

## Original Article

# Mixed ZnO-TiO<sub>2</sub>Suspended Solution as an Efficient Photocatalyst for Decolorization of a Textile Dye from waste water

Mohammad Ali Mooji<sup>1</sup>, Masoumeh Tabatabaee<sup>\*2</sup>

<sup>1</sup> Department of chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran.

Received: 2014/4/11

Accepted: 2015/3/8

---

### Abstract

**Introduction:** In this research mixed ZnO and TiO<sub>2</sub> was used for degradation of an azo dye (Direct Blue 71).

**Material and Methods:** In comparison with just TiO<sub>2</sub> or ZnO as photocatalyst, mixed photocatalyst (ZnO/TiO<sub>2</sub>) is more efficient catalyst for degradation of dye under UV irradiation. The progress of the reactions was monitored spectrophotometrically by measuring the absorbance of dye at special wavelengths. The effects of various parameters such as ZnO/TiO<sub>2</sub> ratio, amount of photocatalyst, pH, initial dye concentration and irradiation time on decolorization rate were systematically investigated.

**Results:** Results show that approximately 90 % of Direct Blue 71 has been eliminated after 70 minutes and optimized condition.

**Keywords:** Photocatalyst; Textile Dyes; Direct Blue 71; Degradation; UV irradiation

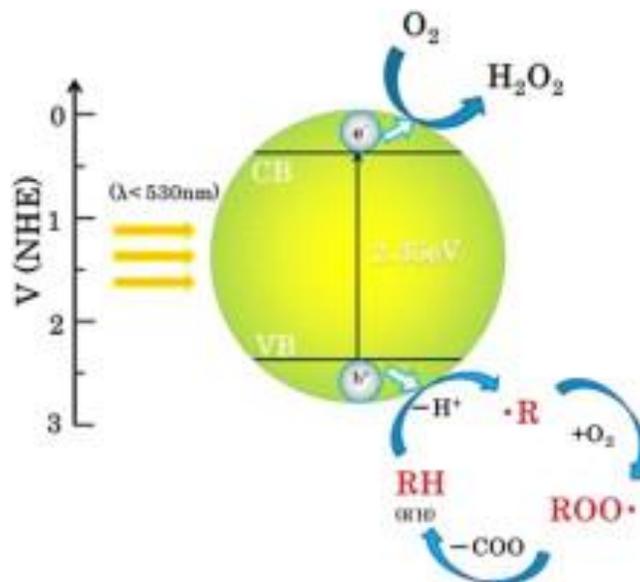
---

\* Corresponding author; +983518117582 E-mail: tabatabaee@iauyazd.ac.ir

## Introduction

Textile industries produce large volume of colored dye effluents which are toxic and removal of dyes from wastewater is a significant environmental issue. For the treatment of dye-containing wastewater, various biological, physical and chemical methods such as microbial biodegradation, membrane filtration, oxidation, ozonation, adsorption, and ultra-filtration have been used<sup>[1-5]</sup>. However, many of these technologies are cost prohibitive, especially when they have been applied for treating large waste streams and some of them merely transfer dyes from the liquid- to the solid-phase, requiring further treatment and causing secondary pollution<sup>[6]</sup>. Thus, there is a need for developing treatment methods that are more effective in elimination dyes from wastewater. Advanced oxidation process (AOPs) is alternative method for the complete degradation of many organic pollutants<sup>[7-11]</sup>. When a photocatalyst absorbs radiation whose energy  $h\nu > E_g$  ( $E_g$  is the semiconductor band gap energy), an  $\bar{e}$  from its filled valance band (VB) is promoted to its conduction band (CB) and valance band holes  $h^+$  are formed (Fig. 1).

Electron would reduce any available species, including  $O_2$ , water and hydroxide ion to form hydroxyl radicals. The  $OH^{\cdot-}$  radicals are very strong oxidizing agents and can easily attack the organic molecules, thus lead finally to their complete mineralization. ZnO and TiO<sub>2</sub> are important photocatalysts with high catalytic activity that have attracted much research attention<sup>[12-14]</sup>. In comparison with TiO<sub>2</sub>, higher photocatalytic activity has been reported for ZnO and it can absorb a larger portion of light spectrum. Studies have shown that the use of metal oxides or sulfide such as WO<sub>3</sub>, MoO<sub>3</sub>, SiO<sub>2</sub>, MgO, ZnO and CdS with TiO<sub>2</sub> can significantly enhance the photocatalytic activity of TiO<sub>2</sub><sup>[15, 16]</sup>. Due to similarity of photodegradation mechanism of ZnO with TiO<sub>2</sub>, it is a suitable semiconductor using with TiO<sub>2</sub><sup>[17-19]</sup>. In continuation of our research on degradation of dyes in the presence of heterogeneous<sup>[14, 20]</sup> or homogeneous<sup>[21]</sup> catalyst, in this paper, we report the results of photocatalytic activity improvement of TiO<sub>2</sub> just with mixing it with ZnO in different weight percent.



**Fig. 1** The photocatalyst interface under UV- illumination

## Materials and Methods

Direct Blue 71 was commercial product. Chemical structures and other characteristics of dye are listed in Table 1. TiO<sub>2</sub> and ZnO powder

were obtained from Merck and used without further purification.

**Table 1.** Chemical Structure and characteristics of dyes

Dye	Abbreviation	Structure	$\lambda_{\max}$ (nm)
Direct Blue 71	DB71		585

## Apparatus

A model UV-Vis spectrophotometer (Shimadzu- 160A) with 10 mm quartz cells was used to make absorbance measurements. To adjust the pH, the Horiba pH meter was used.

## Preparation of photocatalyst

ZnO and TiO<sub>2</sub> (with 20, 40, 60, 80 % (w/w)) were mixed in water (250 mL). The suspension was stirred for 1 h. Photocatalyst was separated, washed and air-dried.

## Photocatalytic degradation

Stock solution of the dyes (100 mgL<sup>-1</sup>) was prepared by dissolving of 100 mg of dye in distilled water and diluted to 1000 mL. Other working solutions were prepared by diluting of this stock solution.

In all cases during the experiment 20 mL of dye solution (80mgL<sup>-1</sup> for DB71) containing the appropriate quantity of photocatalyst was magnetically stirred. In order to achieve the maximum adsorption of the dye onto the heterogenous photocatalyst, the cell was left for 30 min in the dark. The UV irradiation was carried out using Philips lamp (400 W). The colloid solutions of photocatalyst particles were

separated by centrifuged and filtered. Decreasing in the concentration of dye was monitored spectrophotometrically by measuring the absorbance of dyes at special wavelengths. So the degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0}$$

where C<sub>0</sub> is the initial concentration of CV, and C the concentration of CV at time t.

The light source emitted light just above the sample. The intensity level of light is controlled by fixing the distance between the source of light and the sample.

## Results and Discussion

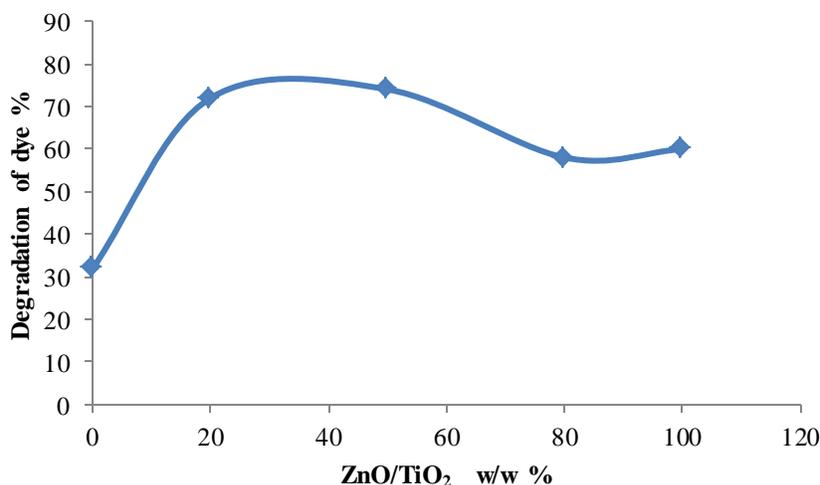
At first, experiments concerning the decomposition of dye (100 mgL<sup>-1</sup>) in the presence of mixed ZnO/TiO<sub>2</sub> (20 % (w/w)) semiconductor and UV illumination, a blank experiment in the absence of hν and another blank experiment in the presence of hν and without semiconductor were performed. Results of these experiments showed that degradation of dye in the presence of ZnO/TiO<sub>2</sub> (20 % (w/w)) as a photocatalyst and UV irradiation could lead

to the disappearance approximately 72 % after 45 minutes. This was contrasted with less than 5 % decolorization for the same experiment performed in the absence of catalyst with UV irradiation and no noticeable changes in the solution absorbance during stirring of dyes and photocatalyst in dark.

### Effect of the ZnO/TiO<sub>2</sub> weight percent on the photocatalytic activity and Comparison with pure TiO<sub>2</sub> or ZnO

To compare the photoactivity of pure TiO<sub>2</sub> or ZnO and ZnO/TiO<sub>2</sub> mixed, 1 g/L TiO<sub>2</sub> and ZnO were used as reference catalyst and a set of parallel experiments were conducted with the

ZnO/TiO<sub>2</sub> weight percent 20, 40, 60 and 80 % (w/w). All the results are presented in Fig. 2. ZnO/TiO<sub>2</sub> mixed catalyst had a higher photocatalytic activity. After 45 minutes of UV light irradiation, 32, 74 and 58 % of the dye in an aqueous dispersion was degraded by TiO<sub>2</sub>, ZnO and ZnO/TiO<sub>2</sub>(50 % (w/w)) respectively. Photodegradation of DB71 with ZnO was reported by our group and results showed that the significant degradation carried out in the presence of H<sub>2</sub>O<sub>2</sub> as oxidation agent<sup>[14]</sup>. Recent experiments showed, the noticeable decolorization of dye solution can be done without any oxidation agent with mixed ZnO/TiO<sub>2</sub> photocatalyst.



**Fig. 2** Effect of the ZnO/TiO<sub>2</sub> weight percent on the photocatalytic activity; Dye = 80 mg/L, [catalyst] = 1 g/L, time = 40 min.

**pH effect on the photo-oxidation of dye**

For pH testing, the pH of dye solution adjusted by 1M sodium hydroxide or 0.1 M cholericacid. The influence of pH on the photo-oxidation of dye was studied; faster degradation of dye was achieved under acidic condition (Table. 2). This dye is negatively charged due to the sulfite

groups (table 1). Decreasingthe pH increases the positive charge on photocatalyst and thus promotes the adsorption of dye to it, which accelerates the decolorization. But due to no significant difference between results in acidic pH and dyesolution, all catalytic experiments were carried out at pH = 6.4 (pH of dye solution).

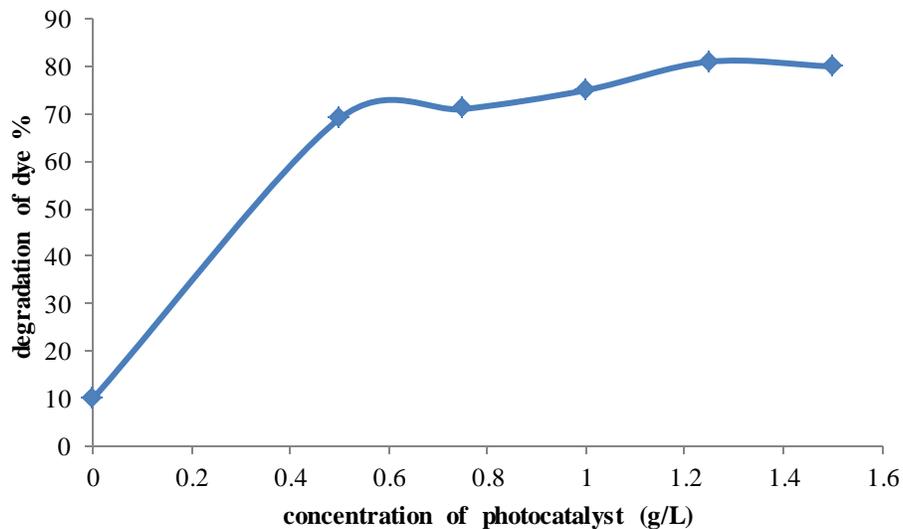
**Table 2.** Effect of pH on degradation of 80 mg/L DB 71 (1 g/L ZnO/TiO2 (50% w/w) and irradiation time 45 min).

pH	Degradation of dye %
2.3	78
4.1	75
6.4 (dye solution)	74
7.8	62
9.2	58

**Effect of catalyst concentration**

In order to avoid the use of excess catalyst, a set of parallel experiments were conducted by varying the amounts of catalyst from 0 to 1.5 g/L

with dye concentration of 80 mg/L and UV irradiation time of 45 minutes. Figure 3 shows that decolorization of dye was increased with increasing amounts of photocatalyst up to 1.25 g/L.

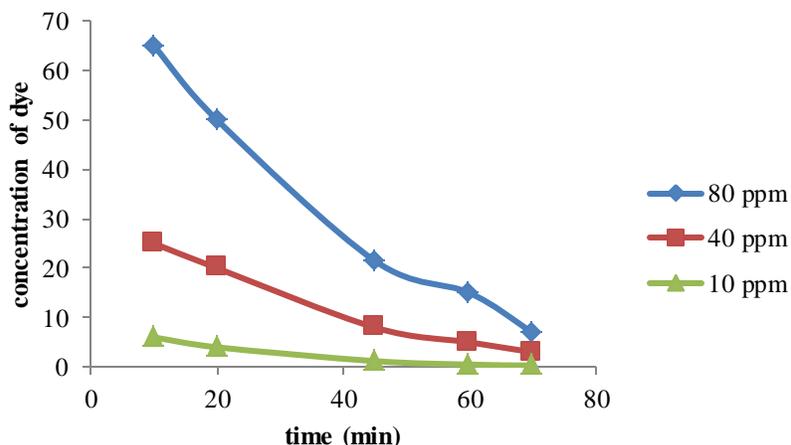


**Fig. 3** photodegradation of DB 71 vs different ZnO/TiO<sub>2</sub> concentration; dye (80 mgL<sup>-1</sup>), ZnO/TiO<sub>2</sub> (50 % w/w) and irradiation time 45 min.

#### **Study of degradation of dye in various initial DB 71 concentration**

After optimizing the catalyst dose, the photocatalytic degradation of DB 71 was carried out by varying the initial concentrations of the dye (10, 40 and 80 mg/L). Figure 4 shows the

time dependent graphs of degradation of DB 71 at different DB 71 concentration solutions (10, 25 and 50 mg/L). As the concentration of the dye was increased, the rate of photodegradation decreased indicating to increase time scan for the complete degradation of dye.



**Figure 4.** Effect of the initial DB71 concentration on photocatalytic degradation (pH = 6.4, ZnO/TiO<sub>2</sub> (50% w/w, 1.25 g/L).

## Conclusion

The photocatalytic oxidation of a azo dye (Direct Fast blue B2R (DB. 71) has been studied using mixed ZnO and TiO<sub>2</sub> as catalyst under UV irradiation. Approximately 90 % of dye has been

eliminated after 70 minutes in the presences of catalyst, UV irradiation and without additional oxidation agent.

## References

1. Ncibi, M. C.; Mahjoub, B.; Seffen, M. Adsorptive removal of textile reactive dye using *Posidonia oceanica* (L.) fibrous biomass. *Int. J. Environ. Sci. Tech.*, 2007,4, 433-440.
2. Forgacs, E.; Cserhatia, T.; Oros, G., (2004). Removal of synthetic dyes from wastewaters: a review. *Environ. Int.*, 30, 953-971.
3. Gharbani, O.; Tabatabaee, S. M.; Mehrizad, A. *Int. J. Environ. Sci. Tech.*, 2008,5, 495-500.
4. Beydilli, M. I.; Pavolsathis, S. G.; Tincher, W. C., (1998). Decolorization and toxicity screening of selected reactive azo dyes under methanogenic condition. *Water Sci. Tech.*, 38 (4-5), 225-232. *Water Sci. Tech.*, 1998, 38, 225-232.
5. Ghasemi, F.; Tabandeh, F.; Bambai, B.; Sambasiva Rao, K. R. S. Decolorization of different azo dyes by *Phanerochaete chrysosporium* RP78 under optimal condition. *Int. J. Environ. Sci. Tech.*, 2010, 7, 457-464.
6. Igbiosa, E. O.; Okoh, A. I., (2009). Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community. *Int. J. Environ. Sci. Tech.*, 6 (2), 175-182

7. Kansal, S.K., Singh, M. and SudD.(2007). Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. *J. Hazard. mater.* 141, 581-590.
8. Giri, R. R., Ozaki, H., Taniguchi S. and Takanami, R.(2008) Photocatalytic ozonation of 2, 4-dichlorophenoxyacetic acid in water with a new TiO<sub>2</sub> fiber *Int. J. Environ. Sci. Tech.*, 5, 17-26.
9. Hoffman M., Martin S., Choi W. and Bahnmann D. (1995) Environmental applications of semiconductor photocatalysis, *Cem. Rev*, 95, 69- 96.
10. Poullos I. and Tsachpinis, I. (1999) Photocatalytic degradation of the textile dye reactive black 5 in the presence of semiconducting oxides, *J. Chem. Technol. Biotechnol.*, 74, 349- 357.
11. Bumpus, J.A.; Triker, J.; Andrzejewski, K.; Rhoads, H.; Tatarko, M. *J. Chem. Educ.* 1999, 76, 1680-1683.
12. Evgenidou, E.; Konstantinou, I.; Fytianos, K.; Poullos, I.; Albanis, T. *Catalysis Today*, 2007, 124, 156-162.
13. Behnajady M.A., Modirshahla N. and Hamzavi, R. (2006) Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst *J. Hazard. mater.* B133, 226-232.
14. Tabatabaee M., Ghotbifard A., Mozafari AA., (2012) Photocatalytic Degradation and Kinetic study of Textile Azo Dyes Direct Blue 71 and Black 19 in ZnO suspended solution *Fresenius Environ.* 21, 1468-1473.
15. Chatterjee D., Dasgupta S. and Rao NN. (2006). Visible light assisted photodegradation of halocarbons on the dye modified TiO<sub>2</sub> surface using visible light. *Sol. Energy Mater. Sol. Cells* 90, 1013-1020.
16. Jing LQ, Qun YC, Wang BQ, Li SD, Jiang BJ, Yang LB, et al. (2006) Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Sol. Energy Mater. Sol. Cells*. 90, 1773-1787
17. Jiang Y., Sun Y., Liu H. Zhu F. and Yin H. (2008) Solar photocatalytic decolorization of C.I. Basic Blue 41 in an aqueous suspension of TiO<sub>2</sub>-ZnO. *Dyes Pigm.* 78, 77-83.
18. Liao DL., Badour CA. and Liao BQ. (2008) Preparation of nanosized TiO<sub>2</sub>/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. *J. Photochem. Photobiol.*, A 194, 11-19.
19. Marcì G., Augugliaro V., López-Muñoz M.J., Martín C, Palmisano L, Rives V., Schiavello M., Tilley R. J. D. and Venezia A.M. (2001). Preparation Characterization and Photocatalytic Activity of Polycrystalline ZnO/TiO<sub>2</sub> Systems. 2. Surface, Bulk Characterization, and 4-Nitrophenol Photodegradation in Liquid-Solid Regime. *J. Phys. Chem. B*, 105, 1033-1040.
20. Tabatabaee, M.; Mirrahimi, S. A. *orient. Photodegradation of Dye Pollutant on Ag/ZnO Nanocatalyst under UV-irradiation* *Orient. J. Chem.* 2012, 28, 243-246.
21. Tabatabaee, M.; Roozbeh, M.; Roozbeh, M. *Catalytic effect of lucunary heteropolyanion containing molybdenum and tungsten atoms on decolorization of direct blue 71* *Chin. Chem. Lett.* 2011, 22, 1501-1504.