

# UV/Solar Photocatalytic Degradation of Jakazol Red 5B: Comparison of Photocatalytic Efficiency of ZnO and TiO<sub>2</sub>

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**Abstract:** In present study, photocatalytic degradation of Jakazol Red 5B (JR5B), an anionic dye has been investigated in a batch reactor under UV/Solar light in slurry mode using ZnO and TiO<sub>2</sub> as a photocatalyst. The variables studied include catalyst dose, solution pH and dye concentration. Optimized concentration was found to be 25 ppm. The degradation rate of JR5B was favourable at pH 7 under UV/ZnO; solar/ZnO and at pH 4 under solar/ TiO<sub>2</sub>; UV/TiO<sub>2</sub> system. Optimum value of catalyst dose was found to be 1 g/l. The disappearance of JR5B obeyed first order kinetics and the value of the rate constants k was 0.174 and 0.029 min<sup>-1</sup> with ZnO and TiO<sub>2</sub> respectively.

**Keywords** — Decolorization, Nanophotocatalyst, Photocatalyst, Photocatalytic activity, TiO<sub>2</sub>, ZnO.

## I. INTRODUCTION

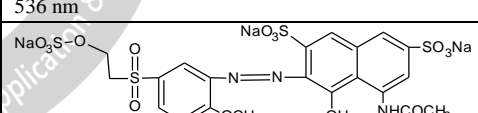
Dyestuff and other commercial colourants have emerged as a focus of environmental remediation efforts [1]. Conventional or non-destructive remediation methods suggested to treat dyes are sedimentation, membrane filtration, adsorption, coagulation-flocculation and precipitation, electrocoagulation and ion-exchange [2-3]. These treatment practices which transfer the pollutants from one phase to another are confined by cost and time factor and huge amount of secondary pollution production [4]. Biodegradation and advance oxidation process (AOP) are destructive techniques employed to treat waste water effluents. Biodegradation means breakdown of pollutants with the use of living micro-organisms (bacteria, algae, fungi or yeast) or enzymes. It is low cost treatment process which cannot be used for most compounds because of its harmful effect on the organism [5].

So, the complete degradation of the pollutants by conventional methods is not possible as they suffer from drawbacks which limit their utilisation on industrial scale. Among AOP, photocatalysis is attractive and effective method for waste water treatment [6]. The photocatalytic degradation focuses on the use of semiconductors which lead to complete the mineralisation of organic pollutants to CO<sub>2</sub>, water and mineral acids [7]. Various semiconductors employed in photocatalysis are TiO<sub>2</sub>, ZnO, CdS, SnO<sub>2</sub>, CuO, WO<sub>3</sub> [8]. Because of non-toxic nature and easy availability, low cost and strong oxidising power, TiO<sub>2</sub> and ZnO semiconductors are extensively used in photocatalysis [7, 9].

Jakazol Red 5B is vinyl sulphone based an anionic azo dye, having versatile applications. It is commonly used for dyeing cotton, viscose, flex and jute but not suitable for silk, wool and polyester and is reasonably photostable to

sunlight. The degradation of Jakazol Red 5B using ZnO and TiO<sub>2</sub> is reported in presence of UV/solar light. The effect of change of pH, amount of catalyst and concentration of dye has also been studied. The chemical structure and other properties of Jakazol Red 5B are given in Table 1.

**Table 1: Main Characteristics of Jakazol Red 5B**

Name of dye	Jakazol Red 5B
IUPAC	Sodium(3-((8-acetamido-1-hydroxy-3,6-disulfonatophthalen-2-yl)diazenyl-4-methoxyphenylsulfonyl)ethylsulfate
Molecular formula	C <sub>21</sub> H <sub>18</sub> N <sub>3</sub> Na <sub>3</sub> O <sub>15</sub> S <sub>4</sub>
Molecular weight	749.6 g/mol
λ <sub>max</sub>	536 nm
Structure	

## II. MATERIALS AND METHODS

### A. Materials

ZnO was purchased from Merck. Titania P-25 (surface area 50 m<sup>2</sup>/g) was obtained from Degussa. Commercially available Jakazol Red 5B (JR5B) was obtained from Nahar Fabrics, Lalru, India and was used without further purification. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1M HCl or 1M NaOH.

### B. Instruments

Photochemical degradation experiments were carried out in specially designed reaction vessels (diameter 0.08 m, volume 500 ml) in the photoreactor equipped with 4 UV tubes each of 30W (Philips). The intensity of UV light was

$2.4 \times 10^{-6}$  einstein / minute measured by chemical method i.e. potassium ferrioxalate actinometry [10]. The experimental set up was reported earlier [11]. Constant stirring of solution was insured by using magnetic stirrers and aeration was done with the help of aquarium aerator. The spectra were taken with UV-VIS Spectrophotometer (Shimadzu 1650); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution.

### C. Procedure

The degradation experiments were carried out by adding 100 mg of photocatalyst (ZnO) or (TiO<sub>2</sub> Degussa) to 100 ml of dye solution and suspension was subjected to irradiation under UV/Solar light. The aqueous suspension was magnetically stirred and aerated throughout the experiment. At different time intervals aliquot was taken out with the help of syringe and then filtered through millipore syringe filter of 0.45  $\mu$ m. The absorption spectra were recorded at  $\lambda_{max}$  536 nm. The rate of degradation was studied in terms of changes in absorption spectra. The decolorization efficiency (%) has been calculated as:

$$\text{Efficiency (\%)} = (C_0 - C) / C_0 \times 100$$

Where  $C_0$  is the initial concentration of dye and  $C$  is the concentration of dye after photo irradiation. Similar experiments were carried out by varying the pH of the solution, concentration of dye and dose of photocatalyst.

## III. RESULTS AND DISCUSSION

### (i) Degradation of Jakazol Red 5B under UV Irradiation

#### A. UV-Vis Spectra

The spectra of JR5B show peaks at 379, 310 and 234 nm in UV region and a main band with a maximum at 536 nm in visible region. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at  $\lambda_{max}$ , i.e., 536 nm which decreased gradually and finally disappeared indicating that the dye had been decolorized.

#### B. Photolysis/Photocatalysis of Jakazol Red 5B

Decolorization of JR5B was investigated under five different experimental conditions through UV alone, UV/TiO<sub>2</sub>, UV/ZnO, Dark/ TiO<sub>2</sub> and Dark/ZnO. Figure 1 depicts the photocatalytic decolorization of JR5B under these experimental conditions. The decolorization rate was recorded in terms of change in intensity of characteristic peak at 536 nm.

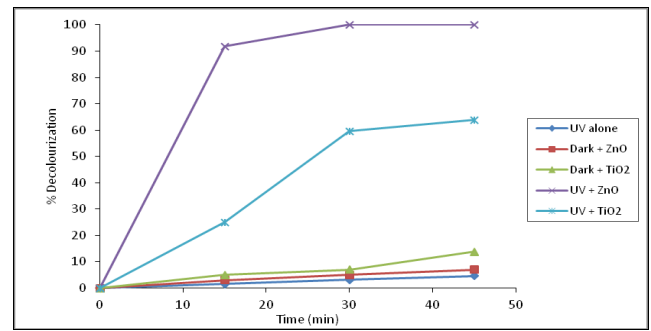


Figure 1: Photocatalytic Decolourization of JR5B Dye (Dye Initial Concentration—25 mg/L, pH—7, Catalyst Dose—1g/L)

Initially blank experiments were performed under UV irradiation without addition of any catalyst (UV alone) and only 4.55% decolourization was observed. The adsorption of the dye was also observed with both catalysts, i.e., Dark/TiO<sub>2</sub> and Dark/ZnO. Only 5% adsorption of the dye was seen in the same time with ZnO and 7% TiO<sub>2</sub> under dark conditions. After that photocatalytic experiments were carried out using both catalysts at fixed dye concentration (25 mg/L) and catalyst loading of 1 g/L. When experiments were performed under UV irradiation with ZnO as photocatalyst (UV/ZnO), the complete decolourization of dye was achieved after 30 min, whereas with TiO<sub>2</sub> as a photocatalyst (UV/ TiO<sub>2</sub>), only 59.64% decolourization of JR5B was observed in the same duration. It indicates that ZnO exhibits higher photocatalytic activity than TiO<sub>2</sub> for the decolourization of JR5B.

#### C. Effect of Catalyst Dose

In order to optimize the dose of catalyst the experiments were performed by varying catalyst concentration from 0.5 g/L to 2.0 g/L. The graph plotted (Figure 2) between amount of catalyst used and percentage degradation reveals that with an increase in catalyst dose degradation efficiency increases upto 1.5 g/L catalyst dose in case of TiO<sub>2</sub> and degradation efficiency is maximum with 1.0 g/L of ZnO as shown in Figure 3. Thus with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface [12]. It has also been reported that the catalyst amount has both positive and negative impact on the photodecomposition rate [13]. Moreover, TiO<sub>2</sub> powders (commercial photocatalysts) have scattering albedo ( $\omega$ ) higher than 0.5 [14], which increases the radiation scattering results in reducing the number of photons absorbed hence further increase in catalyst dose decreases the decolourization efficiency. Therefore the catalyst doses 1.5 (TiO<sub>2</sub>) and 1.0 (ZnO) g/L were fixed for degradation of JR5B.

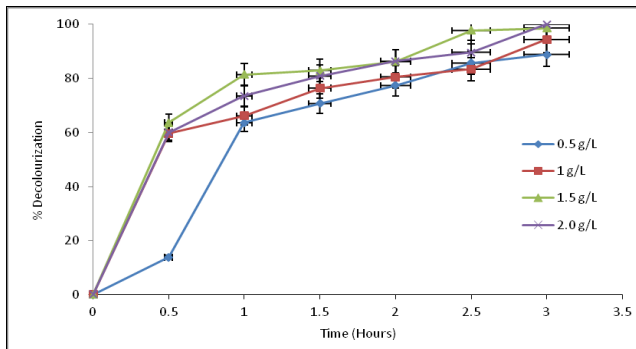


Figure 2: Effect of  $\text{TiO}_2$  Dose on Decolourization Rate of JR5B Dye (Dye Initial Concentration—25 mg/L, pH—7)

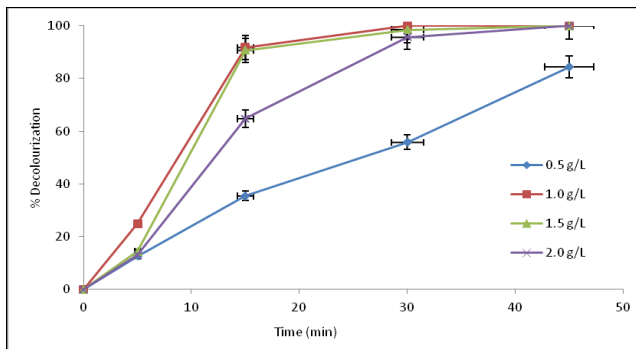


Figure 3: Effect of ZnO Dose on Decolourization Rate of JR5B Dye (Dye initial Concentration—25 mg/L, pH—7)

#### D. Effect of pH

The effect of pH of the solution on the percentage photodegradation was examined in the range 2-10. Figure 4 shows the colour removal efficiency of photocatalysts as a function of pH. The results reveal that the lesser degradation of dye occurs in basic solution and higher in acidic region with  $\text{TiO}_2$ . However in case of ZnO, the maximum degradation occurs at pH 7. The interpretation of pH factor on the efficiency of photocatalytic degradation process can be explained on the basis of acid base property of metal oxide surface and the ionization state of ionizable organic molecule. The point zero charge (pzc) for  $\text{TiO}_2$  (Degussa P25) is 6.8 and for ZnO is  $9.0 \pm 0.3$  [14].  $\text{TiO}_2$  surface is positively charged in acidic media ( $\text{pH} < 6.8$ ) whereas it is negatively charged under alkaline condition ( $\text{pH} > 6.8$ ). ZnO surface is positively charged below pH 9 based on their pzc. JR5B is an anionic dye in aqueous solution. For  $\text{TiO}_2$ , rate of photodecolourization increased with decrease in pH, exhibiting maximum efficiency (100%) at pH 4. Findings of others [15-16] also show that degradation of anionic dyes is more in acidic medium because at pH higher than pzc of titania, its surface becomes negatively charged so adsorption will be less.

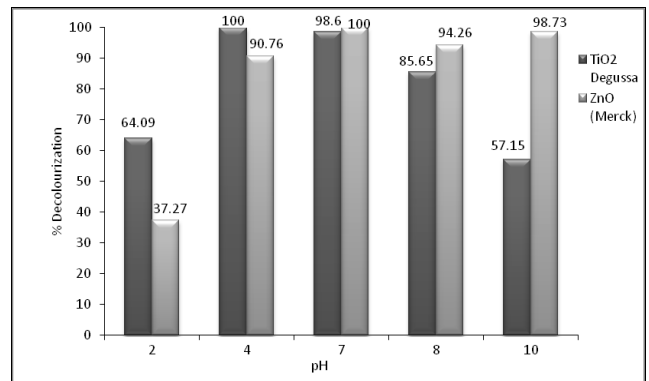


Figure 4: Effect of pH on Decolourization Rate of JR5B Dye (Dye Initial Concentration—25 mg/L,  $\text{TiO}_2$  Dose—1.5 g/L, Time: 3 h, ZnO Dose—1 g/L, Time: 30 min.)

#### E. Effect of Initial Concentration of Jakazol Red 5B

After optimizing the experimental conditions, the photocatalytic discoloration of JR5B was carried out by varying the initial concentration of the dye from 10-100 ppm.

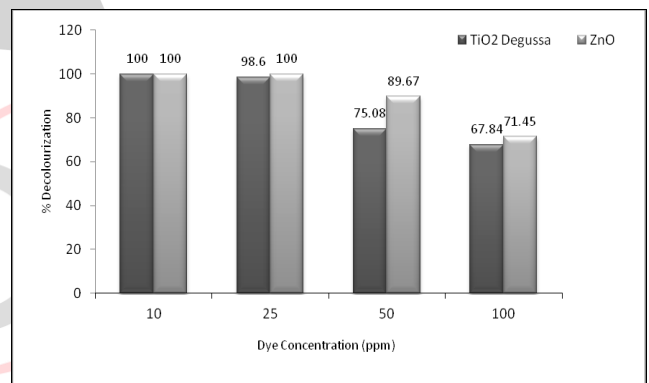


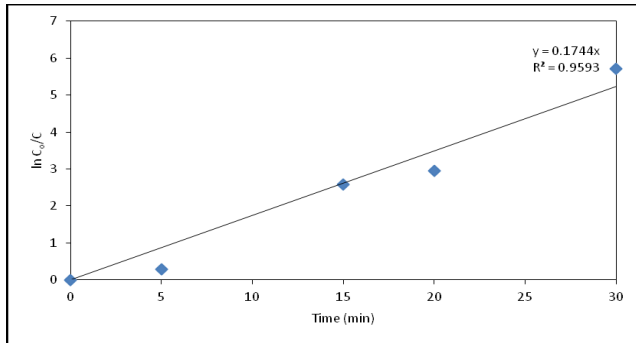
Figure 5: Effect of Initial Concentration of JR5B Dye on Percentage Decolourization under Optimized Conditions ( $\text{TiO}_2$  Dose—1.5 g/L, ZnO Dose—1 g/L, pH—7)

Figure 5 clearly shows that with increase in initial concentration of dye percentage decolourization of JR5B decreases with  $\text{TiO}_2$  as well as ZnO. However percentage degradation for different concentration of dye solution is more with ZnO as compared to  $\text{TiO}_2$ .

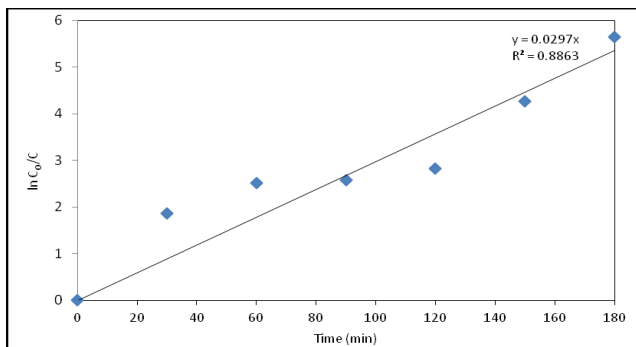
#### F. Kinetic Analysis of Photocatalytic Degradation of Jakazol Red 5B

Figure 6 shows the kinetics of disappearance of JR5B for an initial concentration of 25 mg/L under optimized conditions with ZnO and  $\text{TiO}_2$ . The results show that the photocatalytic decolourization of the dye can be described by the first order kinetic model,  $\ln(C_0/C) = kt$ , where  $C_0$  is the initial concentration and  $C$  is the concentration at any time,  $t$ . The semilogarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be  $R^2 = 0.909$  for  $\text{TiO}_2$  and 0.943 for ZnO. The rate constants for degradation of JR5B using ZnO and  $\text{TiO}_2$  were calculated to be 0.174 and  $0.029 \text{ min}^{-1}$ .

respectively. This constant is a function of many operational conditions and will vary with reactor configuration unless the effect of the photon absorption is included in the rate equation [17].



a) ZnO



b) TiO<sub>2</sub>

Figure 6: Kinetics Analysis for JR5B Dye under Optimized Conditions

a) ZnO b) TiO<sub>2</sub>

(ii) Degradation of Jakazol Red 5B under Solar Irradiation

A. UV-Vis Spectra

Time-dependent UV-Vis spectrum of JR5B dye during photoirradiation with TiO<sub>2</sub> under solar irradiation is shown in Figure 7. The spectra of JR5B shows peaks at 379, 310 and 234 nm in UV region and a main band with a maximum at 536 nm in visible region. The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at  $\lambda_{max}$ , i.e., 536 nm which decreased gradually and finally disappeared indicating that the dye had been decolourized.

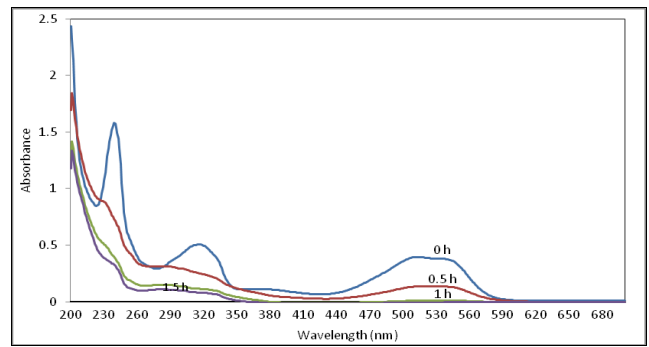


Figure 7: Time-Dependent UV-Vis absorption Spectra for Decolourization of JR5B using TiO<sub>2</sub> under Solar Irradiation

B. Effect of Catalyst Dose

The experiments were performed by varying catalyst concentration from 0.5 g/L to 2.0 g/L for dye solution of 25 ppm at neutral pH. The results obtained with ZnO were same as under UV irradiation i.e. maximum degradation is observed with 1 g/L of the catalyst (Figure 8) whereas optimized dose of TiO<sub>2</sub> is less (1 g/L) under solar irradiation as compared to UV irradiation (1.5 g/L). The rate of decolourization was more under solar irradiation as compared to UV irradiation with both the catalysts. Therefore the catalyst dose 1 g/L was fixed for further studies.

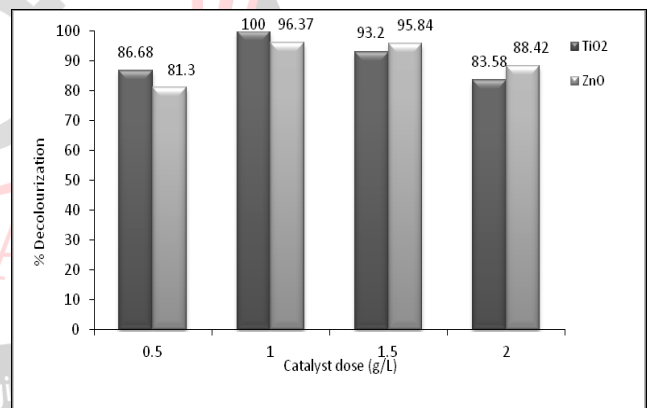
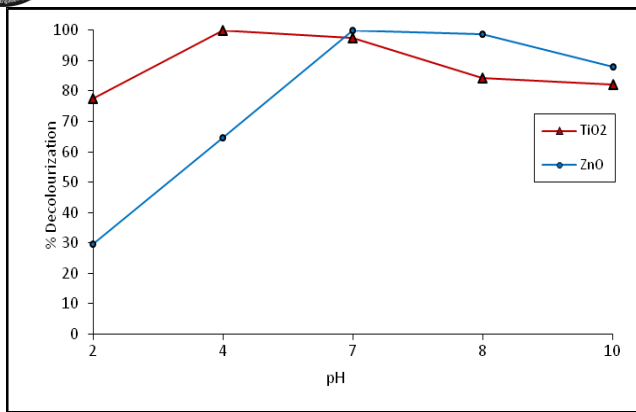


Figure 8: Effect of Catalyst Dose on Decolourization of JR5B under Solar Irradiation (Dye Initial Concentration—25 ppm, Time: 1.5 h, pH—7)

C. Effect of pH

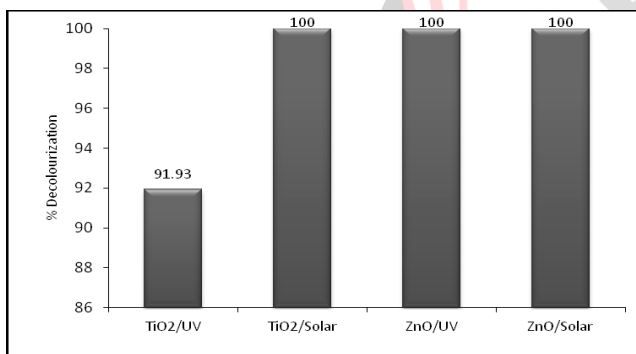
The effect of pH of the solution on the percentage photodegradation of JR5B was examined in the range 2-10 under solar irradiation. Figure 9 shows the colour removal efficiency of JR5B as a function of pH. It has been observed that the maximum decolourization efficiency with TiO<sub>2</sub> was observed at pH 4 and at pH 7 with ZnO.



**Figure 9: Effect of pH on Decolourization of JR5B under Solar Irradiation (Dye Initial Concentration—25 ppm, TiO<sub>2</sub>—1.5 g/L, ZnO—1g/L, Time: 1h)**

#### D. Comparison of Solar/UV Irradiation on Photocatalytic Degradation of JR5B under Optimized Conditions

The comparison of percentage decolourization of JR5B under UV and solar light is shown in Figure 10. It was observed that complete decolourization was achieved in 1 h under solar radiations with ZnO as well as TiO<sub>2</sub> whereas 91.93% decolourization with TiO<sub>2</sub>/UV system and complete decolourization with ZnO/UV was achieved in the same time. It shows the rate of decolourization is faster under solar light as compared to UV light.



**Figure 10: Comparison of Solar/UV Irradiation on Photocatalytic Decolourization of JR5B under Optimized Conditions (Dye Initial Concentration—25 ppm, pH—4 for TiO<sub>2</sub> (1.5 g/L), pH—7 for ZnO (1 g/L), Time: 1 h)**

#### IV. CONCLUSION

Experimental results indicated that decolorisation of dye is facilitated in the presence of catalyst and were favourable with UV/ZnO and solar/ZnO at pH7, which is preferred to be the discharge pH of industrial effluents. As the initial concentration of dye was increased the rate of decolourisation was decreased. The optimum dose of both the catalysts required for complete degradation of the dye solution was 1 g/L. The photocatalytic decolorization followed pseudo-first order kinetics. Comparison of photocatalytic activity of catalysts has clearly indicated that ZnO is more efficient photocatalyst for decolorisation of JR5B at neutral as well as basic media, but TiO<sub>2</sub> shows better efficiency in acidic media.

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