizarin 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 works, is to investigate the potential of ZnO as a photocatalyst under irradiation for the oxidation of textile dyes in aqueous solutions and to evaluate the dependence factors for the color removal rate such as concentration of Dye (AR), photocatalyst semiconductor ZnO, irradiation intensity and pH of the experimental solutions. These are the major variables governing the efficiency of the process.

### Experimental

For the present studies the commercial azo dye Alizarin Red (C.D.H.) and Photocatalyst ZnO (C.D.H., 99% purity) were used for photocatalytic degradation. For the photobleaching process, 1.0 x10<sup>-3</sup>M stock solution of dye Alizarin 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. The concentration of different ingredients in the reaction mixture was [Dye] =2.0x10<sup>-4</sup>M, Zinc Oxide=0.10 g and pH=7.5. To carry out the photobleaching, the reaction mixture was irradiated under light source (200W Tungsten lamp). Water filters

were 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 absorbance using Ultra-Violet spectrophotometer (Systronic Model 106) at 555 nm. The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> ions and evolution of CO<sub>2</sub> were tested by standard procedure.

### Results and Discussion

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst, light to follow the photocatalytic path for the photobleaching of dye. The photocatalytic degradation of Alizarin Red was observed at 555 nm. The optimum conditions for the photobleaching of dye were [Dye] =2.0 x10<sup>-4</sup> M, ZnO =0.10 g, and pH=7.5. The result of photocatalytic bleaching of Alizarin Red is presented in Table 1. It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between 1+ log O.D. and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Alizarin Red follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

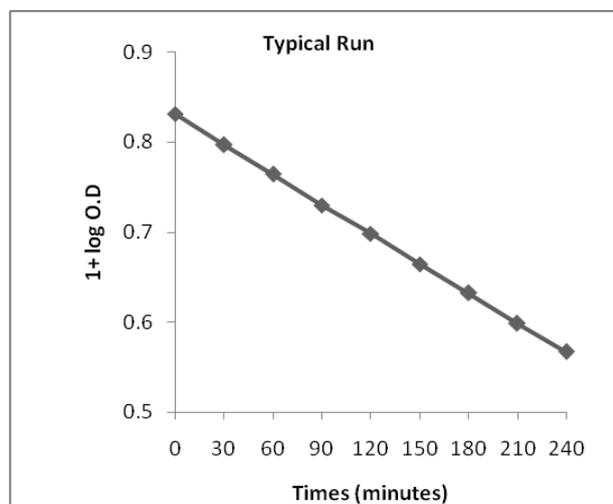
$$\text{Rate Constant (k)} = 2.303 \times \text{Slope} = 4.21 \times 10^{-5} \text{ sec}^{-1}$$

Table.1 Typical Run

[Alizarin Red]= 2.0 x10<sup>-4</sup> M; Zinc Oxide=0.10 g; pH= 7.5; Light Intensity= 80.00mWcm<sup>-2</sup>;

Time (min.)	Optical Density (O.D.)	1+log (O.D.)
0.0	0.678	0.8312
30.0	0.626	0.7966
60.0	0.581	0.7642

90.0	0.537	0.7300
120	0.499	0.6981
150	0.462	0.6646
180	0.429	0.6325
210	0.397	0.5988
240	0.369	0.5670



**Figure.1 Typical Run**

### Effect of pH Variation

The effect of pH on the rate of photocatalytic degradation was studied by keeping all the other experimental conditions constant and changing the initial pH values of Alizarin Red from 4.38 to 10.74, the results of which are illustrated in **Table 2**.

It has been observed that the rate of photocatalytic bleaching of dye increases on increasing the pH. This can be explained on the basis that as the pH of the medium was increased, there is a corresponding increase in the concentration of hydroxyl ions which will adsorb on the semiconductor surface making it negatively charged thus there will be a coulombic attraction between semiconductor surface and cationic dye. This has reflected in an increase of rate of photocatalytic degradation of the dye on increasing pH.

**Table: 2. Effect of pH Variation**

**[Alizarin Red]=  $2.0 \times 10^{-4}$ M; Zinc Oxide = 0.10g; Light Intensity=  $80.00 \text{mWcm}^{-2}$ ;**

pH	$k \times 10^{-5} \text{ s}^{-1}$
4.38	3.45
5.44	3.59
6.50	4.03
<b>7.56</b>	<b>4.21</b>
8.62	3.89
9.68	3.75
10.74	3.03

### Effect of Concentration of Alizarin Red

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentration of Alizarin Red solution. The results are given in **Table 3**. The rate of photochemical degradation has found to increase with increasing concentration of Alizarin Red upto  $2.0 \times 10^{-4}$ M. On further increasing its concentration, a sudden decrease in the rate of degradation was observed.

This may be explained on the basis that on increasing the concentration of dye, more molecules of dye are available for excitation and energy transfer and hence, an increase in the rate is observed. However on increasing the concentration above  $2.0 \times 10^{-4}$ M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of AR was increased, it started acting like a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particle; thus, a decrease in the rate of photocatalytic degradation of Alizarin Red has observed.

**Table: 3. Effect of Dye Concentration**

**pH=7.5; Light Intensity=  $80.00 \text{mWcm}^{-2}$ ; Zinc Oxide = 0.10g;**

[Alizarin Red] $\times 10^{-4}$ M	$k \times 10^{-5} \text{ s}^{-1}$
0.5	1.84
1.0	2.67
1.5	3.73

<b>2.0</b>	<b>4.21</b>
2.5	3.59
3.0	3.45
3.5	2.85

### Effect of Amount Of Semiconductor

The effect of amount of ZnO on the rate of photocatalytic degradation of Alizarin 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 0.10 g, while it becomes almost constant after a 0.10 g (Table. 4). 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, if the amount of semiconductor was further increased, then there will be no increase in the exposed surface area of 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 Alizarin Red. As any increase in the amount of semiconductor after this saturation point 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.

**Table: 4. Effect of Amount of Semiconductor**

**[Alizarin Red]= 2.0 ×10<sup>-4</sup>M; pH =7.5; Light Intensity= 80.00mWcm<sup>-2</sup>;**

Zinc Oxide(g)	K ×10 <sup>-5</sup> sec <sup>-1</sup>
0.04	2.51
0.06	3.20
0.08	3.93
<b>0.10</b>	<b>4.21</b>
0.12	4.23

### Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of Alizarin Red was

also observed. The results obtained 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 increase the rate of reaction because an increase in the intensity of light will increase the number of photons striking per unit area of semiconducting powder.

**Table: 5. Effect of Light Intensity**

**[Alizarin Red]= 2.0 ×10<sup>-5</sup>M; pH =7.5; ZnO= 0.10 g;**

Light Intensity (mWcm <sup>-2</sup> )	k×10 <sup>-4</sup> sec <sup>-1</sup>
20	1.75
40	3.03
60	3.96
<b>80</b>	<b>4.21</b>

### Mechanism

On the basis of the experimental observation, a tentative mechanism for photocatalytic bleaching of Alizarin Red (AR) may be proposed as-



Alizarin 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 of the semiconductor reduces the dye to its leuco form, and ultimately degrades it to the products. In this case however, OH radicals do not

participate as an active species. The fact was confirmed by using 2-propanol as a hydroxyl free radical scavenger, when the rate of bleaching was not affected appreciably.

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### References

1. A. Reife and H.S. Fremann, *Environmental Chemistry of Dyes and Pigments* Wiley New York, 1996.
2. T.F Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.* **2001**, 77, 247.
3. P.P. Zamora, A. Kunz, S.G. Moraes, R. Pelegrini, P.C. Moleiro, J. Reyes and N. Duran, *Chemosphere*, **1999**, 38, 835.
4. L. Ladakowicz, M. Solecka and R. Zylla, *J. Biotechnol.*, **2001**, 89, 175.
5. D. Georgiou, P. Melidis, A. Aivasidis and K. Gimouhopoulos, *Dyes Pigments*, **2002**, 52, 69.
6. I. Arslan, I.A. Balcioglu, T. Tuhkanen and D. Bahnemann, *J. Environ. Engg.*, **2000**, 126, 903.
7. S.K. Chaudhuri and B. Sur, *J. Environ. Engg.*, **2000**, 126, 583.
8. N. Stock, J. Peller, K. Vinodgopal and P.V. Kamat, *Environ. Sci. Technol.*, **2000**, 34, 1747.
9. S. Das, P.V. Kamat, S. Padmaja, V. Au and S.A. Madison, *J. Chem. Soc., Perkins Trans.*, **1999**, 2 1219.
10. Y. Yang, D.T. Wyatt and M. Bahorsky, *Textile Chem. Colorist.*, **1998**, 30, 27.
11. M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahenemann, *Chem. Rev.*, **1995**, 95, 69.
12. W.Z. Tang, An. Huren, *Chemosphere* **1995**, 31, 4157.
13. S. Sakthivel, B. Neppolian, M. Palanichamy, B. Arabindoo, V. Murugesan, *Indian J. Chem. Technol.*, **1999**, 6, 161.
14. A.M. Peiro, J.A. Ayllón, J. Peral and X. Doménech, *Appl. Catal. B: Environ.*, **2001**, 30, 359.
15. [A. Maldotti, A. Molinari, and R. Amadelli, *Chem. Rev.*, **2002**, 102, 3811.
16. S.K. Kansal, M. Singh and D. Sud, *J. Hazard. Mater.*, **2008**, 153, 412-417.
17. S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, and V. Murugesan, *Sol. Energy Mater. Sol. Cells*, **2003**, 77, 65-82.
18. B. Dindar and S. Içli, *J. Photochem. Photobiol. A: Chem.*, **2001**, 140, 263-268.
19. S.K. Pardeshi and A.B. Patil, *Sol. Energy*, **2008**, 82, 700-705.
20. Y. Abdollahi, A. H. Abdullah, Z. Zainal and N.A. Yusof, *Int. J. of Chemistry*, **2011**, 3(3), 31-43.
21. A. Sharma, P. Rao, R. P. Mathur and S. C. Ameta, *J. Photochem. Photobiol. A*, **1995**, 86, 197.
22. H. D. Mansilla and J. Villasnov, *J. Photochem. Photobiol. A*, **1994**, 78, 267.
23. C. Lizama, J. Freer, J. Baeza and H.D. Mansilla, *Catal Today*, **2002**, 76:235-246.