Photocatalytic degradation of indigo carmine by using tungsten doped bismuth vanadate

Ahmad Yasmin*, Ameta Suresh and Kothari Seema
Department of Chemistry, PAHER University, Udaipur-313003 (Raj.), INDIA
*yasminimax@gmail.com

Abstract

The photocatalytic degradation of indigo carmine dye was studied using tungsten doped $BiVO_4$. Bismuth vanadate powder has been synthesized by sol-gel technique. The incorporation of W ions into $BiVO_4$ was confirmed by EDX. The photocatalytic activity was studied using different samples of $BiVO_4$ by variation of pH, concentration of dye, dose of semiconductor and light intensity.

It has been found that degradation of dye is more effective in presence of W doped $BiVO_4$, It shows the role of tungsten ions for enhancing degradation of indigo carmine by reducing the recombination of photogenerated electrons and holes.

Keywords: Photocatalysis, Tungsten, Degradation, $BiVO_4$, Indigo carmine.

Introduction

The water bodies are continuously polluted due to the nonscientific methods of waste water treatment adopted by different industries. The waste water from textile industries contains a significant amount of nonbiodegradable dyes[7]. Complexity of these dye molecules does not favor the natural processes of degradation and secondly, most of the dyes are toxic in nature[3]. Their incomplete degradation may generate more toxic or even carcinogenic byproducts[9,10]. Various physical, chemical and biological methods have been introduced for treatment of dye effluents from industries[21]. Precipitation, coagulation, floatation and oxidizing agent are also used for treatment of dye effluents. Major disadvantages of chemical methods are that they require expensive chemicals and generate some undesired byproducts after dye which may also be polluting in nature[2,17]. Biological methods to degrade dyes were found effective but there is a difficulty in scaling up this process[13].

Photocatalytic degradation of dyes into harmless or less harmful products such as CO_2 and H_2O is a green chemical method. In last few decades, the visible light photocatalysis in presence of semiconductor has attracted more attention[14,25]. The $BiVO_4$ has a band gap of 2.40 eV and therefore, it has been recognized as potentially suitable visible light photocatalyst for degradation of organic pollutants. It has been widely used in the photocatalytic degradation of organic compounds in waste water as well as for O_2 evolution under sunlight irradiation[15,24]. But one of the limitations in the use of $BiVO_4$ is the recombination of photogenerated electrons and holes with a free carrier life time around 40 ns[1]. This low charge migration of $BiVO_4$ photocatalyst can be solved by the introduction of some doping cations into $BiVO_4$ crystal lattice so as to change the crystal symmetry of $BiVO_4$ and thus, increasing the charge migration efficiency to enhance the photocatalytic activities[8]. Many reports are available on the use of coupled $BiVO_4$ with other metal oxides such as Bi_2O_3, V_2O_5, TiO_2, WO_3, CdS, $CuCr_2O_4$ and $CuWO_4$ for water purification and water splitting application.[4-6,11,12,19,26]

One of the most widely used dye in the textile industry is indigo carmine which is also used as an additive in pharmaceutical tablets, capsules and for medical diagnostic purposes[16]. Prado et al[20] compared adsorption of indigo carmine on chitin and chitosan. Nakamura et al[18] decolorized indigo carmine by adsorption on charcoal from the extracted residue of coffee beans. Photocatalytic degradation of indigo carmine using TiO_2 and CaO has also been reported[22,23].

Material and Methods

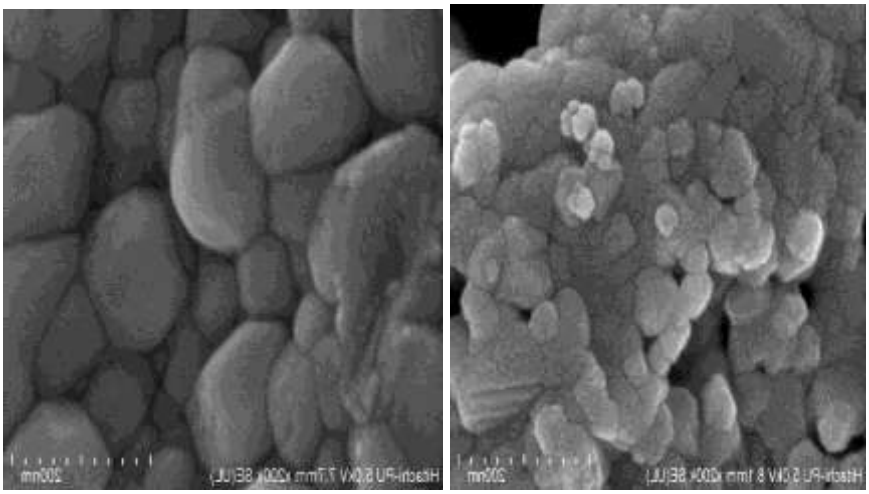
Preparation of catalyst: Bismuth nitrate, ammonium vanadate, citric acid, nitric acid, ammonia and distilled water were utilized as raw material for sol-gel synthesis of $BiVO_4$. The pH value of final solution was adjusted to 7.0. The $BiVO_4$ was placed in a crucible and a certain amount of ammonium tungstate solution was mixed with precursors. After drying and grinding, the powder was calcined at 723 K for 4 h under the ambience of atmosphere. The morphology and chemical composition were investigated by field emission scanning electron microscope and energy dispersive x ray analysis respectively.

The experiments were performed at room temperature and the degradation was monitored at 612 nm by using UV-visible spectrophotometer. The comparative studies were carried out in presence of doped and undoped $BiVO_4$ at 8.0 pH, 4.0×10^{-5} M dye concentration, 0.10 g of semiconductor and 70.0 Wm^{-2} intensity. A 200 Watts bulb with tungsten filament was used for irradiation. It was observed that there is better degradation with doped $BiVO_4$ as compared to undoped one.

Results and Discussion

Characterization

Field Emission Scanning Electron Microscopy (FESEM): The morphology of particles was examined using Field Emission Electron Microscopy (Hitachi PU). The FESEM images of $BiVO_4$ and W-doped (0.8%) $BiVO_4$ are given in fig. 1.



(a) **(b)**

Fig. 1: FESEM Images of (a) Undoped $BiVO_4$ (b) 0.8% W-doped $BiVO_4$

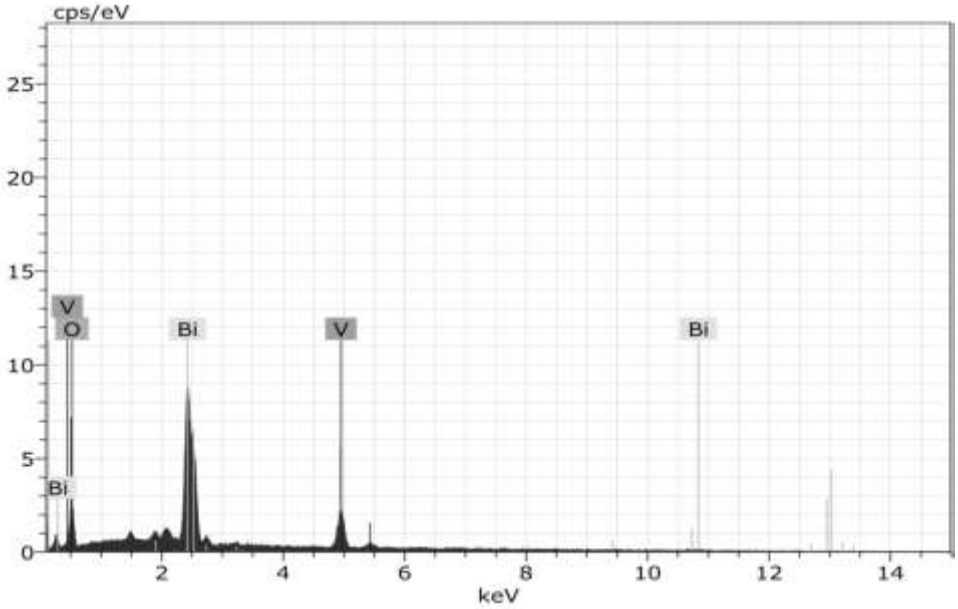


Figure 2(a): Undoped $BiVO_4$

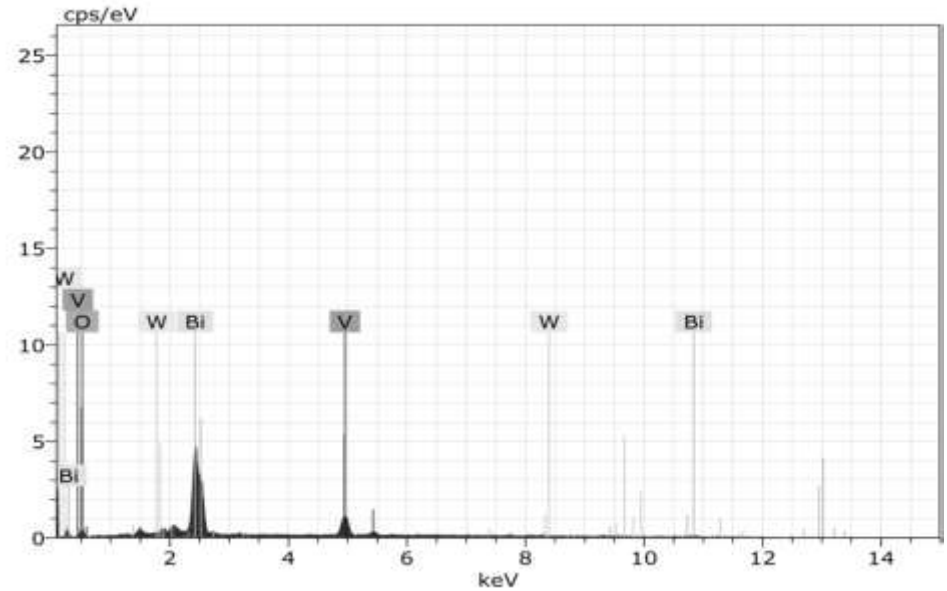


Figure 2(b): W-doped $BiVO_4$

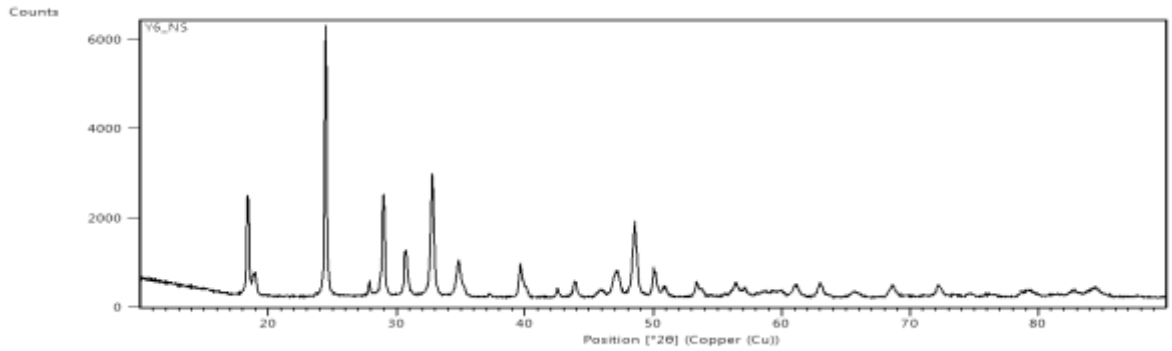


Figure 3(a): Undoped $BiVO_4$

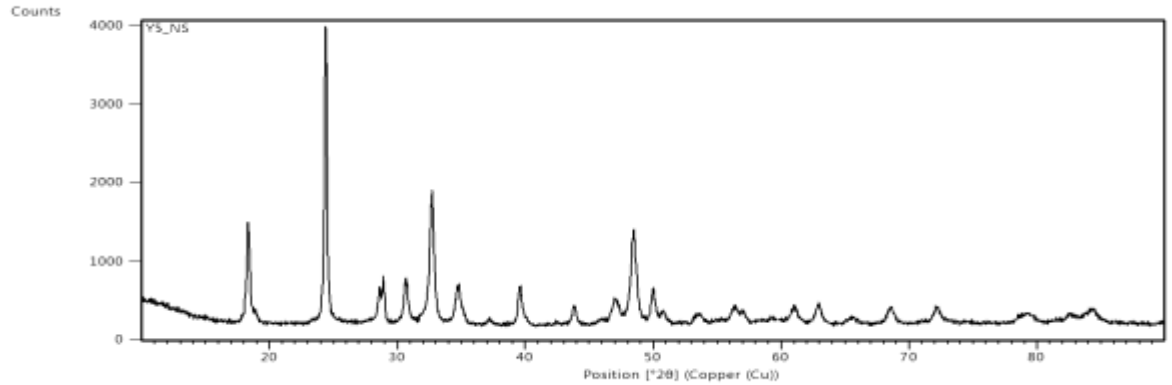


Figure 3(b): W-doped $BiV0_4$

It is clear from these images that undoped $BiVO_4$ has larger particles as compared to 0.8% W doped $BiVO_4$, but the shapes of both are elliptical. The FESEM images of undoped and doped sample are presented in fig. 1.

Energy Dispersive X-Ray Analysis (EDX): EDX analysis was performed to study the chemical composition of the samples. EDX spectra of undoped $BiVO_4$ and W-doped (0.8%) $BiVO_4$ are presented in fig. 2 (a) and 2 (b) respectively. It is clear from the data that undoped sample is pure $BiVO_4$ as it does not contain any signal for impurity while in W-doped $BiVO_4$, there are signals for tungsten which clearly reflect that doping has taken place.

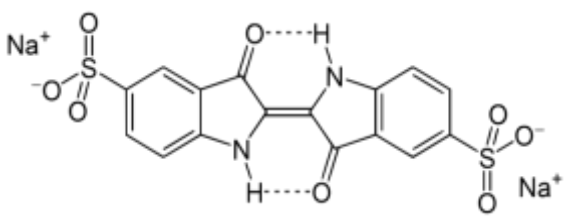
X-RAY Diffraction Analysis: The patterns of X-ray diffraction were recorded for W-doped and undoped $BiVO_4$ with the help of XRD instrument (Pan Analytical X Pert Pro.). The Debye -Scherrer was used to calculate crystallite size of both the samples and these are given in fig. 3(a) and 3(b) respectively.

$D = 0.9\lambda/\beta\cos\theta$

where β = FWHM, λ = X-ray wavelength (CuKα radiation 0.154060 nm). The average size of crystallite was found to be 60.75 nm for undoped $BiVO_4$ which reduces to 41.07 nm.

Photodegradation study: A stock solution of indigo carmine (1.0×10^{-3} M) was prepared by dissolving (0.0466 g) of dye in 100 mL. double distilled water. This stock solution was further diluted. The absorbance of indigo carmine solution was determined with the help of a spectrophotometer (Systronics Model 106) at λ_{max} = 612 nm. The photocatalytic degradation of indigo carmine dye was studied after addition of 0.10 g of W-doped and undoped composite $BiVO_4$ in 50 mL dye solution (4.0×10^{-5} M). The reaction mixture was exposed to visible light with a 200 W tungsten lamp.

Absorbance of solution was measured with the help of a spectrophotometer (Systronics Model 106) at several time intervals. The intensity of light was varied by changing the distance between the light source and reaction mixture. A digital pH meter (Systronics Model CL-54) was used to measure pH of the solution. pH of the dye solution was adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. Control experiments were carried out to confirm that the degradation of *indigo carmine* was photocatalytic in nature. This degradation was also carried out with 1.6% W-doped $BiVO_4$ for comparison.



Structure of Indigo Carmine ($C_{16}H_8N_2Na_2O_8S_2$)

A graph was plotted between log A v/s time which was a straight line showing that photocatalytic degradation of dye follows pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following equation:

k = 2.303 x slope

A typical run has been drawn for the photocatalytic degradation of indigo carmine using photocatalyst where all the parameters were kept constant.

Effect of pH: The rate of change of absorbance and the percentage of degradation of indigo carmine using 0.12 g of both samples were compared at different pH values. The rate of degradation of dye at different pH is compared. The degradation of dye solution was found to increase with increasing pH of the medium reaching an optimum at pH 8.0. There was a decline in rate on increasing the pH further above 8.

Effect of dye concentration: The rate of degradation was observed with change in concentration of dye. On further increment of concentration, the degradation efficiency reduces. In figure 5, we have compared the pattern of degradation of dyes with both the samples.

A TYPICAL RUN

pH = 8 **Amount=0.10 g**
conc.= 4 ×10^{-5} M **Intensity = 70.0 mWcm^{-2}**

Time (min.)	undoped $BiVO_4$		0.8% BiVO4		1.6% W-doped $BiVO_4$	
	Absorbance	1+log A	Absorbance	1+log A	Absorbance	1+log A
00	0.608	0.784	0.697	0.843	0.692	0.840
30	0.592	0.772	0.649	0.812	0.688	0.838
60	0.584	0.766	0.621	0.793	0.653	0.815
90	0.566	0.753	0.608	0.784	0.620	0.792
120	0.554	0.744	0.563	0.750	0.599	0.777
150	0.550	0.740	0.530	0.724	0.588	0.769
180	0.540	0.732	0.495	0.695	0.585	0.767

Rate constant for $BiVO_4$, k = 1.42× 10^{-5}sec^{-1}
Rate constant for 0.8% W-doped Bismuth vanadate, k = 3.02 × 10^{-5} sec^{-1}
Rate constant for 1.6% W-doped Bismuth vanadate, k = 2.12 × 10^{-5} sec^{-1}

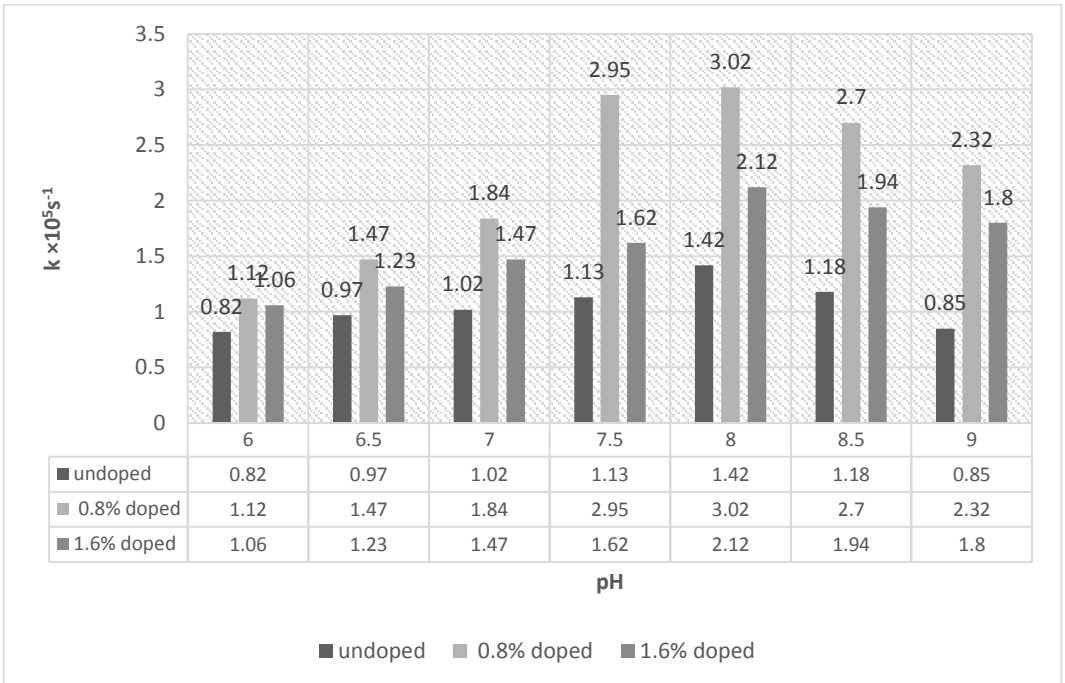


Fig. 4: Effect of pH

It was observed that rate of degradation of indigo carmine increases as the concentration of dye was increased upto 4×10^{-5}M. On further increase in the concentration above this limit, a decreasing trend of the rate was observed.

Effect of catalyst: Experiments were performed with different amounts of undoped as well as W-doped $BiVO_4$. Photodegradation efficiency was found to reach maximum when 0.1 g of undoped and W - doped $BiVO_4$ was used. Use of more than 0.1 g of the photocatalyst resulted in a corresponding decrease in rate of degradation.

Effect of Light intensity: Photodegradation of indigo carmine dye was also carried out using different light Intensities. The rate of degradation was found to increase with increasing light intensity upto 70.0 $mWcm^{-2}$. Higher intensity of light was not used just to avoid any thermal reaction.

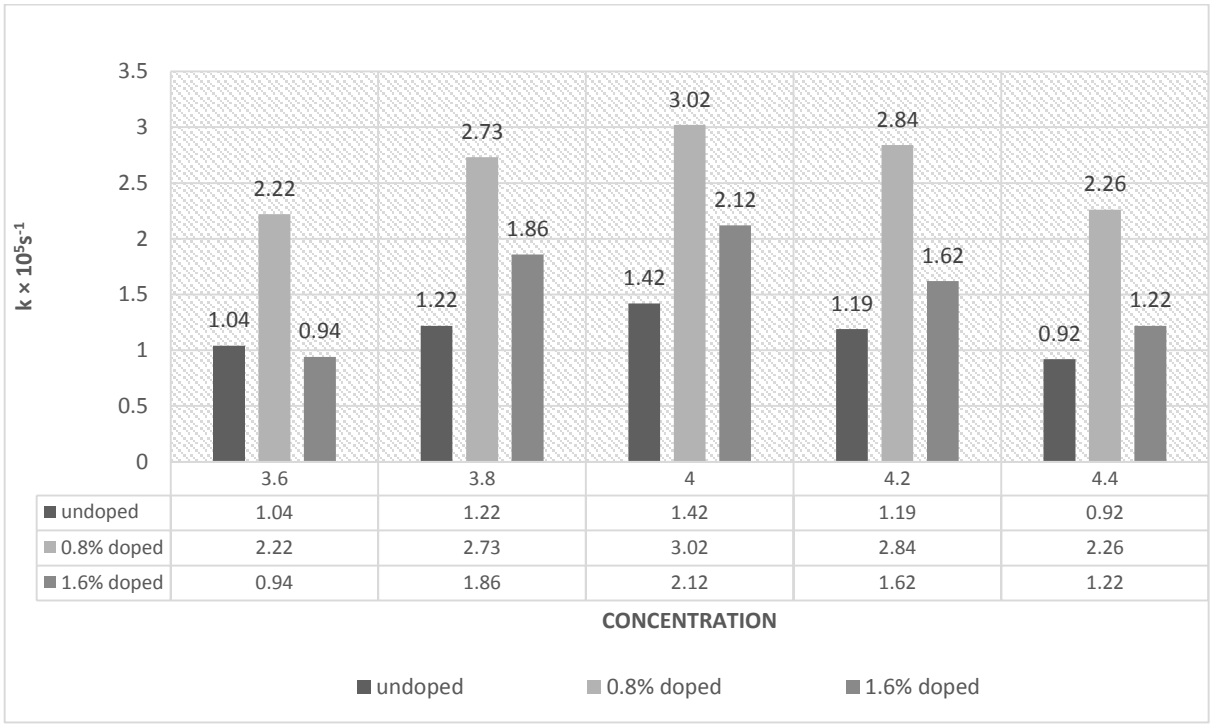


Fig. 5: Effect of dye concentration

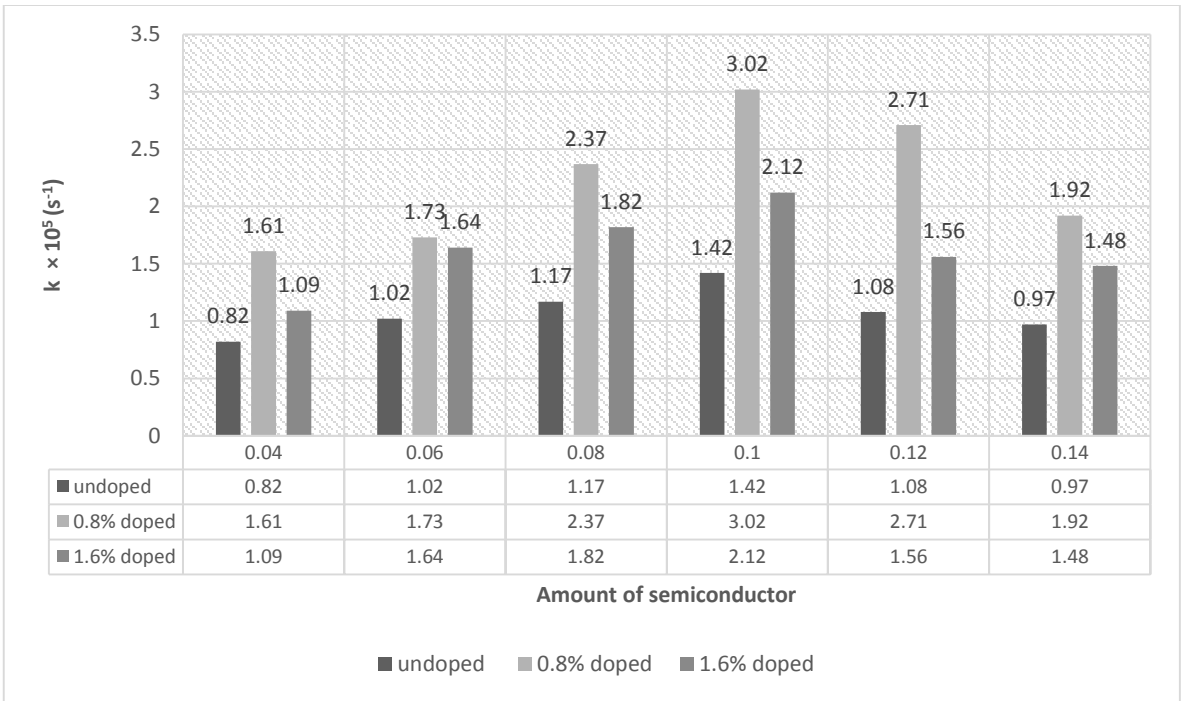


Fig. 6: Effect of amount of photocatalyst

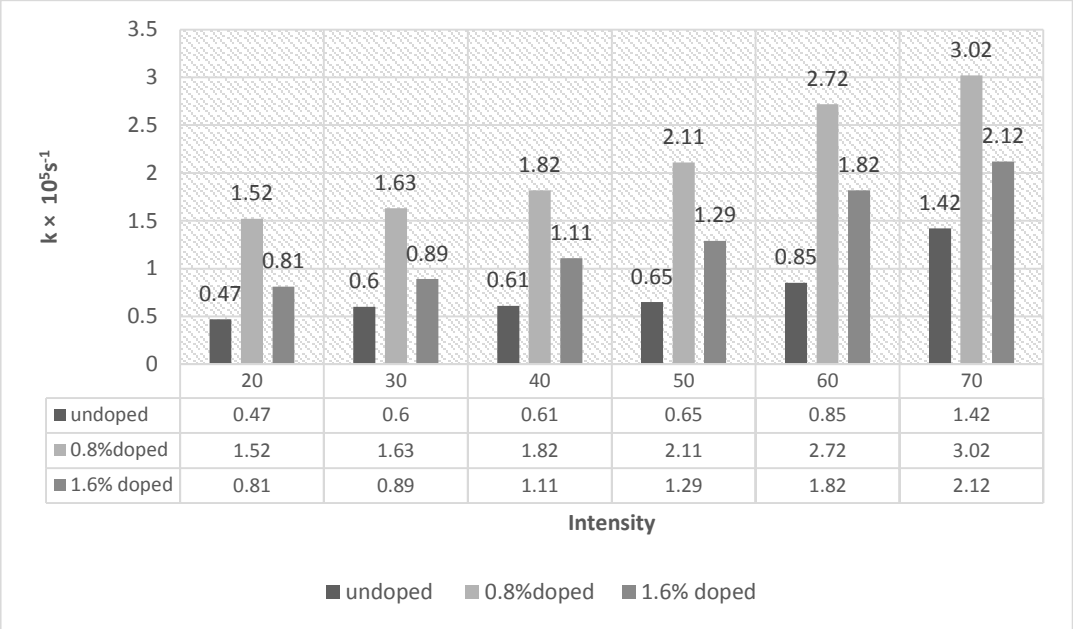


Fig. 7: Effect of light intensity

Mechanism: Mechanism for the photocatalytic degradation of indigo carmine using W doped $BiVO_4$ photocatalysts has been proposed. Electrons in $BiVO_4$ are excited to its conduction band on light irradiation. $^{\bullet}OH$ radicals were not found as active oxidizing species in the present investigations and this was confirmed by using hydroxyl radical scavenger (2-propanol) where the rate of degradation was not affected appreciably. On the basis of the observations, a tentative mechanism for photocatalytic degradation of EB has been proposed as:

$$^{1}IC \xrightarrow{h\upsilon} {}^{1}IC$$
$$^{1}IC_1 \xrightarrow{ISC} {}^{3}IC_1$$
$$BiVO_4 \xrightarrow{h\upsilon} BiVO_4\ (h^{+}\ (VB) + e^{-}\ (CB))$$
$$O_2\ (\text{Dissolved Oxygen}) + e^{-}\ (CB) \longrightarrow O_2^{\bullet -}$$

In basic medium-

$$^{3}IC_1 + O_2^{\bullet -} \longrightarrow \text{Leuco IC}$$
$$\text{Leuco IC} \longrightarrow \text{Products}$$

Indigo carmine absorbs radiation of suitable wavelength and it is excited to its first excited singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the photocatalyst also utilizes the incident light energy to excite its electron from valence band to conduction band, thus leaving behind a hole. The dissolved oxygen accepts the electron from conduction band and is converted to superoxide radical ion, which converts the indigo carmine to its leuco from. The leuco form is ultimately unstable and it will degrade into smaller products.

Conclusion

Tungsten has been used as a metal dopant and it was found that tungsten doped $BiVO_4$ works more efficiently as compared to undoped $BiVO_4$ in the degradation of indigo carmine. When the amount of dopant was kept 0.8%, then rate increases, but it decreases on increasing the % of dopant to 1.6. Here, hydroxyl radical act as active oxidising species as confirmed by scavenger test. This process of photocatalysis degradation is an advanced oxidation process and this method for wastewater purification is eco-friendly in nature.

Acknowledgement

The authors are thankful to SAIF, CIL, Chandigarh, India for FESEM, EDS and XRD analysis.

References

1. Abdi F.F., Savenije J.T., May M.M., Dam B. and Krol, The origin of slow carrier transport in $BiVO_4$ thin film photoanodes: A time resolved microwave conductivity study, *J. Phys. Chem. Lett*., **4**, 2752-2757 **(2013)**

2. Al-Kadasi A., Dris A., Saed K. and Guan K.C.T., Photoluminescence and photocatalysis of the flower like nano-ZnO photocatalysts prepared by a facile hydrothermal method with or without ultrasonic assistance, *Global Nest: The International Journal*, **6**, 222-230 **(2004)**

3. Bae J.S. and Freeman H.S., Aquatic toxicity evaluation of new direct dyes to the Daphnia magna, *Dyes and Pigments*, **3**, 81-85 **(2007)**

4. Bajaj R., Sharma M. and Bahadur D., Visible light driven novel nanocomposite ($BiVO_4/CuCr_2O_4$) for efficient degradation of organic dye, *Dalton Trans.*, **42**, 6736-6744 **(2013)**

5. Chatchai P., Nosaka Y.A. and Nosaka Y., Photo electrocatalytic performance of $WO_3/BiVO_4$ toward the dye degradation, *Electrochim. Acta*, **94**, 314-319 **(2013)**

6. Chen L., Zhang Q., Huang R., Yin S.F. and Luo S.L., Porous peanut like $Bi_2O_3/BiVO_4$ composites with heterojunctions: One step synthesis and their photocatalytic properties, *Dalton Trans*., **41**, 9513-9518 **(2012)**

7. Christie R.M., Environmental aspects of textile dyeing, Wood Head, Boca Raton, Fla, USA **(2007)**

8. Gupta S. and Tripathi, *Chin. Sci. Bull*., **56**, 1639-1657 **(2011)**

9. Hai F.I., Yamamoto K. and Fukushi K., Hybrid treatment systems for dye waste water, *Critical Reviews in Environmental Science and Technology*, **37**, 315-377 **(2007)**

10. Helmer R. and Hespanhol I., Water pollution control-A guide to the use of water quality management principles, E & FN Spon London, UK **(1997)**

11. Jiang H., Nagai M. and Kobayashi K., Enhanced photocatalytic activity for degradation of methylene blue over V_2O_5/$BiVO_4$ composite, *J. Alloys compd.*, **479**, 821-827 **(2009)**

12. Jiang J., Wang M., Li R., Ma L. and Guo L., Febricating CdS /$BiVO_4$ and $BiVO_4$/ CdS hetero structured film photoanodes for photoelectrochemical application, *Int. J. Hydrogen Energy*, **38**, 13069-13076 **(2013)**

13. Khalid A., Arshad M. and Crowley D.E., Accelerated decolourization of structurally different azo dyes by newly isolated bacterial strain, *Applied Microbiology and Biotechnology*, **78**, 361-369 **(2008)**

14. Khatri A., Peerzada M.H., Mohsin M. and White M., A review on developments of dyeing cotton fabrics with reactive dyes for reducing effluent pollution, *J. Clean. Prod*., **87**, 50-57 **(2015)**

15. Kudo A. and Miseki Y., Heterogenous photocatalyst materials for water splitting, *Chem. Soc*., **38**, 253-278 **(2009)**

16. Lakshmi U.R., Srivastava V. Ch., Mall I.D. and Lataye D.H., Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristic for indigo carmine dye, *J. Environ. Manage*, **90**, 710 **(2009)**

17. Mall L.D., Upadhyay S.N. and Sharma Y.C., A review on economical treatment of waste water and effluents by adsorption, *International Journal of Environmental Studies*, **51**, 77-124 **(1996)**

18. Nakamura T., Hirata M., Kawasaki N., Tanada S., Tamura T. and Nakahori Y., Decolorization of indigo carmine by charcoal from extracted residue of coffee beans, *J. Environ. Sci. Health A*, **38**, 55 **(2003)**

19. Pilli S.K., $BiVO_4$/$CuWO_4$ Heterojunction photoanodes for efficient solar driven water oxidation, *Phys. Chem. Chem. Phys*., **15**, 3273-3278 **(2013)**

20. Prado A.G.S., Torres J.D., Faria E.A. and Dias S.C.L., Comparative adsorption studies of indigo carmine dye on chitin and chitosan, *J. Colloid Interface Sci*., **277**, 43 **(2004)**

21. Slokar Y.M. and Majcen le Marechal A., Methods of decolouration of textile waste waters, *Dyes and Pigments*, **37**, 335-356 **(1998)**

22. Subramani A.K., Byrappa K., Ananda S., Loknatha Rai K.M., Ranganathaiah C. and Yoshimura M., Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon, *Bull. Mater. Sci*., **30**, 37-41 **(2007)**

23. Veeranna Kirana Devarahosahalli, Lakshmaiah Madhu Theeta and Narayan Ramesh Thimmasandaran, Photocatalytic degradation of indigo carmine using calcium oxide, *International Journal of Photochemistry*, DOI:10.1155/2014/530570, 530570 **(2014)**

24. Wang D. et al, Photocatalytic water oxidation on $BiVO_4$ with the electrocatalyst as an oxidation cocatalyst: Essential relations between electrocatalyst and photocatalyst, *J. Phys. Chem. C*., **116**, 5082-5089 **(2012)**

25. Yang Y., Xu L., Wang H., Wang W. and Zhang L., TiO_2/graphene porous composite and its photocatalytic degradation of methylene blue, *Mater Design*, **108**, 632-639 **(2016)**

26. Zhang Lili, Tan Guoqiang, Wei Sasha, Ren Huijen, Ao Xia and Luo Yangyang, Microwave hydrothermal synthesis and photocatalytic properties of TiO_2/$BiVO_4$ composite photocatalysts, *Ceram. Int.*, **39**, 8597-8604 **(2013)**.

(Received 16th February 2021, accepted 31st March 2021)