International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2015): 6.391

Oxidative Photodegradation of Evans Blue Dye Using N-Doped Zinc Oxide

Yashwant B. Tambe[1], **Seema Kothari**[2]

Department of Chemistry, PAHER University, UDAIPUR (Raj.) India – 313003

Abstract: ***The photocatalytic degradation of Evans Blue has been studied under visible light in the presence of N-doped ZnO as a photocatalyst. N-doped ZnO was prepared by the solvent free method. The photocatalytic activity of ZnO and N-doped ZnO was compared by investigating the photodegradation of Evans Blue dye under visible light. The effect of different parameters like pH, concentration of the Dye, amount of N-doped ZnO and light intensity on the rate of degradation was also studied. The results revealed that the N-doped zinc oxide photocatalyst shows higher photocatalytic activity compared to pure zinc oxide.***

Keywords: Evans Blue, ZnO, N-doped ZnO, Photocatalytic degradation.

1. Introduction

Dyes constitute one of the pollutants class causing a variety of environmental problems [1]. The colored wastewaters represent a serious environmental problem and a public health concern. The uncontrolled release of colored waste water contaminated with dyes from textile, rubber, paper, and plastic industries have led to serious environmental contamination. These adversely affect the quality of water, inhibit sunlight penetration and reduce photosynthetic reactions. In addition, some dyes are either toxic or carcinogenic. Currently available water treatment technologies either concentrate the pollutants present by transferring them to other phases (adsorption or coagulation) or involve high operating costs with possible generation of toxic secondary pollutants into the ecosystem (sedimentation, filtration, chemical and membrane technologies).

The photocatalytic processes have been applied successfully in the removal of organic pollutants from different classes (pesticides, pharmaceuticals and personal care compounds, halogenated compounds, dyes), where biodegradation of pollutants demonstrated to be inefficient due to the compounds toxicity [2]-[4]. Heterogeneous photocatalysis using metal oxide semiconductors has significant advantages over many processes used in the treatment of aqueous effluents polluted with dyes.

Among the semiconductors, TiO_2 photocatalyst has been extensively investigated. Anatase TiO_2 shows better photocatalytic activity and is used as photocatalyst. It is difficult to prepare phase pure anatase TiO_2, and also preparation of TiO_2 is costly. Zinc oxide (ZnO) can be considered as a suitable alternative to TiO_2 photocatalyst due to its nontoxic nature, good environmental stability, strong oxidizing power, and same band gap energy and is relatively cheaper. The major advantage of ZnO is that it absorbs a large fraction of solar spectrum than TiO_2. ZnO has a wide band gap of about 3.2 eV and can absorb UV light with wavelength below 387 nm, due to the fact that its photocatalytic activity is limited to irradiation wavelength in UV region only. Unfortunately, solar light consists of less than 5% UV radiations and indoor lighting consists of less than 0.1% UV radiations. Therefore it is necessary to modify ZnO in order to utilize major portion of sunlight/indoor lights.

ZnO has been used for the photodegradation of various dye pollutants. Gouvea et al. [5] reported a preliminary study of semiconductor-assisted photochemical degradation of lignin, Remazol, Brilliant Blue R and Kraft E1 paper effluent by using ZnO and Ag-doped ZnO photocatalysts. The effect of transition metal ions such as Mo(VI) doped ZnO has been investigated by Vaya and Sharma [6] for photocatalytic bleaching of eosin yellow. S. Siva Kumar et al. [7] studied the enhanced photocatalytic activity of silver doped ZnO for degradation of Rhodamine 6G. A comparative analysis of structural, optical and photocatalytic properties of ZnO and Ni doped ZnO nanospheres was done by Shashi Kant and Amit Kumar [8]. Behnajady et al. [9] reported the enhancement of photocatalytic activity of ZnO nanoparticles by silver doping with optimization of photodeposition method parameters. Shinde et al. [10] used Ag-doped ZnO thin films for oxidative degradation of Acid Orange 7. Mongkolserm and Pabchanda [11] studied the influence of tin doping on the photocatalytic activity of zinc oxide thin films under UV light. Abdollahi et al. [12] synthesized and characterized various levels of manganese (Mn)-doped ZnO samples. Photodegradation of cresols under visible light showed that 1% Mn-doped ZnO had maximum absorption and rate of photodegradation. Hameed et al. [13] studied the photocatalytic degradation of Acid Red 1 dye using ZnO catalyst in the presence and absence of silver. It was found that the presence of Ag^+ in the catalyst does not significantly enhance the photocatalytic activity of ZnO in the degradation process. Photodegradation of Phenol Red by UV irradiation in the Presence of ZnO Nanoparticles was studied by Tan et al.[14]. Zhang and Zeng [15] used visible light-activated cadmium-doped ZnO nanostructured photocatalyst for the degradation of methylene blue dye. Photocatalytic degradation of phenol was carried out by Kruefu et al.[16] using Niobium-loaded Zinc Oxide nanoparticles (Nb-loaded ZnO NPs). The results indicated that all Nb-loaded ZnO NPs have better photocatalytic activity than the unloaded ZnO nanoparticles.

In the present work, we have reported the use of N-doped ZnO for an effective and efficient photocatalytic degradation of Evans Blue dye.

2. Materials and Methods

Pure ZnO was obtained from S. D. Fine-Chem, Mumbai.

2.1 Preparation of nitrogen-doped ZnO

The N-doped ZnO nanocatalyst was synthesized in a solvent free reaction. 20 g of uncalcined zinc oxide was added to 40 g of urea and grinded in an agate mortar. The mixture was calcined in a ceramic crucible at 400°C for 4 h and cooled. The product was ground to fine powder and labelled as nitrogen-doped zinc oxide (N-doped ZnO).

2.2 Evans Blue

Evans Blue is an azo dye. It is also called as Direct Blue 53. It appears as a dark blue powder. It is soluble in water and its maximum absorbance is at 610 nm in an aqueous solution. Evans Blue is pharmacologically active, acting as a negative allosteric modulator of the AMPA and kainate receptors and as an inhibitor of vesicular glutamate transporters. Evans blue dye has been used as a viability assay on the basis of its penetration into non-viable cells.

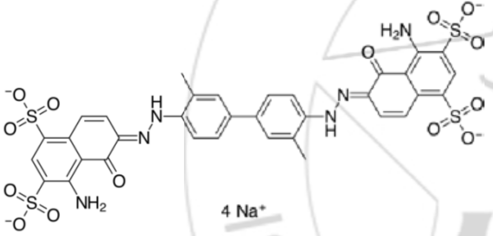

Figure 1: Structure of Evans Blue

2.3 Experimental Technique

Evans Blue dye was used as a model system in the present investigation to compare the photocatalytic activity of pure ZnO and N-doped ZnO. All the solutions were prepared in doubly distilled water. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp (Philips; light intensity = 60.0 mWcm^{-2}). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solution was measured with the help of digital pH-meter. 1.0 × 10^{-3} M solution of Evans Blue was prepared which was used as stock solution. The stock solution was further diluted as and when required. The absorbance of Evans Blue dye solution was determined with the help of a spectrophotometer at λ_{max} = 610 nm. The progress of reaction was observed by measuring absorbance of the reaction mixture containing dye and semiconductor at regular time intervals during exposure. A decrease in absorbance of Evans Blue solution was observed with increasing time of exposure. A plot of 1 + log A against time was found linear for pure ZnO and nitrogen doped ZnO, which indicates that the degradation of Evans Blue follows pseudo-first order kinetics. The rate constant was calculated with the help of the equation, k = 2.303 x Slope.

3. Results and Discussion

3.1 A Typical Run

A 1.5 × 10^{-5} M solution of Evans Blue was prepared in doubly distilled water and 0.14 g of N-doped ZnO was added to it. The pH of the reaction mixture was adjusted to 8.0 and this solution was exposed to a 200 W tungsten lamp at 60.0 mWcm^{-2}. A decrease in absorbance of Evans Blue solution was observed with increasing time of exposure. The results are shown in Table 1 and graphically presented in Fig. 2. Here, a comparative observation was made for pure ZnO and N-doped ZnO, which confirmed that the rate of degradation was 2.5 times increased in the case of N-doped ZnO as compared to pure ZnO.

Table 1: A typical run
pH =8.0, [Evans Blue] = 1.5 × 10^{-5} M, N-doped ZnO = 0.14 g, Light intensity = 60 mWcm^{-2}

Time (min)	Pure ZnO		N-doped ZnO	
	Abs.	1+log A	Abs.	1 + log A
0	0.62	0.79	0.62	0.79
15	0.57	0.76	0.51	0.71
30	0.51	0.71	0.42	0.62
45	0.47	0.67	0.33	0.52
60	0.45	0.65	0.29	0.46
75	0.42	0.62	0.23	0.36
90	0.39	0.59	0.19	0.28
105	0.36	0.56	0.16	0.20
120	0.33	0.52	0.13	0.11
Rate constant (k)	0.85 x 10^{-4}sec^{-1}		2.19 x 10^{-4}sec^{-1}	

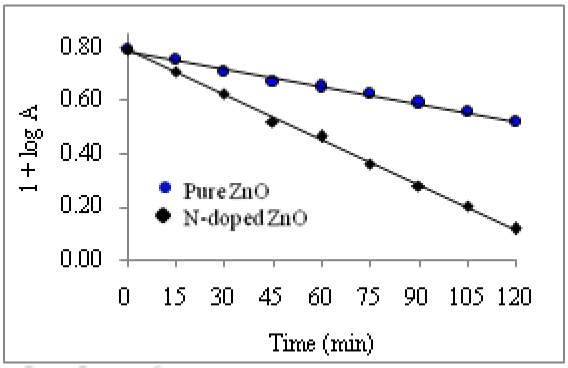

Figure 2: A typical run

3.2 Effect of pH

The effect of pH on the rate of degradation of Evans Blue was investigated in the pH range 4.0 to 11.0. The results are reported in Table 2 and graphically represented in Fig. 3.

Table 2: Effect of pH
[Evans Blue] = 1.5 × 10^{-5} M, N-doped ZnO = 0.14 g, Light intensity = 60.0 mWcm^{-2}

pH	Rate constant (k) x 10^{4} (sec^{-1})
4.0	0.96
5.0	1.44
6.0	1.46
7.0	1.53
8.0	**2.19**
9.0	1.83
10.0	1.75
11.0	1.51

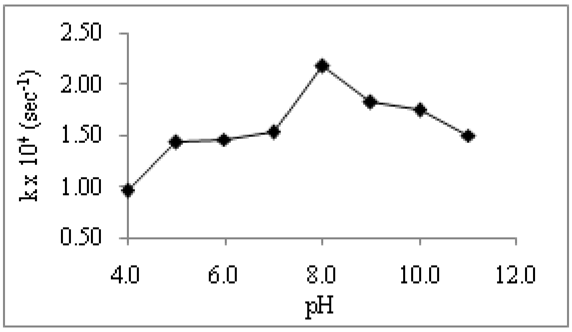

Figure 3: Effect of pH

It has been observed that the rate of degradation was increased with increase in pH from 4.0 to 8.0; further increase in pH results in a decrease in the rate of reaction. The increase in the rate of photocatalytic degradation with increase in pH may be due to generation of more $^{\bullet}OH$ radicals, which are produced from the interaction of OH^- and hole (h^+) of the semiconductor. These $^{\bullet}OH$ radicals are responsible for the oxidative degradation of dye. After pH 8.0, the rate decreases because more OH^- ions are available and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of anionic Evans Blue to the semiconductor surface will be retarded due to repulsion between two negatively charged species. This results into decrease in the rate of degradation.

3.3 Effect of Evans Blue concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of Evans Blue solution. The results are tabulated in Table 3 and graphically represented in Fig. 4.

Table 3: Effect of Evans Blue concentration
pH = 8.0, N-doped ZnO = 0.14 g, Light intensity = 60.0 mWcm^{-2}

[Evans Blue] x 10^5 M	Rate constant (k) x 10^4 (sec^{-1})
1.00	1.10
1.25	1.83
1.50	**2.19**
1.75	1.76
2.00	1.46
2.25	1.31
2.50	0.73
2.75	0.59

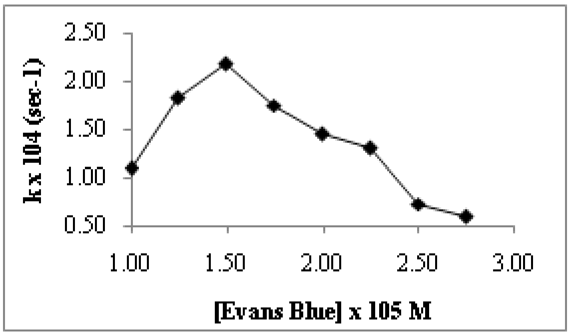

Figure 4: Effect of Evans Blue concentration

It was observed that the rate of photocatalytic degradation of the dye increases on increasing the concentration of Evans Blue up to 1.5 × 10^{-5} M. It may be attributed to the fact that as the concentration of the Evans Blue was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye. There was a decrease in degradation rate on increasing the concentration of dye above 1.5 × 10^{-5} M. This may be because of the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach surface of the photocatalyst at the bottom of reaction vessel.

3.4 Effect of amount of N-doped ZnO

The effect of amount of N-doped zinc oxide on the rate of photodegradation of Evans Blue was observed by keeping all other factors identical. The results are tabulated in Table 4 and graphically represented in Fig. 5.

Table 4: Effect of Amount of N-doped ZnO
pH = 8.0, [Evans Blue] = 1.5 × 10^{-5} M, Light intensity = 60.0 mWcm^{-2}

N-doped ZnO (g)	Rate constant (k) x 10^4 (sec^{-1})
0.02	0.37
0.04	0.66
0.06	0.80
0.08	1.25
0.10	1.56
0.12	1.97
0.14	**2.19**
0.16	2.19
0.18	2.19

The rate of reaction was found to increase on increasing the amount of semiconductor, N-doped zinc oxide. The rate of degradation reached to its optimum value at 0.14 g of the photocatalyst, because as the amount of the semiconductor was increased, it provides more exposed surface area for degradation of dye molecules. Beyond 0.14 g, the rate of reaction becomes almost constant. After a particular value (0.14 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

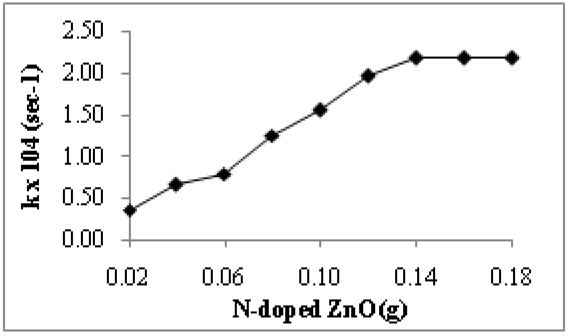

Figure 5: Effect of amount of N-Doped ZnO

3.5 Effect of light intensity

The effect of light intensity on the photocatalytic degradation of Evans Blue was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are given in Table 5 and graphically presented in Fig. 6.

Table 5: Effect of light intensity
pH = 8.0, [Evans Blue] = 1.5 × 10^{-5} M, N-doped ZnO = 0.14 g

Light intensity ($mWcm^{-2}$)	Rate constant (k) x 10^5 (sec^{-1})
20.00	0.61
30.00	0.94
40.00	1.68
50.00	2.02
60.00	**2.19**
70.00	2.19

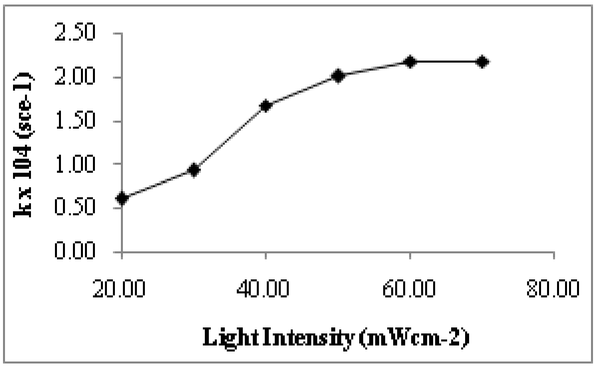

Figure 6: Effect of light intensity

These data indicate that photocatalytic degradation of Evans Blue was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. The rate of reaction remained constant as the intensity of light was increased beyond 60 $mWcm^{-2}$.

3.6 Mechanism

On the basis of above observations, a tentative mechanism is proposed for the photocatalytic degradation of Evans Blue using N-doped ZnO semiconductor.

Evans Blue (EB) absorbs radiation of suitable wavelength and it is excited to its first singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting N-doped ZnO also utilizes the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of •OH radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger (isopropanol), where the rate of degradation was drastically reduced.

$$^{1}EB_0$$

4. Conclusion

Nitrogen doped zinc oxide was prepared and used for the photocatalytic degradation of Evans Blue dye. Different rate affecting parameters like pH, dye concentrations, catalyst amount and light intensity were studied for the dye degradation. The observations revealed that Evans Blue dye could be degraded successfully by using N-doped ZnO under visible light. In comparative study, it was found that the N-doped ZnO has shown enhanced photocatalytic activity than pure ZnO.

References

[1] S. A. Abo-Farha, “Photocatalytic degradation of monoazo and diazo dyes in wastewater on nanometersized TiO_2”, Journal of American Science, 6, pp. 130-142, 2010.
[2] F.A. Caliman, M. Gavrilescu, “Pharmaceuticals, personal care products and endocrine disrupting agents in the environment – A review”, Clean – Soil, Air,Water, 34, pp. 277-303, 2009.
[3] M. Gavrilescu, K. Demnerova, J. Aamand, S. Agathos, F. Fava, “Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation”, New Biotechnology, 32, pp. 147–156, 2014.
[4] L.Pereira, A.V. Coelho, C. A. Viegas, “Enzymatic biotransformation of the azo dye Sudan Orange G with bacterial CotA-laccase”, Journal of Biotechnology, 139, pp. 68–77, 2009.
[5] C. Gouvea , F. Wypych , S. Moraes , N. Duran , P. Peralta-Zamora, “Semiconductor-assisted photodegradation of lignin dye, and kraft effluent by Ag-doped ZnO”, Chemosphere, 40, pp. 427-432, 2000.
[6] D. Vaya and V. K. Sharma, “Study of synthesis and photocatalytic activities of Mo doped ZnO”, J. Chem. Pharm. Res., 2 (3), pp. 269-273, 2010.
[7] S. Siva Kumar, V. Ranga Rao and G. Nageswara Rao, “Enhanced Photocatalytic Activity of Silver Doped ZnO for Degradation of Rhodamine 6G”, Asian Journal of Chemistry, 24 (12), pp. 5837-5840, 2012.
[8] S. Kant and A. Kumar, “A comparative analysis of structural, optical and photocatalytic properties of ZnO and Ni doped ZnO nanospheres prepared by sol-gel method”, Adv. Mat. Lett3 (4), pp. 350-354, 2012.
[9] M. Behnajady, N. Modirshahla, M. Shokri, A. Zeininezhad & H. Zamani, “Enhancement of

photocatalytic activity of ZnO nanoparticles by silver doping with optimization of photodeposition method parameters", J. Environ. Sci. and Health: Part A, 44 (7), pp. 666-672, 2009.

[10] S. S. Shinde, C. H. Bhosaleand K. Y. Rajpure, "Oxidative degradation of Acid Orange 7 using Ag-doped zinc oxide thin films", J. Photochem. Photobiol. B, 117, pp. 262-268, 2012.

[11] P. Mongkolserm and S. Pabchanda, "Influence of Tin Doping on the Photocatalytic Activity of Zinc Oxide Thin Films under UV Light", J. Chem. Chem. Eng., 6, pp. 631-637, 2012.

[12] Y. Abdollahi , A. H. Abdullah, Z. Zainal and N. A. Yusof, "Synthesis and Characterization of Manganese Doped ZnO Nanoparticles", Int. J. Basic & Applied Sci., 11 (4), pp. 44-50, 2011.

[13] B. Hameed, U. Akpan, K. Wee, "Photocatalytic degradation of Acid Red 1 dye using ZnO catalyst in the presence and absence of silver", Desalination & Water Treatment, 27 (1-3), pp. 204-209, 2011.

[14] T. K. Tan, P.S. Khiew, W. S. Chiu, S. Radiman, N.M. Huang, H.N. Lim, "Photodegradation of Phenol Red in the Presence of ZnO Nanoparticles", World Academy of Science, Engineering & Technology, 55, pp. 791-796, 2011.

[15] D. Zhang and F. Zeng, "Visible light-activated cadmium-doped ZnO nanostructured photocatalyst for the treatment of methylene blue dye", J. Mat. Sci., 47 (5), pp. 2155-2161, 2012.

[16] V. Kruefu, H. Ninsonti, N. Wetchakun, B. Inceesungvorn, P. Pookmanee and S. Phanichphant, "Photocatalytic Degradation of Phenol Using Nb-loaded ZnO Nanoparticles", Engineering Journal, 16 (3), pp. 91-99, 2012.