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Use of Tungsten Doped Bismuth Vanadate as Photocatalyst for Degradation of Azure B

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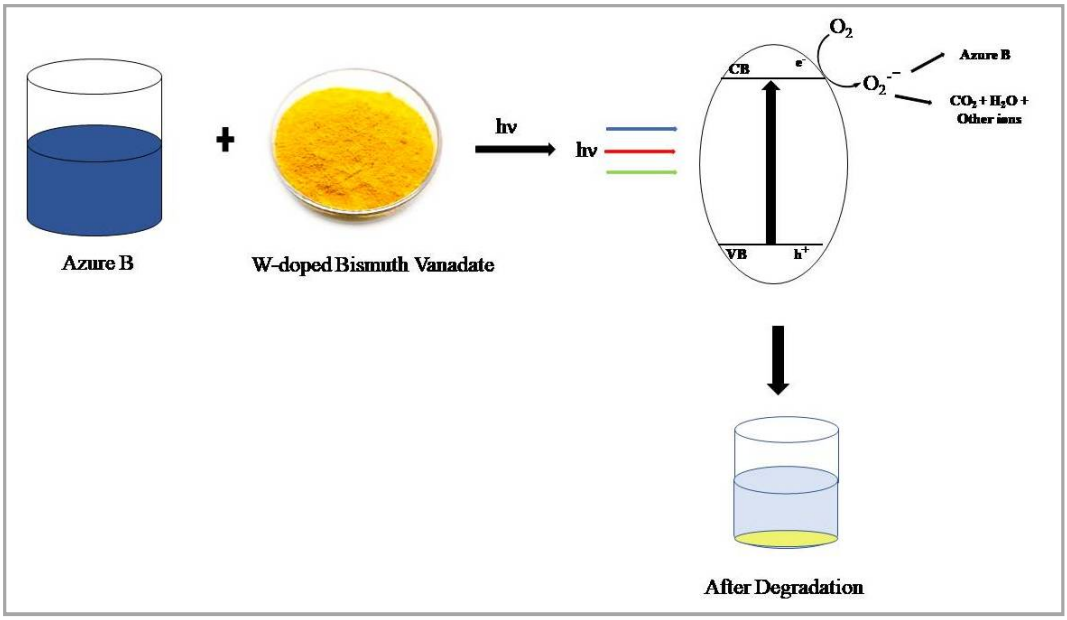
ABSTRACT

Dye wastes are major pollutants of water. Advanced oxidation process (AOP) such as photcatalysis has been used as an alternative and effective option for treatment of industrial wastewater, especially in case of non–biodegradable compounds. The degradation of azure B can be catalysed in presence of light. Bismuth vanadate has photocatalytic activity, which can be enhanced by metal doping such as tungsten. Effect of different operational parameters like pH, concentration, amount of bismuth vanadate, dosage of dopants, light intensity, etc. was studied on the rate of degradation and conditions were optimized as: pH (8.5), concentration of dye (2.0×10^{-5} M), amount of photocatalyst (0.10 g), and light intensity (70.0 mWcm^{-2}). On the basis of observations, a suitable mechanism for the photocatalytic degradation of Azure B dye has been proposed involving oxygen anion radical as an active oxidizing species.

Graphical Abstract:



Keywords: Bismuth vanadate, Photocatalytic, Tungsten, Doped, Azure B.

INTRODUCTION

The photocatalytic degradation of two dyes with similar structure (Azure A/B) and Sudan III/IV) dyes, but different functional groups, were studied by Aarthi *et al*., [1]. The photocatalytic activity of two TiO_2 samples was compared solution combustion synthesized TiO_2 and Degussa P-25. It was reported that photodegradation rate was dependent on polarity of solvents and it increases with increasing polarity. Some Cu-loaded $BiVO_4$ (Cu–$BiVO_4$) catalysts were synthesized Xu et al.[2] via impregnation method. The photocatalytic activities of as–prepared Cu–$BiVO_4$ was evaluated for degradation of methylene blue (MB) and it was found that it depends mostly on the Cu content as well calcination temperature. The optimum calcination temperature and Cu loading were found to be 300°C and 5 at.%, respectively. It was revealed that efficient *N*-demethylation of MB was there, when Cu–$BiVO_4$ was used as a catalyst.

The ZnO–reduced graphene oxide (ZnO–RGO) nanocomposites was synthesized by Rabieh *et al*., [3] via a hydrothermal method and then used as an efficient photocatalyst for photodegradation of azure B dye. A synergistic effect was observed between photocatalytic potential of the nanocomposites and surface adsorption characteristic on the photodegradation of azure B. It was indicated that photocatalytic activity of ZnO was significantly improved on hybridization with RGO sheets. Rabieh *et al*., [4] also synthesized ZnO nanostructure assembled by nanosheets via a ultrasound–assisted route without using any template or surfactant. It was reported that ZnO sample was in hexagonal phase with clew-like microspheres consisting of nanosheets with an average thickness of 50 nm. As–synthesized ZnO was used for the photocatalytic degradation of azure B under UV light. They also confirmed the role of hydroxyl radicals as main active oxidizing species in this photodegradation process.

Yang *et al*., [5] synthesized Ag_2O@Ag-modified $BiVO_4$ composites via a pH-mediated chemical precipitation method. It was revealed that methylene blue (MB) and rhodamine B (RhB), and their mixture can be degraded in presence of light and as–prepared composites. It was also reported that composites with Ag_2O : $BiVO_4$ (1 : 10) exhibited the highest degradation efficiency and RhB or MB could be completely degraded in 15 and 48 min, respectively. Adepu et al.[6] synthesized mesoporous titanosilicate/bismuth vanadate (BVTS) under mild conditions. It was reported that the BVTS heterostructures exhibited increased photocatalytic activity in the degradation of rhodamine B dye (RhB) in presence of sunlight. The optimum photocatalytic activity of BVTS 1 was almost 6.5 and 3.5–folds more than bismuth vanadate and titanosilicate, respectively. It was revealed that RhB was degraded in 60 min over BVTS 1 nanocomposites under visible light irradiation.

Soltani *et al*., [7] photocatalytically reducted grapheme oxide (GO) to reduced graphene oxide (rGO) in presence of visible-light using $BiVO_4$ (BVO). It was observed that the photocatalytic degradation of methylene blue (MB) was enhanced due to smaller particle sizes, which were two–folds as compared to BVO. The complete photodegradation could be achieved in 60 min. The monoclinic bismuth vanadate (m-$BiVO_4$) nanoparticles were prepared by Sajid et al.[8] via hydrothermal method. It was reported that particles were highly dispersed and have a uniform size of 50–70 nm. These nanopaticles were used for photocatalytic degradation of crystal violet and rhodamine-B under visible light. The m-$BiVO_4$ nanoparticles showed enhanced photocatalytic response for the degradation for both these dyes under visible light.

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Chaudhary *et al*., [9] prepared a composite of reduced graphene oxide and nickel sulfide via mechanochemical method. The photocatalytic performances of as–prepared rGO/NiS composite, rGO and NiS were evaluated using azure B model system. The composite exhibited good photocatalytic activity as compared to NiS as well as rGO. The photocatalytic performance of rGO/CuS composite, rGO and CuS was evaluated by Ruchi *et al*., [10] using a model system of azure B. Optimum conditions were obtained for photocatalytic degradation of azure B by the variation of different operational parameters such as pH, concentration of azure B, amount of composite, and light

intensity. It was concluded that composite showed good photocatalytic activity as compared to individual CuS and rGO.

Bismuth vanadate nanoparticles were synthesized by Josephine et al.[**11**] via co-precipitation method at different pH (9, 10 and 11). It was revealed that as–synthesized nanoparticles were monoclinic single-phase $BiVO_4$. The photocatalytic degradation of rhodamine B dye was evaluated in presence of $BiVO_4$. Vyas *et al*., [**12**] prepared water-soluble carbon quantum dots (CQDs) (6 nm) by carbonization of pomegranate *(Punica granatum)* peels. The amorphous nature of CQDs and the monoclinic nature of CuO NRs were confirmed. It was observed that CuO NRs decorated with CQDs exhibited maximum photocatalytic activity for the degradation of azure B (97 %) than CuO NRs alone.

Justinabraham *et al*., [**13**] doped vanadyl phosphate (VP) with graphitic carbon nitride to form VP/g-C_3N_4 (VP/GCN) composite. As–prepared materials after perxomonosulfaric activation were evaluated for the photocatalytic degradation of azure B under visible light. It was reported that degradation efficiency of as-prepared composite was found to be around 93% for azure B dye effluent within 2 h. Banu *et al*., [**14**] synthesized graphene oxide (GO) and GO/CuO nanocomposites via modified Hummer's and hydrothermal methods, respectively. The photocatalytic degradation of azure-B dye was selected as a model system to evaluate the photocatalytic efficiency of GO/CuO nanocomposite. It was revealed that heigher catalytic activity of GO/CuO nanocomposite was mainly due to synergistic effect between GO and CuO nanoparticles such as small size of GO/CuO NPs and high surface area. It was revealed that GO/CuO nanocomposite exhibited long-term durability and good stability based on recycling.

MATERIALS AND METHODS

Field Emission Scanning Electron Microscopy (FESEM): The morphology of particles was examined using Field Emission Electron Microscopy (Hitachi PU). The higher resolution provides the structural differences between undoped and doped samples. It provides information about morphology of samples. It was observed that particles of undoped $BiVO_4$ were larger in size, which decreases on doping with tungsten.

Energy Dispersive X-ray Spectroscopy (EDX) Analysis: Energy dispersive X-ray spectroscopy data revealed the presence of 33.49, 37.79, 19.65 and 9.07% of bismuth, vanadium, oxygen and tungsten, respectively. It indicates that there was no impurity in the sample and it contain only these elements.

X-ray Diffraction (XRD): The patterns of X-ray diffraction were recorded for undoped and W-doped $BiVO_4$ with the help of XRD instrument (Pan Analytical X Pert Pro.). The X–ray diffraction data were used to calculate particle size of undoped and W-doped $BiVO_4$using Debye-Scherrer formula and it was found to be 60.75 nm for undoped and 41.7 nm for 0.8% doped W–$BiVO_4$.

Materials: Bismuth nitrate ($Bi(NO_3)_3.5H_2O$), ammonium metavanadate (NH_4VO_3), citric acid, nitric acid, and ammonia were used in synthesis of bismuth vanadate. Then it was doped with tungsten using ammonium wolframate ($(NH_4)_6W_7O_{24}.6H_2O$) solution. All chemicals used were of analytical grade and used without further purification. Azure B was purchased from Himedia Chemicals. All the solutions were prepared in double distilled water.

Synthesis of W-Doped Bismuth Vanadate: The process of synthesis of undoped and W–doped $BiVO_4$ was used as earlier [**15**]. A stock solution of azure B(1.0×10^{-3} M) was prepared by dissolving (0.0305g) of dye in 100 mL double distilled water. This stock solution was further diluted as and when required. The absorbance of azure B solution was determined with the help of a spectrophotometer (Systronics Model 106) at λ_{max} =644 nm. The photocatalytic degradation of azure B was studied after addition of 0.10 g of W–doped or undoped $BiVO_4$ in 50.0 mL dye solution ($2.0\times 10^{-}$

^{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 at regular 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. The pH of dye solution was adjusted by addition of previously standardized 0.1N sulphuric acid and 0.1N sodium hydroxide solutions. Control experiments were carried out to confirm that the degradation of azure B was photocatalytic in nature. The degradation of azure B was also carried out with 0.8% and 1.6% W–doped $BiVO_4$ for comparison.

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

$$k=2.303 \times \text{slope}$$

A typical run has been presented in table 1 for the photocatalytic degradation of azure Busing undoped and W–doped $BiVO_4$ as photocatalysts, keeping all other parameters constant.

Table1. Typical Runs

Time (min)	Undoped $BiVO_4$		0.8% W–doped$BiVO_4$		1.6% W–doped $BiVO_4$	
	Absorbance (A)	1+log A	Absorbance (A)	1 + log A	Absorbance (A)	1 + log A
00	0.776	0.8899	0.758	0.8797	0.708	0.8500
15	0.672	0.8274	0.543	0.7348	0.543	0.7348
30	0.596	0.7752	0.398	0.5999	0.422	0.6253
45	0.579	0.7152	0.292	0.4654	0.325	0.5119
60	0.447	0.6503	0.209	0.3201	0.254	0.4048
75	0.380	0.5798	0.155	0.1903	0.199	0.2988
90	0.336	0.5263	0.141	0.1492	0.155	0.1903
105	0.292	0.4653	--	--	0.120	0.0792
120	0.251	0.3996	--	--	--	--

pH = 8.5, [Azure B] = 2.0×10^{-5} M , Amount of photocatalyst = 0.10 g,
Light intensity = 70.0 $mWcm^{-2}$

Rate constant with undoped bismuth vanadate, $k=1.57\times10^{-4}sec^{-1}$, Rate constant with 0.8% W–doped bismuth vanadate, $k = 3.57 \times 10^{-4}$ sec^{-1}, Rate constant with1.6%W–doped bismuth vanadate, $k=2.83\times10^{-4}sec^{-1}$

RESULTS AND DISCUSSION

Effect of pH: The effect of pH was investigated by varying the initial pH of solution from 6.0 to 9.0. The results are given in figure 1. It was found that degradation efficiency increases with an increase in pH and then decreases. An electron from the conduction and is removed by dissolved oxygen to generate $O_2^{\bullet-}$an ion radicals. An increase in rate of degradation with increase in pH may be due to availability of more $O_2^{\bullet-}$radicals. A decrease in rate of photocatalyticdegradation may be due to neutral form of azure B (that exists in basic media), which does not face any attraction towards negatively charged surface of the photocatalyst.

Effect of Dye Concentration: The effect of variation of concentration of azure B has been observed in the range from 1.6×10^{-4} M to 2.4×10^{-4} M for undoped, 0.8% and 1.6% W–doped $BiVO_4$. Results are reported in figure 2. It has been observed that rate of degradation increases with increasing concentration of dye but decreases on increasing the concentration of the dye further. On increasing the concentration of dye, the degradation rate increases due to more availability of molecules for

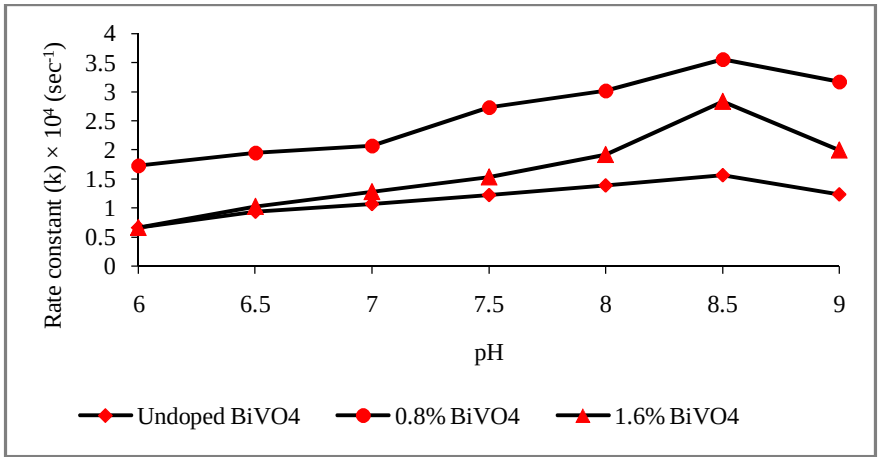

Figure 1. Effect of pH.

excitation and energy transfer but after a certain concentration, the rate of photocatalytic degradation was observed to decrease. This may be due to inner filter effect of dye molecules, which do not allow incident light to reach the semiconductor and thus, resulted in a decrease in rate of degradation on further increasing the concentration of dye. pH = 8.5, Amount of photocatalyst = 0.10 g, Light intensity = 70.0 mWcm^{-2}.

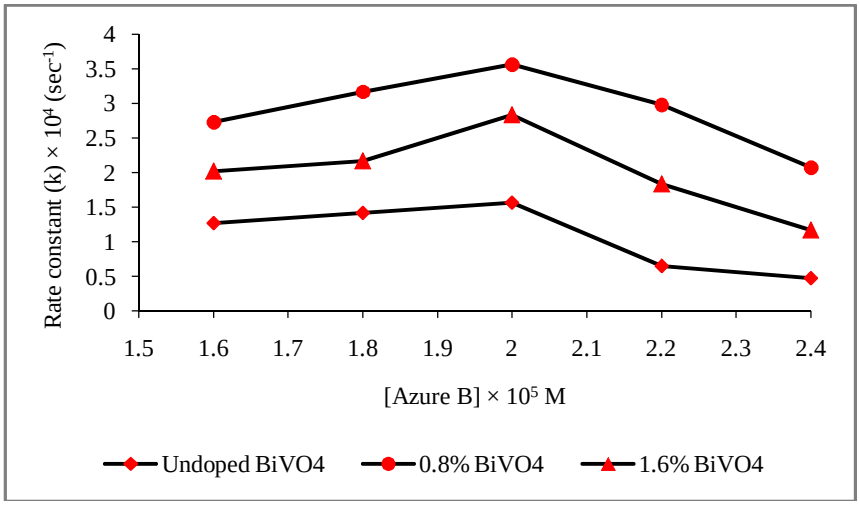

Figure 2. Effectofdyeconcentration.

Effect of Amount of Photocatalyst: The effect of variation of amount of photocatalyst on dye degradation was investigated in the range of 0.04g to 0.14g and results are presented in Figure 3. It was observed that rate of degradation increases on increasing the amount of photocatalyst but upto a certain amount of photocatalyst (0.1 g), for undoped, 0.8% and 1.6% doped $BiVO_4$.After this amount, the rate ofreaction decreases. It may be explained on the basis that as the amount of photocatalyst was increased, the exposed surface area of photocatalyst will also increase. As a result, there is a rise in the rate of reaction, but with further increase in the amount of photocatalyst, there is no increase in exposed surface area of photocatalyst, but only the thickness of the layer will increase, which allow e^- – h^+ recombination more probable, and hence, a decrease in rate of photocatalytic degradation was observed. pH = 8.5, [Azure B] = 2.0 × 10^{-5} M, Light intensity = 70.0 mWcm^{-2}.

Effect of Light Intensity: The influence of light intensity on rate of degradation of dye was also investigated by changing the light intensity from 20.0 to70.0 mWcm^{-2}. The observations are reported in figure 4. The observed data indicated that the rate of reaction increases with increasing light intensity

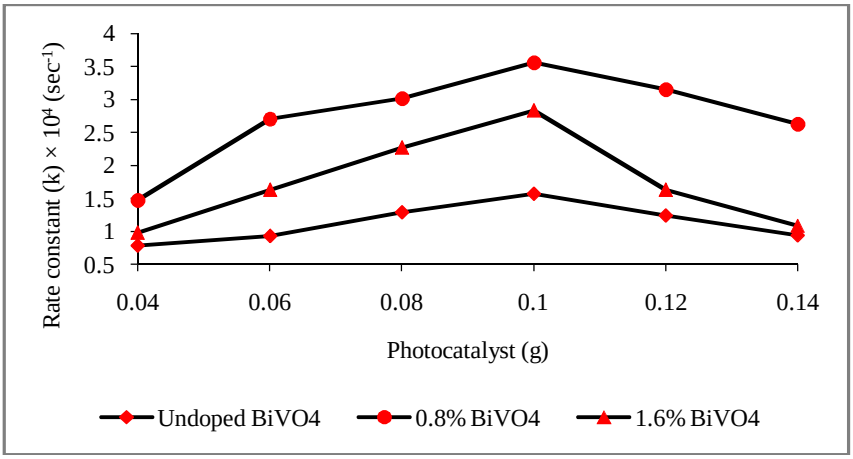

Figure3. Effect of amount of photocatalyst.

and the maximum rate was found at 70.0 $mWcm^{-2}$ for different samples. It may be due to fact that as the light intensity was increased, the number of photons striking per unit time per unit area of photocatalyst will also increase, resulting in a higher rate of degradation. Further increase in the light intensity may initiate some side thermal reactions and therefore, higher intensities of light have been avoided. pH = 8.5, [Azure B] = 2.0×10^{-5} M, Amount of photocatalyst = 0.10 g**.**

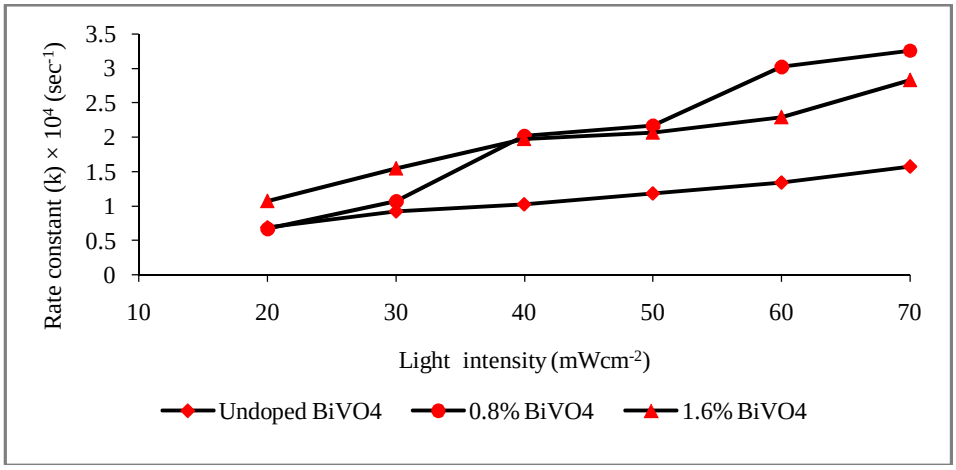

Figure 4. Effect of light intensity.

Mechanism: ˙OH radicals were not found participating as an active oxidizing species in the present investigation as confirmed by using specific hydroxyl radical scavenger (2–propanol), where the rate of degradation was not decreased appreciably. On the basis of the observation, a tentative mechanism for photocatalytic degradation of Azure B has been proposed as-

$$^{1}\text{Azure B}_0 \xrightarrow{h\upsilon} {}^{1}\text{Azure B}_1 \quad ...(1)$$

$$^{1}\text{Azure B}_1 \xrightarrow{ISC} {}^{3}\text{Azure B}_1 \quad ...(2)$$

$$\text{Photocatalyst} \xrightarrow{h\upsilon} \text{SC } (e^-)\text{ (CB)} + h^+\text{ (VB)} \quad ...(3)$$

$$O_2\text{(Dissolved oxygen)} + e^-\text{ (CB)} \longrightarrow O_2^{\bullet -} \quad ...(4)$$

$$O_2^{\bullet -} + {}^{3}\text{Azure B}_1 \longrightarrow \text{Leuco Azure B} \quad ...(5)$$

$$\text{Leuco Azure B} \longrightarrow \text{Products} \quad ...(6)$$

Azure B 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 $BiVO_4$ and W-$BiVO_4$ also utilize the incident light energy to excite itselectron from valence band to conduction band; thus, leaving behind a hole. The dissolved oxygen accepts electron from conduction band and it is converted to superoxide radical ion ($O_2^{\bullet-}$), which converts azure B into its leuco from. Aleuco form is relatively unstable and ultimately, it degrades to smaller products.

CONCLUSION

The doped and undoped $BiVO_4$ samples were synthesized by sol-gel method. The experimental results showed that degradation efficiency of azure B was affected by various working parameters like pH, concentration, amount of semiconductor and light intensity. The photodegradation of azure B was found to increase by doping bismuth vanadate and optimum value was found with 0.8% W–$BiVO_4$. The optimum conditions were pH = 8.5, concentration of dye = 2.0×10^{-5} M, amount of photocatalyst = 0.10 g, and light Intensity = 70.0 $mWcm^{-2}$. The rate of degradation was increased more than two folds as compared to undoped $BiVO_4$. An adverse effect was observed on increasing the concentration of dopant above 0.8%. This decrease may be due to blocking of active sites by this amount and there are no free active sites now. Photocatalytic degradation has emerged as a promising technology for wastewater treatment and it can be also considered as an eco-friendly pathway because of its benign approach. The time is not far off, when this technique will be firm-footed and almost replace other existing methods of waste water treatment.

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REFERENCES

[1]. T. Aarthi, P.Narahari, G.Madras, Photocatalytic degradation of Azure and Sudan dyes using nano TiO_2, *J. Hazard. Mater*, **2007**, 149(3), 725-734.
[2]. H. Xu, H. Li, C. Wu, J. Chu, Y.Yan, H. Shu, Z. Gu, Preparation, characterization and photocatalytic properties of Cu-loaded $BiVO_4$, *J. Hazard. Mater*, **2008**, 153(1-2), 877-884.
[3]. S. Rabieh, K. Nassimi, M. Bagheri, Synthesis of hierarchical ZnO–reduced graphene oxide nanocomposites with enhanced adsorption–photocatalytic performance, *Mater. Lett.*, **2016**, 162, 28-31.
[4]. S. Rabieh, K. Nassimi, M. Bagheri, Clew-like hierarchical ZnO nanostructure assembled by nanosheets as an efficient photocatalyst for degradation of azure B, *J. Mater. Sci.: Mater. Electr.*, **2016**, 27(10), 10052-10058.
[5]. Q. Yang, F. Chen, X. Li, D. Wang, Y. Zhong, G. Zeng, Self-assembly Z-scheme heterostructured photocatalyst of Ag_2O@Ag-modified bismuth vanadate for efficient photocatalytic degradation of single and dual organic pollutants under visible light irradiation, *RSC Adv.*, **2016**, 6(65), 60291-60307.
[6]. A. K. Adepu, V.Katta, V.Narayanan, Synthesis, characterization, and photocatalytic degradation of Rhodamine B dye under sunlight irradiation of porous titanosilicate (TS)/bismuth vanadate ($BiVO_4$) nanocomposite hybrid catalys, *New J. Chem.*, **2017**, 41(6), 2498-2504.
[7]. T. Soltani, A. Tayyebi, B. K.Lee, Enhanced photoelectrochemical (PEC) and photocatalytic properties of visible-light reduced graphene-oxide/bismuth vanadate, *App Surface Sci.*, **2018**, 448, 465-473.

[8]. M. M.Sajid, N. Amin, N. A.Shad, Y.Javed, Z. Zhang, Hydrothermal fabrication of monoclinic bismuth vanadate (m-$BiVO_4$) nanoparticles for photocatalytic degradation of toxic organic dyes, *Mater. Sci. Eng., B*, **2019**, 242, 83-89.
[9]. R. Chaudhary, S. C. Ameta, R.Ameta, Photocatalytic degradation of azure B under visible light irradiation by reduced graphene oxide–NiS composite, *Macedonian J. Chem. Chem. Eng*., **2019**, 38(1), 107-114.
[10]. Ruchi, A. K. Rai, J. P. Bhatt, R. Ameta, S. C. Ameta, Photocatalytic degradation of azure B by reduced graphene oxide-copper sulphide composite (rGO-CuS): A green approach towards environmental remediation, *J. Applicable Chem.*, **2019**8(2), 794-800.
[11]. A. J. Josephine, C. R. Dhas, R. Venkatesh, D. Arivukarasan, A. J. Christy, S. E. S. Monica, S. Keerthana, Effect of pH on visible-light-driven photocatalytic degradation of facile synthesized bismuth vanadate nanoparticles, *Materials Research Express*, **2020**, 7(1).
[12]. Y. Vyas, P. Chundawat, P. B.Punjabi, C. Ameta, Green and facile synthesis of luminescent CQDs from pomegranate peels and its utilization in the degradation of azure B and amido black 10B by decorating it on CuO nanorods, *Chemistry Select*, **2021**, 6(33), 8566-8580.
[13]. R. Justinabraham, A. Durairaj, S. Ramanathan, J. Wesley Ramachandran, D. Padmanabhan, S. A. Jayam, Novel $VOPO_4$/g-C_3N_4-PMS system for organic pollutant degradation: Assessment of toxicity by Danio rerio, *J. Water Process Eng*., **2021**, 44, doi: 10.1016/j.jwpe.2021.102422.
[14]. R. Banu, N. Salvi, S. Gupta, C. Ameta, R. Ameta, P. B.Punjabi, A facile synthesis of GO/CuO nanocomposite with enhancing photocatalytic activity for the degradation of azure-B dye and its antimicrobial behavior, *Arabian J. Sci. Eng*., **2022**, 47, 365–378.
[15]. Y. Ahmad, S. Ametam, S. Kothari, Photocatalytic degradation of indigo carmine by using tungsten doped bismuth vanadate, *Res. J. Chem. Environ*., **2021**, 25 (7), 86-92.