IJBPAS, May, 2021, 10(5): 1441-1456

ISSN: 2277–4998

International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS)

'A Bridge Between Laboratory and Reader'

www.ijbpas.com

SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION AND PHOTOCATALYTIC DEGRADATION STUDY OF W, N-CODOPED ZnO OVER REACTIVE BLUE 160 UNDER NATURAL SUN LIGHT IRRADIATION

E. KRISHNAN[1], M. RAVISHANKAR[*1] M. SIVAKUMAR[2] AND S. SIVAKUMAR[#2]

1: Department of Chemistry, Rajah Serfoji govt college (Autonomous), Thanjavur, India

2: Department of Chemistry, E. R. K Arts and Science College, Harur, India

***Corresponding Author: M. Ravishankar: E Mail: ravishankar1in@yahoo.co.in**

Received 19th June 2020; Revised 21st July 2020; Accepted 26th Aug. 2020; Available online 1st May 2021

https://doi.org/10.31032/IJBPAS/2021/10.5.5070

ABSTRACT

The photocatalytic activity of W, N-codoped ZnO was investigated by the degradation of Reactive Blue 160 (RB 160) under natural sunlight irradiation. A series of W, N-codoped TiO_2 photocatalyst with different mole ratio (0.02 mol%, 0.03 mol%, 0.04 mol%, 0.05 mol%, and 0.06 mol%) were prepared sol-gel technique. The pure ZnO was low photocatalytic activity, due to its poor surface properties, gets photocorrosion and low utilization of visible light. These problems were minimised by adding dopant (W and N) with ZnO. The photocatalytic activity of W, N-codoped ZnO was remarkably higher than that of the as-prepared sample like pure TiO_2. The highlighted photocatalytic properties of W, N-codoped ZnO were confirmed by XRD, SEM and UV-DRS. W, N-codoped TiO_2 photocatalyst has photostability and long durability.

Keywords: W, N-Codoped TiO_2, sol-gel route, Photocatalytic Degradation, Reactive Black 5 and Natural Sun Light

INTRODUCTION

Water is one of the basic requirements for all domestic and commercial activities of the human. But human activities pollute the water bodies with diverse variety of contaminants depending upon the nature of the process. Among the industrial processes, textile dyeing and dye manufacturing affect the quality of the surface and ground water to a great extent. Wastewater generated by these industries containing residual dyes, which are intensely coloured and cause disturbance to the ecological system of the receiving water. It has been reported that about 15% of dyes produced in the world is lost during the dyeing process and is released in textile effluents **[1]**. Other than the dyes, textile effluents also contain high concentration of recalcitrant organic compounds and dissolved salts which are added to the water during dyeing and finishing process.

The dyes are usually had a synthetic origin and a complex aromatic molecule structure which make them more stable and more difficult to be biodegraded . It has been reported that only 47% to 87% of dyes stuff is biodegradable **[2-3]**. It has been documented that radical colour is usually due to insoluble dyes which have low biodegradability. So textile waste waters make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. If these effluents are improperly treated they will pose bad threats to all species on the earth because the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products.

Reactive dyes, one of the prominent and most widely used types of azo dyes, are typically azo-based chromophores combined with different reactive groups. They are extensively used in many textile-based industries because of their favorable characteristics, such as bright colour, water fastness and simple application. However, up to 50% of reactive dyes are lost through hydrolysis during the dyeing process and therefore, a large quantity of the dyes appears in waste water **[4-5]**.

The recent development in water decontaminant process is concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade more number of recalcitrant molecules into biodegradable compounds and are called advanced oxidation process (AOP's).

Among the different AOP's, photocatalytic methods has been powerful and simple for the degradation mechanism to remove organic pollutants. Semiconductor metallic oxide nanomaterials have been used to remove organic dyes from aqueous solution. Metal oxides have exhibited good photocatalytic activities under sunlight and have been used to degrade poisonous organic dyes to non-poisonous forms.

Recently, the degradation of pollutants was carried out with unique semiconductor metal oxide nanoparticles which include TiO_2, ZnO, WO_3, In_2O_3 and SnO_2. Among these, ZnO showed superior properties, including an absorption range within the visible region, high photo-stability, good sensor abilities, light-emitting diodes, and solar light harvesting **[6-7]**. The photocatalytic performance of ZnO was not effective for the degradation of organic dyes due to an extensive band gap (3.37 eV) and the recombination of electron–hole pairs. Unfortunately, the sunlight spectrum includes only about 5–7% of UV light. This minimum amount of UV light in the sunlight spectrum has particularly ruled out the use of the natural source of light for photocatalytic decolorization of pollutants. In addition, functionalized ZnO nanoparticles had been proven to have distinctive properties which include biocompatibility, a non-toxic nature, highly stability and good photo-catalytic potential **[8-9]**.

Doping and introducing impurities in ZnO nanoparticles have rendered them more photocatalytically active over a wide range of wavelengths (UV region to visible region) by reducing the bandgap energy **[10]**. ZnO nanoparticles have been modified with different dopants consisting of N and S atoms for enhancing the photocatalytic oxidation of organic dyes under UV light irradiation. Nitrogen-doped ZnO nanoparticles in the form of nanorods and nanowires have been used for water splitting applications **[11]**.

Doping of two kinds of atoms into wide band gap semiconductor oxides (ZnO or TiO_2) has attracted considerable interest, since it could result in a higher photocatalytic activity and improved characteristics compared with single-element doping into semiconductor oxides. Nd, C-codoped TiO_2 synthesized by X. Wu et.al exhibit enhanced photocatalytic activity, due to the absorption of whole range of visible light region.

However, from the literature survey the use of ZnO doped with metal and non metal in photocatalytic systems is still insufficient. In this connection, the aim of this work is to evaluate the photocatalytic performance of ZnO doped with N and W (non metal and metal) to remove reactive blue 160 dye from aqueous solution under solar light irradiation.

2. MATERIALS AND METHODS

This work deals with the method of preparation of catalyst, characterization techniques and the experimental set-up used for the carrying out the photocatalytic degradation process.

2.1 Chemicals used

Reactive blue 160 a widely used in textile dye with two monochlorotriazine anchor groups supplied by Vexent dyeaux India Pvt. Ltd, Mumbai (Minimum dye content 70%) were used for photocatalytic degradation studies.

Commercial name: Blue HERD

Chemical formula: $C_{38} H_{23} Cl_2 N_{14} O_{18} S_5 Na_5$

Molecular weight: 1309.84

Water solubility: 70g/L at 293k

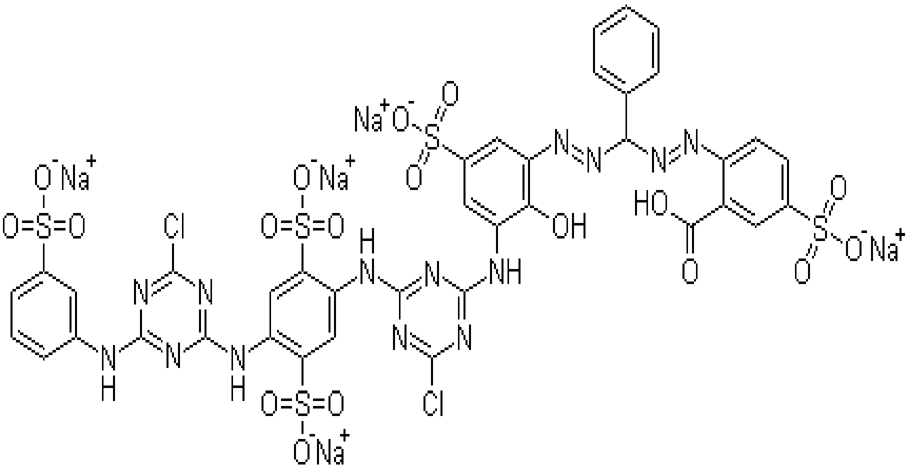


Figure 1: Structure of Reactive Blue 160

Zinc chloride (extra pure) (98%), Sodium tungstate (AR) Urea (AR) and sodium bicarbonate (99%) were supplied by Merck India Pvt. Ltd; dye solutions for photocatalytic studies were prepared in double distilled water. Sodium hydroxide and hydrochloric acid (both AR grade from Qualigens) were used for modifying the pH of the solutions. Hydrogen peroxide (Qualigens) and ammonium peroxydisulphat (Loba) was used as oxidant in combined oxidant photocatalytic degradation studies. Potassium dichromate (AR), Silver sulphate (GR), mercury sulphate (GR) 99% Ferroin (GR) and Sulphuric acid were used for COD analysis.

2.3 Preparation of W, N- codoped ZnO photocatalyst

In the preparation of W, N- codoped ZnO, 10 g of zinc chloride and 0.06 g of Sodium tungstate were dissolved in 100 ml of double distilled water. To that solution 6.2 g of sodium bicarbonate was then added in portions with vigorous stirring for several minutes. The precipitate formed was washed several times with distilled water to remove NaCl formed. Added 0.01 mol % of sodium tungstate and urea completely washed the precipitate to the suspension. The precipitate was then dried at 100ºC to remove the water. The solid obtained after drying was grinded in an agate mortar and pressed into a ceramic crucible. The material was calcinated at 500ºC for 4 hrs. The undoped ZnO was synthesised in the same procedure without adding sodium tungstate**.**

2.4 Characterization of Photocatalyst

Characterization: X-ray powder diffraction (XRD) patterns of the photocatalysts were recorded on a Philips X'pert-MPD diffractometer in the 2h range 20°–80° using Cu Ka radiation. The data were collected with a step of 0.028 (2h) at room temperature. The phase structure of the products was determined by comparing the experimental X-ray powder patterns to the standard compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). The crystallite sizes were calculated from the peak width using the Scherrer equation. The surface morphologies and particle size were observed by Scanning Electron Microscopy (JEOL.JSM-6360LV). UV-visible diffuse reflectance spectra were acquired by a Perkin-Elmer Lambda 35 spectrometer. BaSO4 was used as the reflectance standard.

2.5 Photocatalytic studies

All the photocatalytic experiments were performed under natural sunlight on clear sky days during the period of January to March-2019. In a typical experiment, 50 ml of dye solution (concentration 50 mg l^{-1}) was taken with 50 mg of photocatalyst in a 250 ml glass beaker. Then the dye solution was kept in direct sunlight with continuous aeration and the concentration of the dye remains was measured periodically by measuring its light absorbance at the visible λ_{max} by using Elico SL- 171 Visible spectrophotometer. In order to avoid the variation in results due to fluctuation in the intensity of the sunlight, a set of experiments have been carried out simultaneously. Oxidant combined photocatalytic degradation process were also done as mentioned method. For pH studies the pH of the dye solutions were modified to different values (3, 5, 7, 9 and 12) by using 0.1M HCl and NaOH solution.

2.6 Chemical Oxygen demand (COD)

For the analysis of COD, 0.4g of H_gSO_4 was added to 20 ml of the degraded dye solution in a 250 ml round bottom flask. To that 10ml of 0.25N $K_2Cr_2O_7$ was added and mixed well. Then 30 ml of H_2SO_4-$AgSO_4$ reagent (prepared by dissolving 0.5g of $AgSO_4$ in 30ml of Concentrated H_2SO_4) was added slowly with constant stirring. After that few pieces of pumice stones were added and the flask was fitted with a condenser and reflux for 2 hours. The solution was cooled and diluted to 150ml with distilled water and the entire content was titrated against 0.25 N Ferrous Ammonium Sulphate (FAS) solution using ferrion as indicator.

$$\text{COD in mg l}^{-1} = \frac{(V_1\text{-}V_2) \times N \times 8}{x}$$

Where V_1 & V_2 are the volume of FAS solution consumed for blank and test sample respectively, N is the normality of FAS solution and x is the volume of sample taken for analysis.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of the photocatalyst

3.1.1 X-ray diffraction studies

The powder XRD patterns of ZnO and W, N- codoped ZnO were as shown in **Figure 3.2.** Both samples were identified by XRD as a single phase containing ZnO (JCPDS card nos.: 89-1397; 89-0511; 36-1451). The high intensity of the peaks indicates that both ZnO and W, N- codoped ZnO are of high crystallinity. The mean crystallite sizes of the samples calculated by using the Scherrer formula for ZnO and W, N- codoped ZnO was given in the **Table 3.1**. The result shows that W doping increases the particle size of the ZnO. An XRD pattern of W, N- codoped ZnO indicates the uniform dispersion of W and N ions.

3.1.2 SEM analysis of the photocatalyst

The SEM micrographs of ZnO and W, N- codoped ZnO were shown in **Figure 3.3a and 3.3b** respectively. The micrographs show that ZnO particles have blunder particle morphology whereas W, N- codoped ZnO has uniform arrangement-like pattern composed of spherical of ZnO.

3.1.3 Diffused Reflectance UV-Visible analysis of the photocatalyst

Diffused reflectance spectra UV-visible spectra of ZnO and W, N- codoped ZnO were given in **Figure 3.4.** The results show that the absorption onset of ZnO and W, N-codoped ZnO were 390 nm and 480 nm respectively. Therefore W, N- codoped ZnO can utilize visible l ight than the pure ZnO for photoexcitation process and expected to have more activity in the solar radiation than the undoped ZnO. The red shift in the light absorption of ZnO on W and N doping has been interpreted by Kim et al., as the sp-d exchange interaction between the band electrons and the localized “d” electrons of the transition metal ion at the cationic site **[12-14]**.

3.2 Photocatalytic studies

3.2.1 Kinetics study of Reactive Blue 160

The kinetics of degradation of Reactive Blue 160 over ZnO and W, N-codoped ZnO photocatalyst has been studied in natural sunlight. The normalized C/C_0 Vs time plots for the dyes were given in **Figure 3.5 a**. The data were also analysed with the Langmuir–Hinshelwood kinetic model:

$$r = \left(\frac{kKC}{1 + KC}\right)$$

Where r is the specific degradation reaction rate the dye ($mgl^{-1}min^{-1}$), C the concentration of the dye ($mg\ l^{-1}$), k the reaction rate constant (s^{-1}) and K is the dye adsorption constant. When the concentration (C) is small enough, the above equation can be simplified in an apparent first-order equation:

$$\left(-\frac{dC}{dt}\right) = r = kKC = k_{app}C$$

After integration, we will get

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}\,t$$

Where C_0 is the initial concentration ($mg\ l^{-1}$), C is the concentration of the dye after t minutes of illumination and k_{app} is the apparent first order rate constant. The plots obtained were shown as **Figure 3.5 b.** The photocatalytic degradation of Reactive Blue 160 on W, N-codoped ZnO was found to be faster than that of the undoped ZnO. The W, N-codoped ZnO shows higher activity than the undoped ZnO, the reason is due its band gap difference of ZnO and W, N-codoped ZnO. It was reported that transition metal like W can trap photogenerated electron-hole pair in the semiconductor and minimize their recombination.

3.2.2 Effect of pH of the dye solution on W-doped ZnO

The influence of initial pH of the dye solution on degradation efficiency of W, N-codoped ZnO was shown in **Figure 3.6.** The photocatalytic degradation of the Reactive Blue 160 reaches the maximum, when pH of the dye solution was pH 3. The point of zero charge of ZnO was pH 9. Therefore its surface becomes positively charged when the pH of the solution was below 9 and the density of positive charge in the surface of ZnO increases with the decrease of pH value. Due to the anionic nature of the Reactive Blue-160, its adsorption on positively charged W, N-codoped ZnO surface was very high **[15]**. The photogenerated holes easily oxidise dye molecule when dye molecules are adsorbed on the photocatalyst surface of the photocatalyst. Hence the rate of degradation of Reactive Blue-160 was maximum at pH 3.

3.2.3 Effect of dosage of the photocatalyst

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 25 to 150 mg L^{-1}. The percentage of Reactive Blue 160 degraded in 60 minutes for various catalyst dosages were given **Figure. 3.7.** It can be observed that the efficiency of the photocatalytic degradation of both dyes increases with the increase of the photocatalyst amount from 25 to 100 mg L^{-1}. The enhancement of the removal efficiency on increase of the dosage of photocatalyst was due to the increase of active sites available for the photocatalytic reaction.

3.2.4 Chemical Oxygen Demand (COD) analysis

The Chemical oxygen Demand test is widely used as an effective technique to measure the organic load in the wastewater and also to estimate the degree of mineralization of organic pollutant in water treatment **[16]**. The analysis measure the organic load present in the water in terms of the total quantity of oxygen required to oxidize them to CO_2 and water**.** The reduction in COD values of the Reactive Blue 160 solution before and after the treatment was estimated. **Table 3.2** gives the percentage of degradation of dye calculated from spectrophotometric data and COD values for ZnO and W, N-codoped ZnO. The reduction in COD values of the treated dye solution indicates that the dye solution was not only decolourised but also mineralized into smaller molecules like CO_2**,** NO_2 and so on**.** The mineralisation of Reactive Blue 160 has lower percentage than the degradation; it might be due to the presence of triazine groups, which are reported chemically more stable than phenyl groups.

3.2.5 Effect of addition of hydrogen peroxide

Effect of H_2O_2 on the photodegradation efficiency of W, N codoped ZnO photocatalyst for the degradation of RB 60 (100 mg/L) was also carried out same experimental conditions. The degradation efficiency of W, N codoped ZnO was increases with increasing amount of H_2O_2 0 mM (36%) to 10 mM (100%) under light irradiation (**Figure 3.8**). Further increasing H_2O_2 beyond 8 mM decreased the degradation efficiency. Hence, 8 mM of H_2O_2 is the optimal level for the degradation. The enhancement of degradation efficiency by the addition of H_2O_2 is due to the increased production of hydroxyl radicals and increasing the e^-_{CB}-/ h_{VB}^+ charge separation process as given in equations,

$$H_2O_2 + e^-_{CB} \longrightarrow {}^{\bullet}OH + {}^{-}OH \quad (1)$$

$${}^{\bullet}OH + RB\ 160 \longrightarrow \text{Degrade products} \quad (2)$$

Unexpectedly, the potential of photocatalytic efficiency decreases due to the presence of excess H_2O_2. This excess of H_2O_2 endagers the potential of photocatalytic activity by scavenging the highly valuable $^{\bullet}OH$ radical and produces much feeble $^{\bullet}OOH$. Further, the $^{\bullet}OOH$ reacts with remaining strong $^{\bullet}OH$ radical, leading to the formation of unfavorable H_2O and O_2. In addition, the photocatalytic oxidation found to be inhibited when the excess H_2O_2 reacted with oxidative h^+ on catalyst surface (Eq. (5)).

$$H_2O_2 + {}^{\bullet}OH \longrightarrow {}^{\bullet}OOH + H_2O \quad (3)$$

$${}^{\bullet}OOH + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (4)$$

$$H_2O_2 + {}_{(VB)}h+ \longrightarrow O_2 + H^+ \quad (5)$$

The photodegradation capacity of H_2O_2 was also investigated in without photocatalysts (photolysis) on the degradation of RB 160 dye solutions under UV-visible light irradiation. Without W, N codoped ZnO and 10 mM (W, N codoped ZnO), H_2O_2 alone causes 18% and 25%, respectively, after 120 min irradiation.

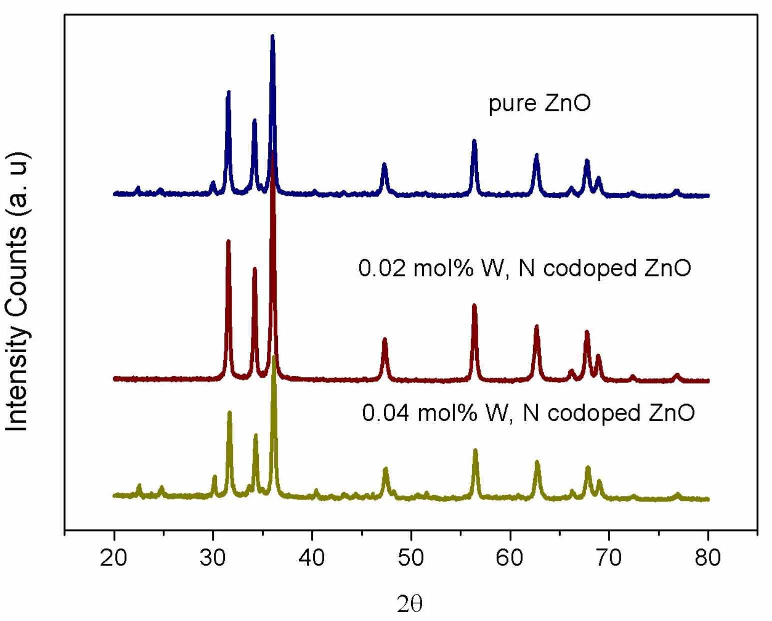
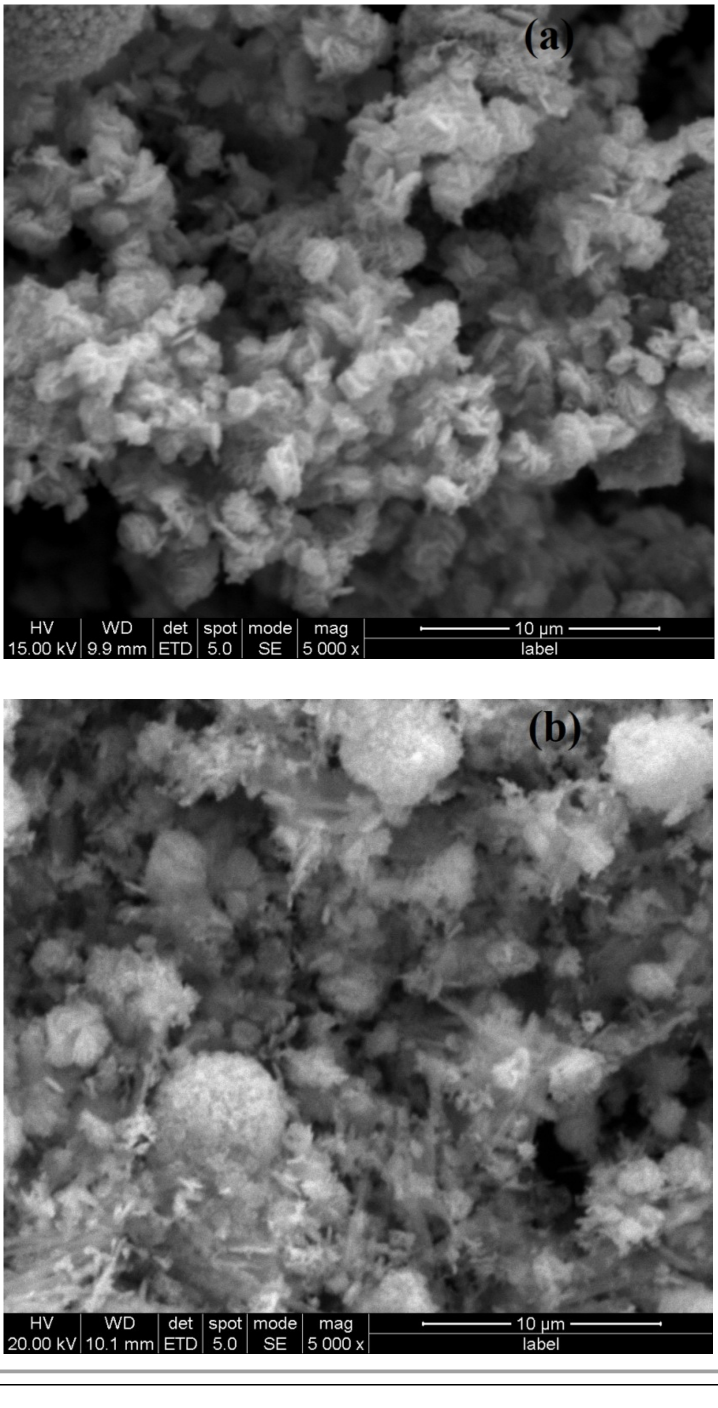


Figure 3.2: XRD patterns of ZnO and W, N- codoped ZnO

Table 3.1: XRD calculation results of ZnO and W, N- codoped ZnO

Photocatalyst	$d_{(101)}$-spacing (Å)	Full Width Half Maximum	Average crystallite size (nm)
ZnO	**2.4753**	**0.342°**	**73**
0.007% W, N- codoped ZnO	**2.4810**	**0.510°**	**49**
0.02% W, N- codoped ZnO	**2.4710**	**0.400°**	**49**



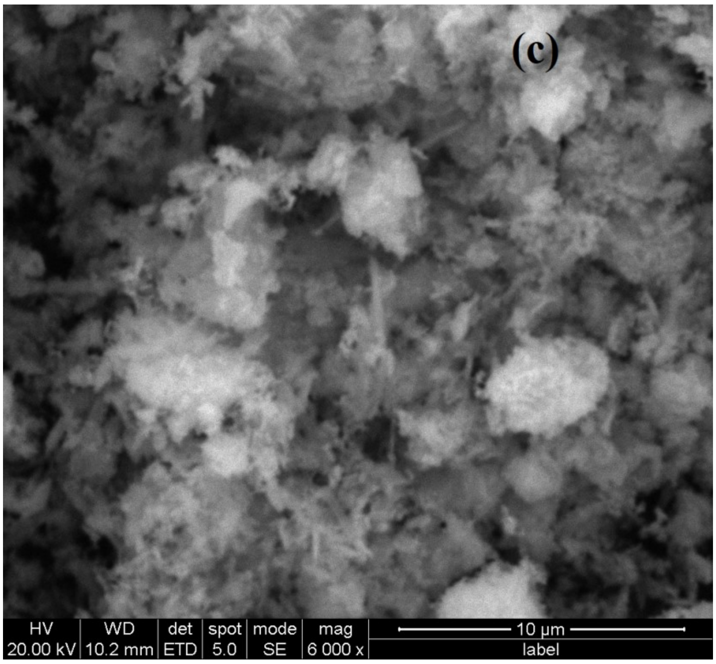


Figure 3.3: SEM micrograph of (a) ZnO, (b) 0.04 % W, N codoped ZnO and (c) 0.05 % W, N codoped ZnO photocatalyst

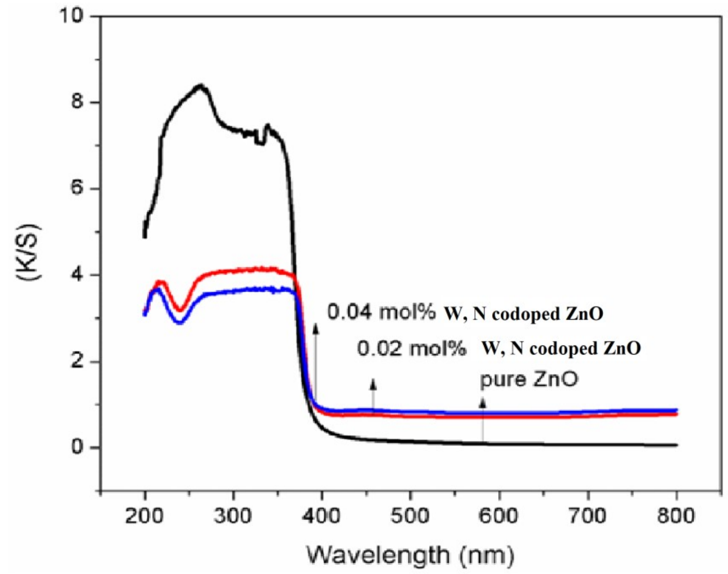


Figure 3.4: Diffused Reflectance UV-Visible spectra of ZnO and W, N-codoped ZnO

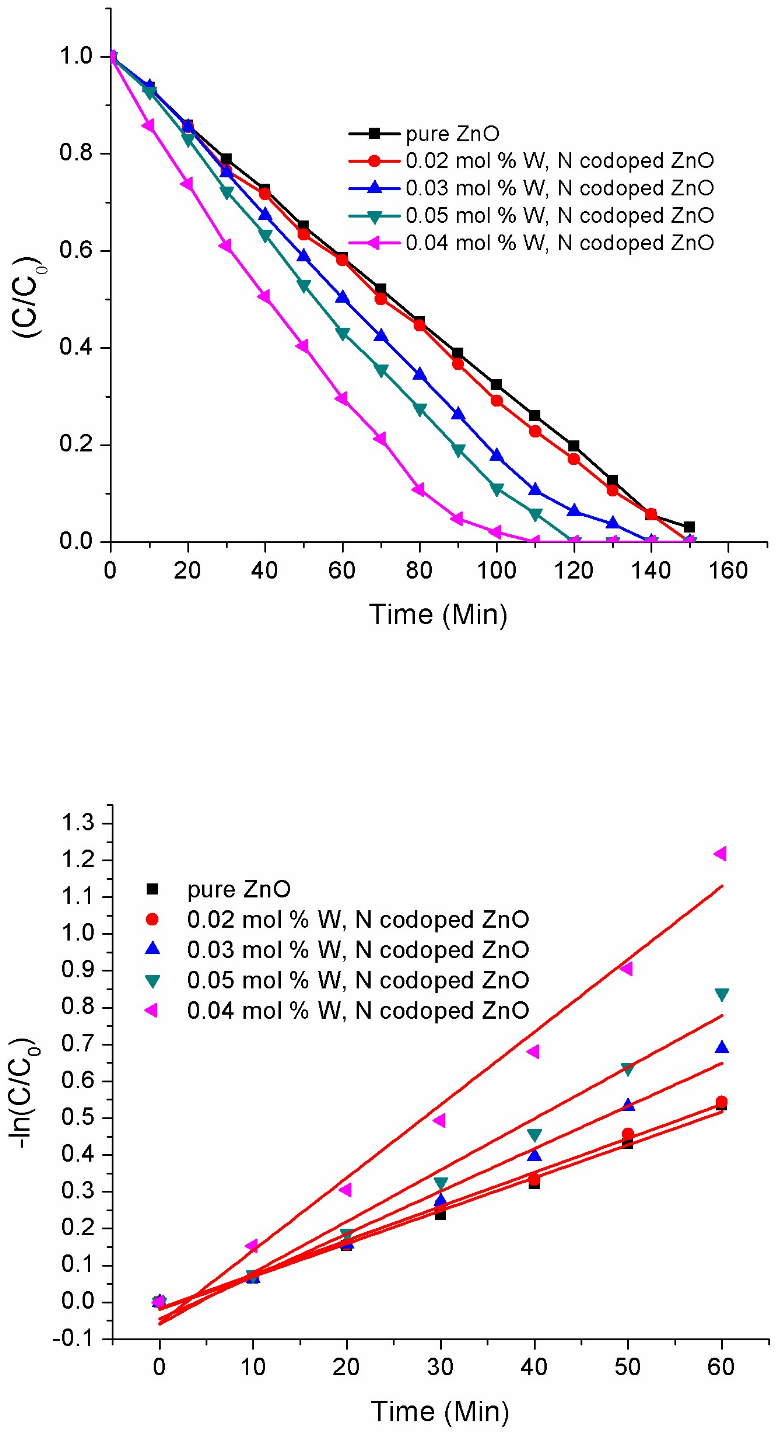


Figure 3.5 (b): Effect of time on the photocatalytic degradation of dyes. 3.5b Apparent first order kinetic plots the degradation of Reactive Blue 160

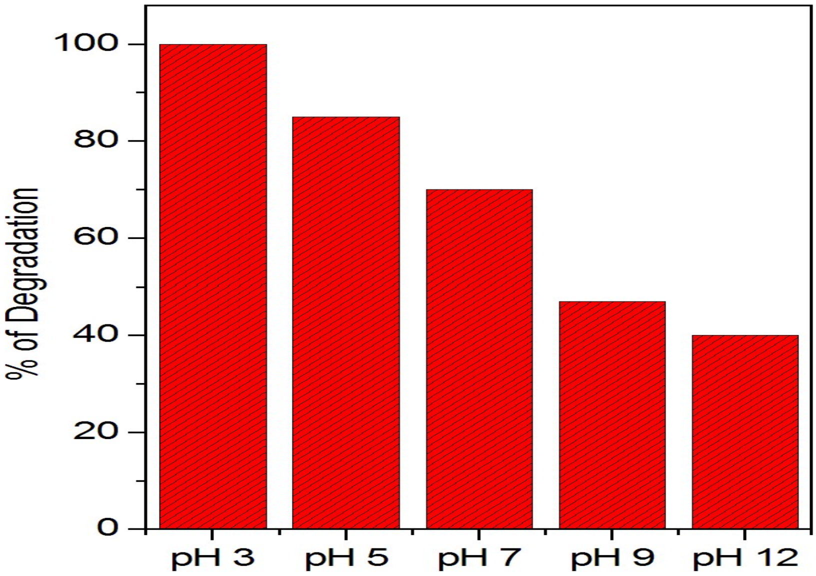


Figure 3.6: Effect of pH on the degradation of RB 160

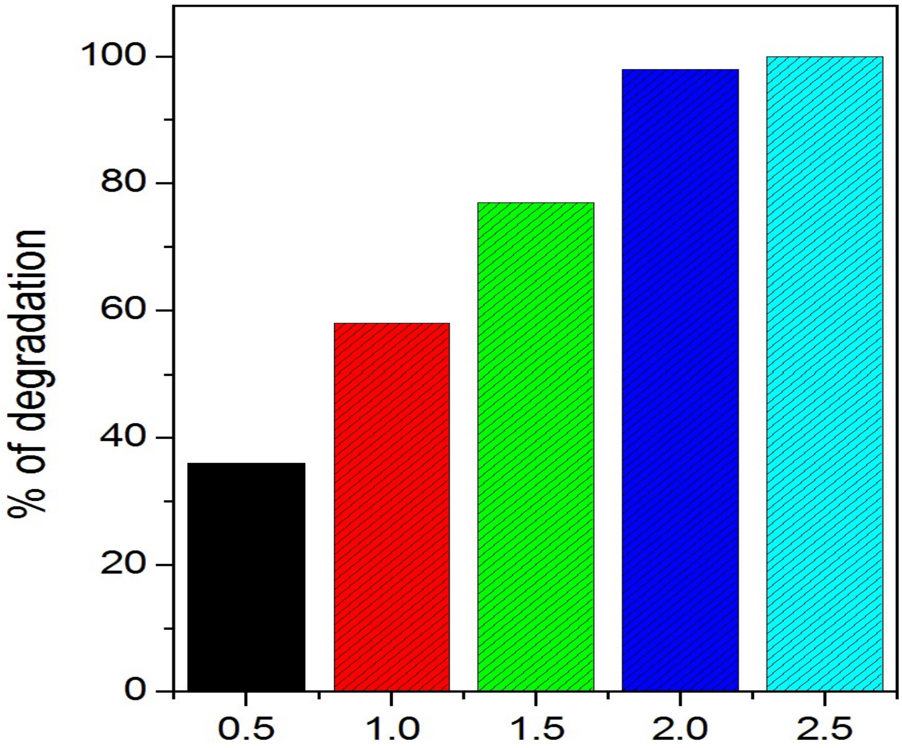


Figure 3.7: Effect of dosage of the photocatalyst

Table 3.2: COD analysis of the degraded Reactive Blue solution (Irradiation time: 2 hrs)

	Reactive Blue 160	
Photocatalysts	% of degradation	% of reduction in COD
ZnO	100	66
W, N codoped ZnO	100	71

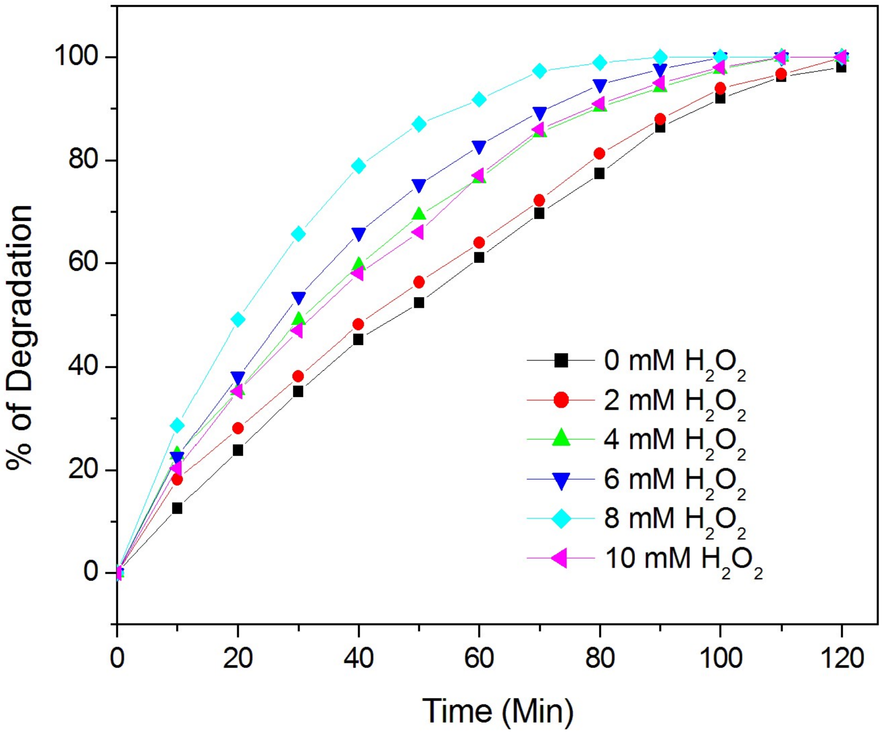


Figure 3.8: Effect of concentration of H_2O_2 on degradation of dyes

4. CONCLUSION

Highly crystalline ZnO and W, N-codoped ZnO were synthesized by a simple precipitation followed by thermal decomposition of carbonates. The W, N-codoped ZnO catalyst shows an absorption threshold extended into the visible region and also has smaller particle size compared to ZnO. Based on this study following conclusion has been obtained. W, N-codoped ZnO have higher activity in sunlight than the parent ZnO. Addition of 1mM of H_2O_2 increases the rate of degradation of the dyes but increasing of concentration of oxidant beyond 8 mM not much increase of degradation due to the formation of less reactive peroxy radical. Photocatalyst dosage of 100 mg l^{-1} is optimum for the degradation of dye. Acidic pH is more suitable for the degradation of Reactive Blue 160. Reactive Blue 160 was highly mineralized when extended the reaction time. The overall results of this study show that the W, N-codoped ZnO is an efficient photocatalyst for the degradation of

Reactive Blue 160 from aqueous solution. It could also be applied for treatment of other organic dyes.

Acknowledgments

The author is indebted to Supervisor for his constant encouragement and support.

Conflict of interests

The authors declare that they have no conflict of interest

REFERENCES

[1] Mitchell V G, Mein R G and Mcmahon T A. Utilising Stormwater and Wastewater Resources in Urban Areas, Australian Journal of Water Resources 2002; 6: 31-43.

[2] Zita J, Kry’sa J, and Mills A, Correlation of Oxidative and Reductive Dye Bleaching on TiO2 Photocatalyst Films, Journal of Photochemistry and Photobiology A: Chemistry 2009; 203: 119-124.

[3] Pichat P, Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial, Marcel Dekker Inc, New York, Basel, 2003, 77.

[4] Kanna M, Wongnawa S, Mixed Amorphous and Nanocrystalline TiO_2 Powders Prepared by Sol-Gel Method: Characterization and Photocatalytic Materials Chemistry and Physics 2008; 110(1):166-175.

[5] Li G, Chen L, Dimitrijevic N. M and Gray K A, Visible light photocatalytic properties of anion-doped TiO_2 materials prepared from a molecular titanium precursor, Chemistry and Physics 2008; 451: 75-79.

[6] Yu J. G, Ma T. T, Liu S. W, Enhanced photocatalytic activity of mesoporous TiO_2 aggregates by embedding carbon nanotubes as electron-transfer channel Physical Chemistry Chemical Physics 2011; 13: 3491.

[7] Pron A and Rannou P, Processible conjugated polymers: From organic semiconductors to organic metals and superconductors Progress in Polymer Science 2002; 27: 135−190.

[8] Fang Z, Eshbaugh A and Schanze A, Low-Bandgap Donor−Acceptor Conjugated Polymer Sensitizers for Dye-Sensitized Solar Cells, Journal of American Chemical Society 2011; 133: 3063−3069.

[9] Barman S, Deng F and McCreery R L, Conducting Polymer Memory Devices Based on Dynamic Doping Journal of American Chemical Society 2008; 130: 11073−11081.

[10] Chuang C H, Lin Y Y, Tseng Y H, Chu T H, Lin C C, Su W F, Chen C W, Hybrid Zinc Oxide Conjugated Polymer Bulk Heterojunction Solar Cells, Journal of Physical Chemistry C 2010; 114: 18717−18724.

[11] Janáky C, Tacconi N. R. D, Chanmanee W, Rajeshwar K, Preparation and Strongly Enhanced Visible Light Photocatalytic Activity of TiO2 Nanoparticles Modified by Conjugated Derivatives of Polyisoprene, Journal of Physical Chemistry C 2012; 116: 25806-25815.

[12] Kalikeri S, Kamath N, Gadgil D J Shetty Kodialbail V, Visible light-induced photocatalytic degradation of Reactive Blue-19 over highly efficient polyaniline-TiO_2 nano-composite: a comparative study with solar and UV photocatalysis. Environmental Science Pollution Research Intermediate 2018; 25(4): 3731-3744.

[13] Vanja Gilja, Katarina Novakovic, Jadranka Travas-Sejdic, Zlata Hrnjak-Murgiv Marijana Kraljic Rokovic and Mark Žic, Stability and Synergistic Effect of Polyaniline/ TiO_2 Photocatalysts in Degradation of Azo Dye in Wastewater, nanomaterials 2017; 7: 1-16.

[14] Lin Y, Li D, Hu J, Xiao G, Wang J, Li W and Fu X, Highly Efficient Photocatalytic Degradation of Organic Pollutants by PANI-Modified TiO_2 Composite Journal of Physical Chemistry C, 2012; 1165764-5772.

[15] Yang C, Dong W, Cui G and Zhao Y, Enhanced photocatalytic activity of PANI/TiO_2 due to their photosensitization-synergetic effect Electrochimica Acta 2017 DOI: 10.1016/j.electacta.2017.07.037

[16] Mais L, Mascia M, Palmas S and Sechi E, Photoelectrochemical oxidation of phenol with nano-structured TiO_2 -PANI electrodes under solar light irradiation, Separation and Purification Technology, 2018.
DOI: 10.1016/j.seppur.2018.03.074