SOLAR LIGHT INDUCED PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN USING $BiVO_4$ CATALYST

Prafulla Kumar Panda, Debapriya Pradhan* and Suresh Kumar Dash

Department of Chemistry, ITER, Siksha 'O' Anusandhan (Deemed to be University), Bhubaneswar, Odisha 751030, India

Email ID: debapriyapradhan3@gmail.com

ABSTRACT

A visible light active bismuth vanadate ($BiVO_4$) nanoparticle was created using a simple, low-cost, and energy-efficient co-precipitation method.X-ray diffraction and Fourier-transform infrared spectroscopy were used to investigate the crystal structure, phase, and details of chemical bonds in the prepared $BiVO_4$.The optical property of the catalyst, as well as a thorough evaluation of its morphology, was measured using ultraviolet-vis diffuse reflectance spectroscopy and FE-SEM analysis.The elemental composition and purity of the catalyst were determined using EDAX analysis.The degradation of MG under solar light radiation was used to scrutinise the photocatalytic efficiency of the catalyst. Within 75 minutes, $BiVO_4$ demonstrated 95% degradation efficiency. To evaluate the degradation efficiency of the catalyst, various parameters (pH, concentration, dose, and time) are investigated.

Keywords: $BiVO_4$ NPs, malachite green dye, Photocatalytic degradation, electron/hole recombination, solar light irradiation.

DOI Number: 10.48047/NQ.2022.20.20.NQ109154 **NeuroQuantology2022;20(20): 1518-1526**

INTRODUCTION

Hygienic water is required for all forms of life to exist. Environmental protection and remediation are the most pressing issues for humans in the twenty-first century, owing to rapid industrial expansion, depleted water resources, uncontrolled ground water development, environmental pollution, and global warming causing abnormal climatic changes [1]. Various industrial sectors, including textiles, dyeing, and printing, emit huge volumes of synthetic organic colours as effluent.Traditional water purification procedures, such as adsorption, flocculation-sedimentation, ion exchange, biological treatment, and filtration, have been shown to be inadequate and expense, potentially resulting in additional contamination[2-6].In this regard, heterogeneous photo catalysis, with its high oxidation power, low operating temperature, and green-chemistry-related procedures, has gotten a lot of attention in recent decades, promising a tantalising path to meeting global challenges related to the environment, energy, and sustainability thanks to abundant sunlight resources [7].

Various studies have been conducted on semiconductors such as TiO_2, ZnO, and others that lack efficiency due to fast charge recombination, reduced absorption, greater band gap, and very low reusability.Among the various nano materials, transition metal oxide are found to attract considerable attention for photocatalytic degradation due to the high stability under U.V light , low cost , high resistivity towards corrosion & their relative abundances.The major drawback in using these semiconductors is their large band gap (> 3 e.v) electron hole recombination which reduce their photocatalytic efficiency , moreover they absorb around 2% to 3% of sun's spectrum & active in U.V range[8]. An effective photocatalyst requires large surface area, narrow band gap, fast charge carrier transformations & ability to absorb solar light under visible region .$BiVO_4$ has gained significant attention among the several investigated oxides with activity under visible light irradiation. This oxide has piqued the interest of researchers owing to its potential uses in a variety of technical domains, since it possesses intriguing features such as Ferro elasticity [7], ionic conductivity [8,] and

eISSN 1303-5150

photochromism[9-10].$BiVO_4$ is an n-type semiconductor with excellent chemical and photo stability properties.

Furthermore, its flexible optical and electrical features, as well as a band gap of 2.4 eV, make it an attractive choice for solar energy harvesting[11].For the fabrication of $BiVO_4$ photocatalyst, many techniques have been described, including solid-state reaction, sonochemical, organic decomposition, precipitation, hydrothermal, sol-gel, and others[12].Kudo et al.[13] used an aqueous technique to synthesise highly crystalline monoclinic and tetragonal $BiVO_4$ by reacting the layered potassium vanadates KV_3O_8 and $K_3V_5O_{14}$ with $Bi(NO_3)_3$ for three days at 20 C. Guo et al.[14] investigated the photocatalytic degradation of methylene blue using a simple surfactant-free $BiVO_4$ catalyst. Sarkar et al. [15]used a precursor-mediated growth approach to create a spherical-shaped $BiVO_4$ photocatalyst and examined the photocatalytic degradation of Rhodamine B under visible light irradiation. Dong et al.[16] produced sponge-like $BiVO_4$ films with polystyrene (PS) as a pore-forming material and F-doped SnO_2 (FTO) glass as a substrate and demonstrated photoelectrocatalytic phenol degradation under visible light irradiation. Deebasree et al.[17] used a sol-gel-assisted ultra sonication approach to create a $BiVO_4$ photocatalyst and evaluated the decolourization of methylene blue under visible light irradiation. Chen et al. [18]used a microwave hydrothermal technique to create a $BiVO_4$ photocatalyst and examined the total water-splitting mechanism.In this study, a simple Co-precipitation method was used to synthesise $BiVO_4$ photocatalyst, which was then used to degrade Malachite green (MG) under solar light. The effects of various experimental parameters on the photo degradation of MG were investigated, including initial dye concentration, pH, amount of catalyst loading, and agitation time.

MATERIALS AND METHODS

Materials

For preparation of $BiVO_4Bi(NO_3)_35H_2O$ (Aldrich, 99.99%), NH_4VO_3 (Aldrich, 99.99%),Concentrated HNO_3 solution and NaOH (Merck 99.99% purity) chemicals were used.

Preparation of $BiVO_4$

BiVO4 was synthesised using a simple co-precipitation method. In a 1:1 molar ratio, $Bi(NO_3)_3$ $5H_2O$ and NH_4VO_3 were dissolved in 1M HNO_3 solution. After observing a reddish yellow colour, a 1M NaOH solution was added drop by drop to raise the pH value to 10 while vigorously stirring. The resulting pale yellow colour solution was centrifuged and washed several times with distilled water. The filtrate was then dried in an oven before being calcined in a muffle furnace at 500^0c degrees Celsius for 3 hours. The yellow-colored sample was then finely powdered and collected.

Sample Characterisation

Powder Xray diffraction was used to characterise the structure using a PAN analytical Diffractometer with Cu-K radiation (PW 1830, Philips, Japan) and CuKα radiation, equipped with a Vantec high speed detector. The samples' X-ray diffraction data were collected in the 2θ range of 10-80°.The morphology of the samples was examined using field emission microscope (ZEISS SUPRA 55).A Perkin Elmer Spectrum version 10.4.3 FTIR spectrophotometer was used to determine the bond vibrational frequencies of the components, while a Perkin Elmer Lamda365 spectrophotometer was used to acquire UV-DRS spectra (to investigate the materials' optical properties).Spectrophometer (Systronics 2202) was used for study of photocatalytic degradation.

Photocatalytic Experiment

The photocatalytic efficiency of $BiVO_4$ against MG dye was investigated. A stock solution with a concentration of 100 ppm was prepared for photocatalytic degradation. The photo catalyst's efficiency was evaluated by varying parameters such as pH (3,5,7,9,11), concentration (20,40,60,80ppm), catalyst dose (0,20,30,40mg), and irradiation time (15,30,45,60,75min). Before exposing the photocatalyst-enhanced dye solution to sunlight, it was kept in the dark for 30 minutes to achieve adsorption-desorption equilibrium.

eISSN 1303-5150

RESULTS AND DISCUSSION

Materials Characterisation

XRD Analysis

The phase formation of crystalline solids is identified using X-ray diffraction (XRD) analysis which is shown in Figure.1 depicts the XRD patterns of $BiVO_4$.The observed diffraction peaks at 2θ values of 18.690, 28.918, 30.54, 34.5, 35.2, 39.8, 42.37, 45.7, 46.5, 46.9, 49.9, 53.2, 55.7, 58.2, 59.0, 63.2, 65.5, 69.7, 74.3, 75.5, and 76.4 correspond to (001), (013), (004), (200), (020), (211), (015), (123), (204), (024), (2 All of the peaks are associated with the monoclinic phase of $BiVO_4$ (JCPDS No. 83–1699). Using the Debye-Scherrer formula, the average crystallite size of the $BiVO_4$ NPs was calculated to be 34.8 nm.

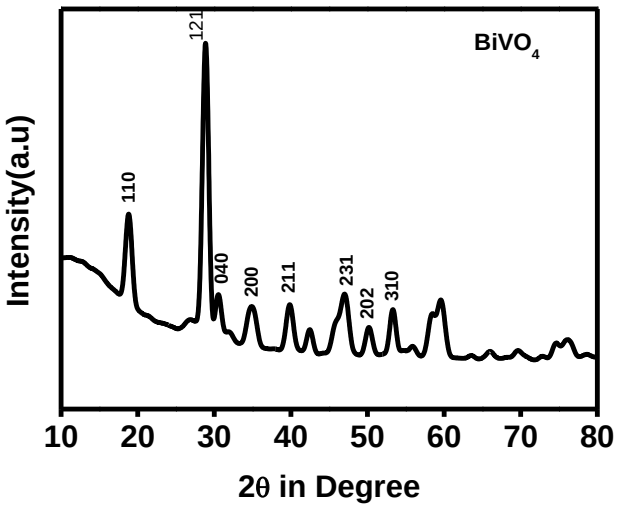


Figure.1. XRD pattern of $BiVO_4$

All of the diffraction peaks on the product's X-ray diffraction pattern belonged to $BiVO_4$, implying that the synthesised product was of high purity. The XRD spectrum of the product shows sharp diffraction peaks, indicating that the synthesised $BiVO_4$ is crystalline.[19]

FTIR Analysis

FT-IR spectroscopy is an important analytical technique for determining sample structure and identifying chemical bonds in a molecule. The FT-IR spectrum was captured in the 500-4000 cm^{-1} wave number range. As shown in Figure.2 the asymmetric and symmetric stretching bands of the VO_4 unit were attributed to the main absorption bands observed at 725.32 and 830.24 cm^{-1}. The asymmetric stretching and symmetric stretching vibrations of the V-O bond are characterised by the absorption band at 700-900 cm^{-1}. All of the spectra show a weak stretching vibration of the C-O bond derived band at 1383 cm^{-1} and a bending vibration of absorbed H_2O molecules at 1650 cm^{-1}, which could be due to atmospheric CO_2 absorption during the experiment[20].

eISSN 1303-5150

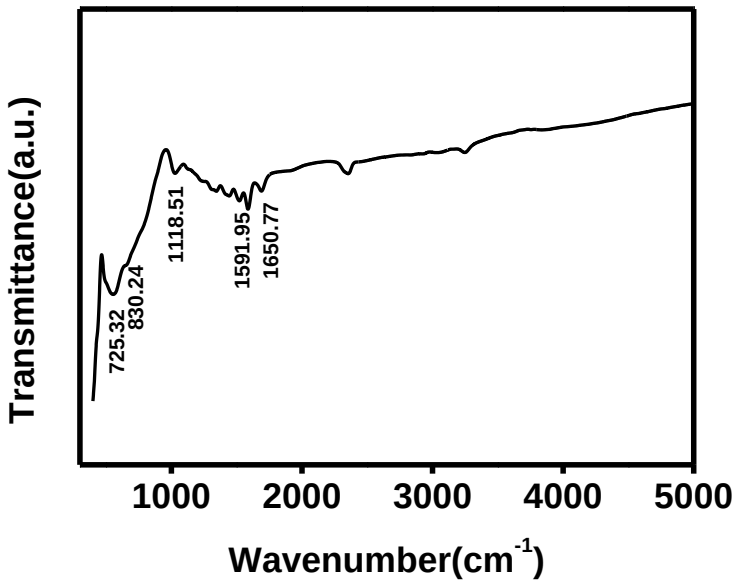


Fig.2 FTIR graph of $BiVO_4$

Scanning Electron Microscopy (SEM)

Under different magnifications, field emission scanning electron microscopy (FESEM) is used to examine the morphology and elemental composition of $BiVO_4$ which is shown in Figure.3 .The as-prepared $BiVO_4$ exemplifies nanoparticle aggregation with a large number of irregular smaller crystals. The EDS analysis of $BiVO_4$ is shown in Figure.4 that confirmed the presence of Bi, O and V in the NPs. The weight and atomic wt. percentage of Bi, O, V are found to be 67.7, 16.3 and15.9% and 19.6, 61.6 and18.8% respectively. The element analytical results agreed well with those previously reported[21].The absence of other elements proven the purity of $BiVO_4$ NPs.

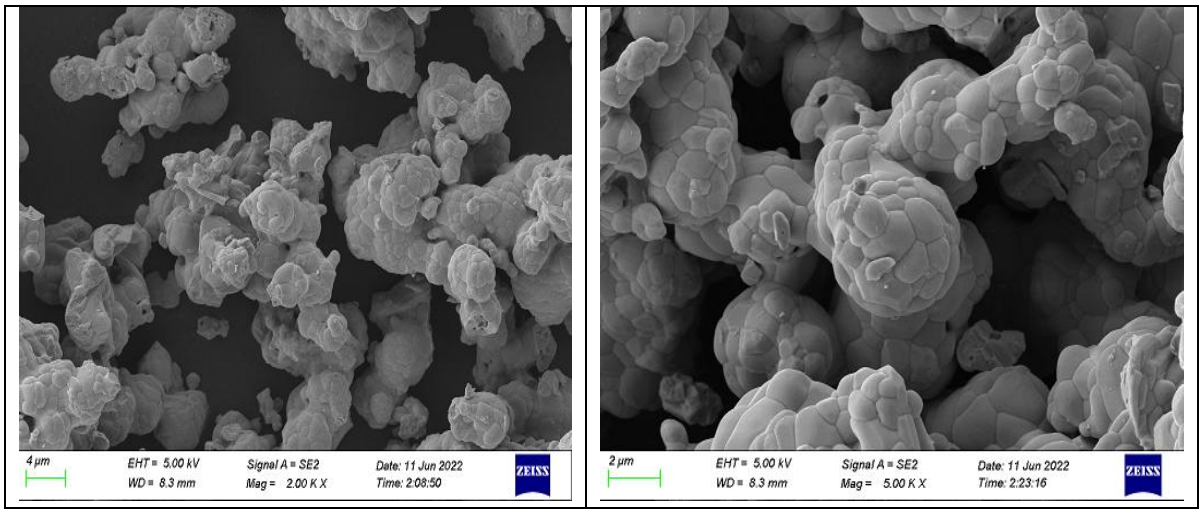
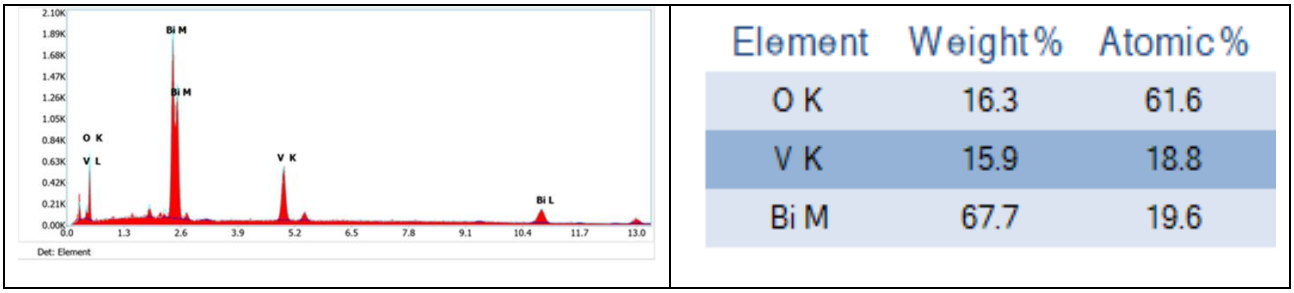


Figure.3 FESEM image of $BiVO_4$



Element	Weight%	Atomic%
O K	16.3	61.6
V K	15.9	18.8
Bi M	67.7	19.6

Figure.4. EDS analysis of $BiVO_4$

eISSN 1303-5150

UV-DRS Analysis

UV-DRS was used to evaluate the photon absorption abilities of the prepared $BiVO_4$.The absorption spectrum of $BiVO_4$ is shown in Figure 5, and the corresponding band gap energy (see Figure 5 inset) was calculated using the equation 1.

$$\alpha hv = A\,(hv - Eg)^{1/2} \qquad (1)$$

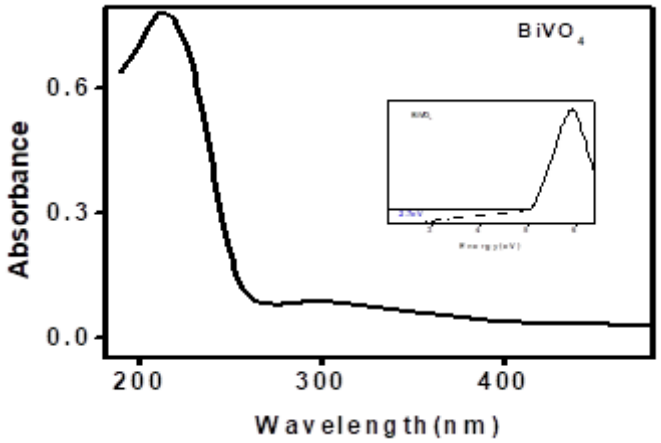


Figure.5. UV-DRS analysis and Band gap energy determination of $BiVO_4$

where α, v and h represents the absorption coefficient, frequency of the light and Planck's constant, respectively. The Tauc plot $(\alpha hv)^2$ versus photon energy (hv) curve can be used to calculate the band gap energy value. $BiVO_4$ band gap energy was calculated to be 2.6 eV, confirming its potential as a visible light driven photocatalyst. The UV-Vis absorption spectrum of $BiVO_4$ demonstrates strong optical absorption in the 200-600 nm wavelength range, indicating that $BiVO_4$ can efficiently absorb visible light and acts as a solar energy driven active photocatalyst for dye degradation. The semiconducting electronic structure is well understood to play an important role in photocatalytic activity[22].

Effect of Various parameters on Photocatalytic Degradation

EFFECT OF PH

The effect of pH on the photo degradation efficiency of MG was investigated under solar irradiation at pH 3.0, 5.0,7.0, 9.0, and 11.0 in the presence of a fixed amount of $BiVO_4$ (20mg). The natural pH of the MG solution was 7, and $BiVO_4$ demonstrated photocatalytic degradation efficiency of 65% in 90 minutes. The pH of the MG solution was adjusted using diluted HCL and NaOH solution to investigate the effect of pH on degradation efficiency. Figure 6 depicts the photo catalyst's photo degradation efficiency at various pH levels. As a result, decreasing the pH results in a simultaneous decrease in degradation efficiency, with 11 exhibiting the highest efficiency (88%). The degradation efficiency differed depending on the pH. The less degradation occurs in acidic pH due to electrostatic repulsion because the dye and catalyst surface are both positive. When the pH is raised, there is a strong attraction between the surface of the catalyst and the dye molecule[23-24] .

eISSN 1303-5150

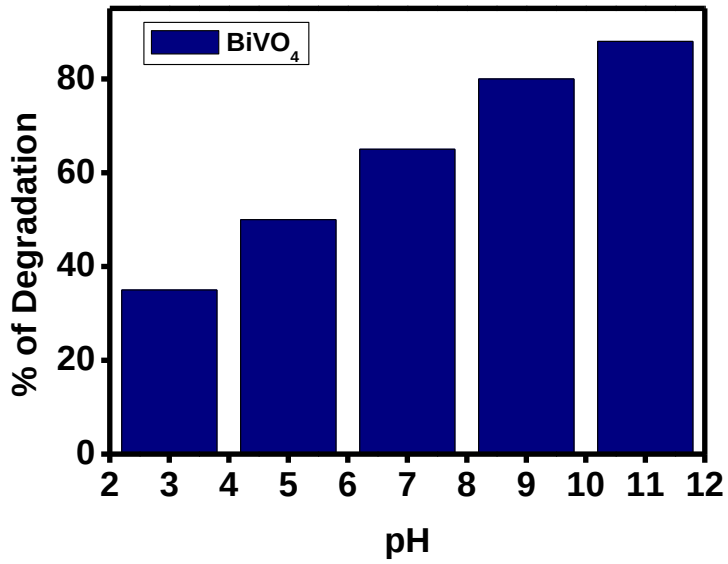


Figure.6. Degradation of MG by $BiVO_4$ with changing pH values.

Effect of Concentration

The effect of dye concentration(20,40,60,80 ppm) on degradation efficiency was investigated by varying the MG concentration while keeping the catalyst loading and solution pH constant which is shown in figure7.From figure 7 it is shown that $BiVO_4$ gave maximum degradation efficiency of 92% on 20 ppm MG solution.The decrease in degradation efficiency with increasing dye concentration is due to an increase in the number of dye molecules, which restrict the incident of light on the catalyst's surface, resulting in the formation of active radical species[25].

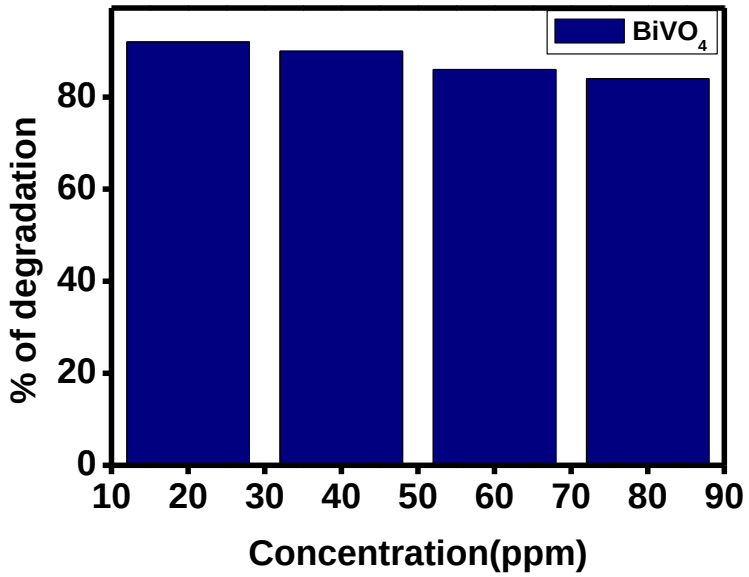


Figure.7. Degradation of MG by $BiVO_4$ with changing initial concentration

Effect of Catalyst Dose

The impact of the effect of $BiVO_4$dose on photo degradation efficiency was examined by varying the amount of catalyst within the range 10-40 mg while keeping pH and concentration constant. From figure 8 it is shown that the maximum degradation of 92% was achieved by 10 mg catalyst dose and there is

eISSN 1303-5150

decrease in the degradation% with increasing the catalyst dose.However, at a higher catalyst loading there is turbidity in suspensions and light penetration is restricted. The photo degradation rate of MB decreased as a result of the reduced light penetration.

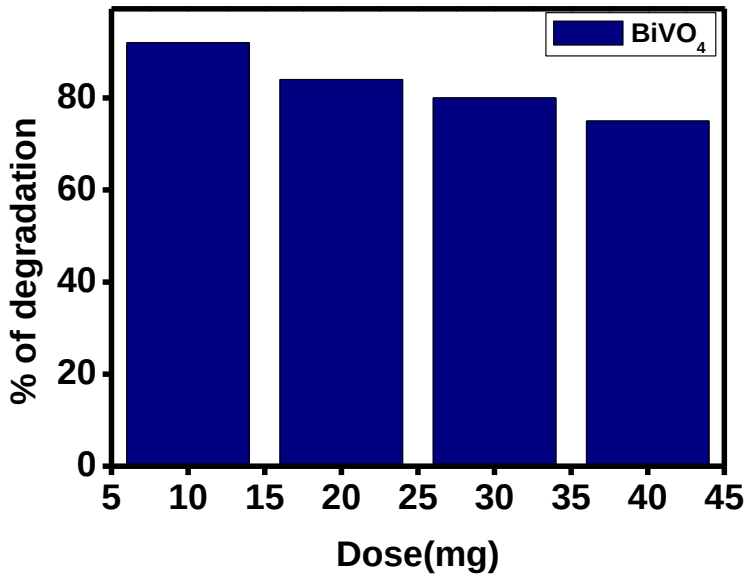


Figure.8. Degradation of MG by $BiVO_4$ with changing Catalyst dose(mg)

Effect of Time

To investigate the effect of time on the degradation of MG, different ageing times (15,30,45,60,75 min) were used. The degradation percentage increased with time, reaching a peak of 95% at 75 minutes. The degradation vs time and time variant curve is shown in figure 9.Because of the decrease in dye concentration, there is a minimal difference in degradation percentage between times 60 and 75 minutes.

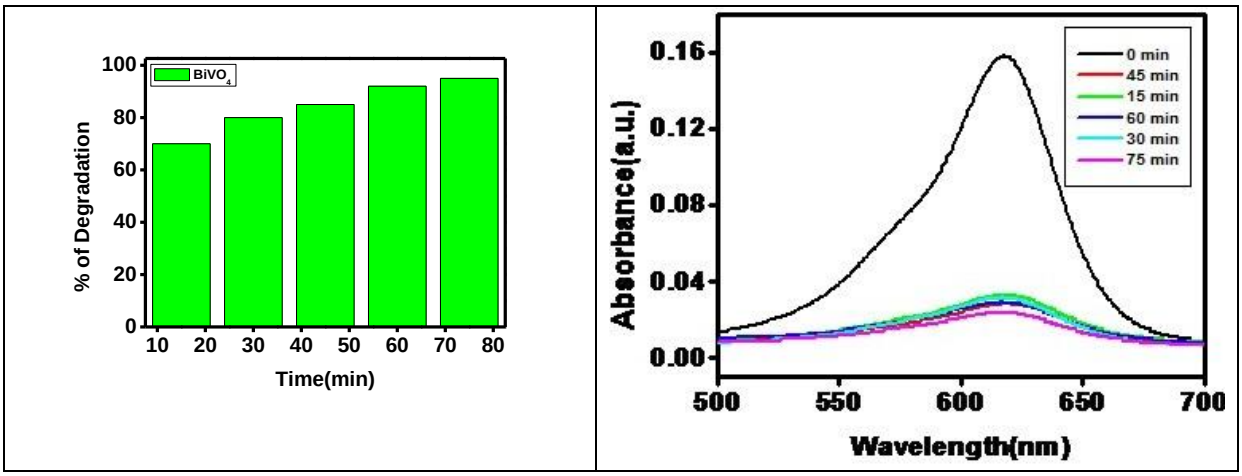


Figure.9. Degradation of MG by $BiVO_4$ with changing time.

Degradation Mechanism of MG

In a photocatalytic reaction, semiconductor materials absorb photons (light energy) and produce excess electrons (e^-) and holes (h^+) in the conduction band (CB) and valence band (VB), respectively. •OH radicals are formed when the h^+ in the VB reacts with H_2O. Thus, the generated radicals and e^- in the CB are involved in production of superoxide radical which causes the MG degradation, and degradation products are produced (CO_2, H_2O, etc.)[26] as shown in figure 10.

eISSN 1303-5150

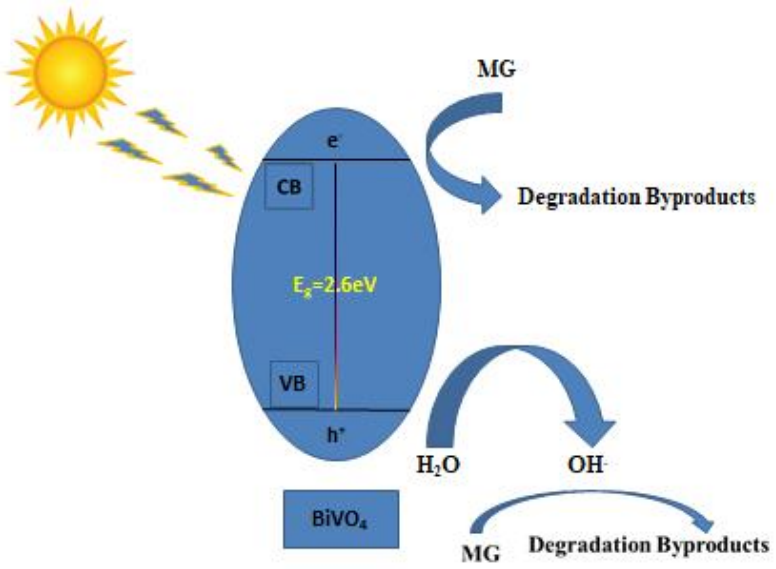


Figure. 10. Possible mechanism for Photocatalytic degradation of MG by $BiVO_4$.

CONCLUSION

$BiVO_4$ was developed using the coprecipitation method and characterised using standard techniques (XRD,FTIR,FE-SEM,UV-DRS). The photocatalytic activity of the material was tested by photo degrading Malachite Green in aqueous solution. The material showed a superior capacity to decolorize the dye solution. The photocatalytic efficiency of the photocatalyst was studied by varying parameters like pH, initial concentration, catalyst dose and time. Within 75 minutes, $BiVO_4$ exhibited 95% photocatalytic degradation towards the MG dye at pH ~11 with 10 mg catalytic dose. The photo-degradation mechanism of MG by $BiVO_4$ revealed the involvement of hydroxide and superoxide radicals in dye degradation

ACKNOWLEDGMENTS

The authors are grateful to the Department of chemistry, ITER, Siksha 'O' Anusandhan (Deemed To Be University), Bhubaneswar, for providing the help in infra structure, experimental work and in providing chemicals.

REFERENCES

1 E. Baldev, D. MubarakAli, A. Ilavarasi, D. Pandiaraj, K. A. S. S. Ishack and N. Thajuddin, Colloids Surf., B., 105, 207–214 (2013).

2 N.M. Mubarak, J.N. Sahu, E.C. Abdullah, N.S. Jayakumar, Sep. Purif. Rev., 43, 311–338(2014)

3 L. Mohanty, D.S. Pattanayak, R. Singhal, D. Pradhan, S.K. Dash, Inorg. Chem.Comm., 138, 109286(2022)

4 D. Pradhan, P.K. Panda, S.K. Dash, Design Engineering, 8, 167-174(2021)

5 D. Pradhan, P.K. Panda, A. Mishra, E. Falletta, S.K. Dash, Env. Qual. Mgmt, 1-16(2022), Article in Press.

6 L. Mohanty, D.S. Pattanayak, S.K. Dash, J. Indian Chem. Soc.,98 (11), 100180(2021).

7 Y. Sun, B. Qu, Q. Liu, S. Gao, Z. Yan, W. Yan, B. Pan, S. Wei, Y. Xie, Nanoscale 4, 3761–3767(2012).

8 I. Khan, K. Saeed and I. Khan, Arabian J. Chem., 12, 908–931 (2019).

9 M. Long, W. Cai, J. Cai, B. Zhou, X. Chai, Y. Wu, J. Phys. Chem. B., 110, 20211–20216(2006)

10 H. Jiang, H. Endo, H. Natori, M. Nagai, K. Kobayashi, Mater. Res. Bull., 44,700–7006 (2009).

11 Y. Hu, J. Fan, C. Pu, H. Li, E. Liu, X. Hu, J. Photochem. Photobiol. A., 337, 172-183(2017).

12 Sun, J.X.; Chen, G.; Wu, J.Z.; Dong, H.J.; Xiong, G.H.,Appl. Catal. B Environ.,132–133, 304–314 (2013).

13 Kudo, A.; Omori, K.; Kato, H.,J. Am. Chem. Soc., 121, 11459–11467(1999).

eISSN 1303-5150

14 Guo, M.; He, Q.; Wang, A.; Wang, W.; Fu, Z.,Crystals., 6, 81 (2016).
15 Sarkar, S.; Chattopadhyay, K.K.,Phys. E.,58, 52–58 (2014).
16 Dong, L.; Zhang, X.; Dong, X.; Zhang, X.; Ma, C.; Ma, H.; Xue, M.; Shi, F.,J. Colloid Interface Sci., 393, 126–129(2013).
17 Deebasree, J.P.; Maheskumar, V.; Vidhya, B.,Ultrason. Sonochem.,45, 123–132 (2018).
18 Chen, S.H.; Jiang, Y.S.; Lin, H.Y.,ACS Omega.,5, 8927–8933 (2020).
19 M. Arumugam and M. Y. Choi.,Bull. Korean Chem. Soc.,1229-5949 (2020).
20 P.Pookmanee, S.Kojinok , R.Puntharod , S.Sangsrichan& S.Phanichphant.,Ferroelectrics., 456:1, 45-54(2013).
21 Y. Shen, M. Huang, Y. Huang, J. Alloy. Compd., 496, 287–292 (2010).
22 Liu, W.,J. Hazard Mater., 181, 1102–1108 (2010).
23 V. K. Gupta, R. Jain, A. Mittal, M. Mathur, S. Sikarwar, J. Colloid Interface Sci., 309, 464(2007).
24 A. Franco, M. C. Neves, M. M. RibeiroCarrott, M. H. Mendon, M. I. Pereira, O. C. Monteiro, J. Hazard. Mater., 161, 545(2009).
25 S. K. Kansal, M. Singh, D. Sud, J. Hazard. Mater., 153, 412 (2008).
26 Y. Yan,S.Sun,Y.Song,X.Yan, Journal of Hazardous Materials., 250–251, 106–114(2013).

eISSN 1303-5150