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Bismuth vanadate, an agile photocatalyst for the degradation of malachite green dye

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Abstract

Visible light-active bismuth vanadate (BiVO_4) nanoflakes were successfully synthesized by co-precipitation technique. As prepared BiVO_4 was characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Monoclinic forms of BiVO_4 having average size of 37.76 nm were obtained. V-O, Bi-O and VO_4^{3-} groups were observed by FTIR. The elemental mapping image showed 49.25% Bi, 9.69% V and 41.06% O which were found to be distributed homogeneously. As prepared BiVO_4 was applied in the photocatalytic degradation of malachite green dye (MG). The maximum degradation was found to be 72.72% in 120 min using 500 W halogen lamp irradiation which may be due to the synergistic effect of lamp light and a stream of air. The optimum catalyst dose was found to be 0.1 g per 100 mL of 10 ppm dye concentration with the initial pH being 6.

Keywords: Photocatalyst, co-precipitation, nanoparticles, photodegradation, irradiation

Introduction

In recent years, semiconductor photocatalysis has become a facile method for the removal of organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment, industrial and health applications [1]. TiO_2 , the most common photocatalyst being non-toxic, non-poisonous, chemically inert and biostable, has been preferred material for environment pollution remediation for a long time [1]. However, the use of TiO_2 is limited because it has got wide band gap energy of 3.2 eV and only responds to UV light which is about 3-4% of the solar spectrum [2].

In these days, attention has been given to visible-light driven photocatalysts such as CdS [3], ZnS [4], Ag_3PO_4 [5], Bi_2O_3 [6], BiVO_4 [7-9], Bi_2WO_6 [10], having narrow band gap (E_g) than TiO_2 to efficiently utilize solar energy and indoor light [11]. BiVO_4 which has band gap (E_g) of 2.4 eV, is one of the visible light active photocatalysts that has been used in photocatalytic degradation of organic compounds in waste water as well as for O_2 evolution under sunlight irradiation [12]. It has also been used in degradation of pharmaceutical wastes, antibiotics and bacteria [13, 14]. In this study, it has been used for photocatalytic degradation of malachite green dye (MG).

Malachite green (MG) is a triphenylmethane dye which is also known as aniline green, basic green 4, diamond green B, victoria green B etc [15]. It is a cationic dye with molecular formula $\text{C}_{23}\text{H}_{25}\text{N}_2\text{Cl}$ available as chloride salt. It is also available in oxalate, acetate forms [16]. The color of the crystals is normally dark green with metallic luster while the aqueous solutions appear blue-green. MG has been used in dyeing silk, leather and paper as well. It is also used as a biological stain for microscopic analysis of cell biology and tissue samples. In recent decades, it has been widely used as antibacterial, antiseptic, fungicidal, algicidal and parasiticidal in aquaculture [17-19].

Despite its uses, it is now regarded as cytotoxic, irritant, genotoxic, mutagenic and carcinogenic substance. This toxicity is mainly related to the leuco forms of MG [17-19] such as MG leucocarinol and leuco malachite green (LMG) as shown in Fig. 1

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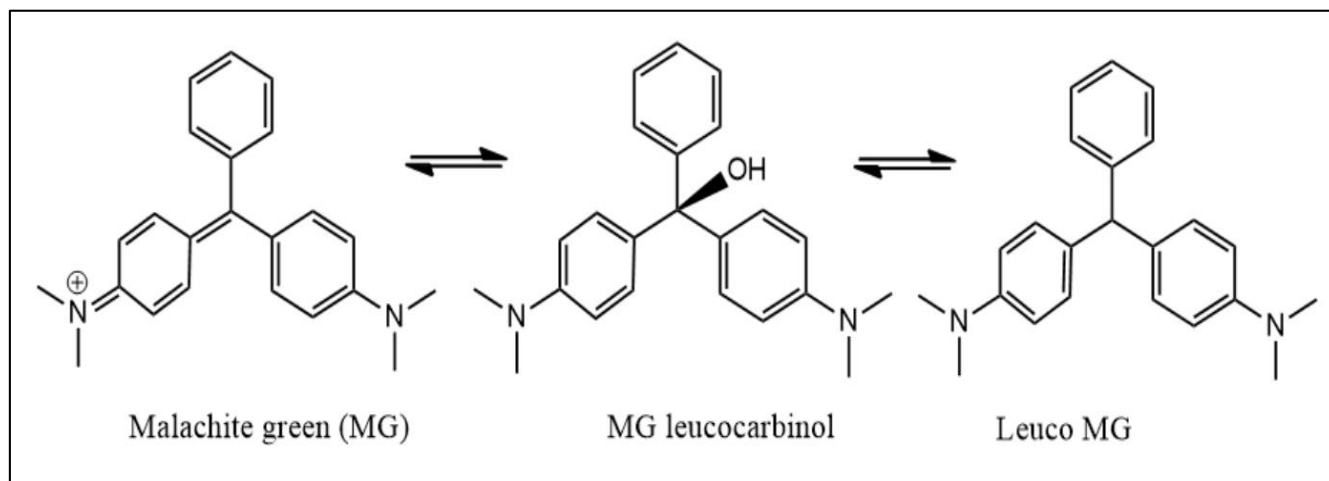


Fig 1: Conversions between MG (left), MG leucocarbiniol (middle), and LMG (right).

In aqueous solutions, these three forms are interconvertible to each other at equilibrium pKa being 6.9. Hence, it can reside as reduced form as leucomalachite green in fish serum, liver, kidney, muscles, other tissues and eggs for longer period. It may be introduced into human body through intake of such fishes [18]. Consequently, it is not permitted in the USA and EU. Nevertheless, despite the large amount of data on its toxic effects, it is still widely used for fishery disinfection because of its low price and high efficiency [17-19].

Various methods such as hydrolysis, adsorption, volatilization, and biodegradation have been employed to remove or degrade this toxic dye from water bodies [17]. However, photocatalysis has emerged as an effective way for this purpose due to its high efficiency and low-cost as well as recyclability of the photocatalyst. MG has been photodegraded under natural conditions under sunlight [17] as well as in the presence of photocatalysts such as BiWO₆ [20], TiO₂ nanotubes [21], bimetal cerium-cadmium oxide [22], naked niobium oxide (Nb₂O₅) [23], as well as several bismuth oxides as Bi₂O₃ and its doped and composite forms [6]. Here, MG has been tried for photodegradation in presence of visible light of 500W halogen lamp using BiVO₄ as photocatalyst.

Materials and Method

AR grade bismuth nitrate was purchased from Merck Specialties Private Limited, Mumbai and LR grade ammonium vanadate (NH₄VO₃) from S.D. Fine Chem. Limited, Mumbai and were used without further purification. Distilled water has been used throughout the experiments. The Bruker D2 Phaser was used to record the X-ray diffraction pattern to study the phase state. A monochromatized Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation at energy resolution of 180 eV was used. The surface morphology of the as-prepared BiVO₄ particles was obtained using mini SEM (Nanoeye, Co.) applying current of 120 mA and voltage of 30 kV. Elemental analysis of the material was performed by using a UNICAM PU 700 spectrometer. The FTIR spectra were obtained by using Shimadzu IRAffinity-1 and were recorded from 4000-400 cm⁻¹ wavenumber. Visible spectrophotometer (2306, AB1211010, Electronics India) was used to measure pH of solutions.

Preparation of BiVO₄

BiVO₄ was prepared by facile co-precipitation method [9]. First of all, bismuth nitrate solution was prepared by dissolving 1.498 g AR grade Bi(NO₃)₃·5H₂O in 100 mL (4M) HNO₃ solution at 70 °C. It was added dropwisely with

continuous stirring condition to ammonium vanadate solution prepared by dissolving 0.362 g NH₄VO₃ in 100 mL (2M) NH₄OH solution. After proper mixing, the solution pH was adjusted to 9 using (5M) NaOH solution. Then a yellow suspension was obtained, and the solvent was evaporated slowly at 70 °C. The dried material was then ground to fine powder. Thus, BiVO₄ was prepared.

Determination of working pH

The 100 mL of 10 ppm MG solutions prepared in different pH (4-8), were kept in dark for 180 min and absorbance was monitored at 617 nm using visible spectrophotometer (2306, AB1211010, Electronics India) at 30 min interval of time.

Photocatalytic activity

The photocatalytic activity of as-prepared BiVO₄ in visible light was studied by degrading malachite green dye (MG) at ambient temperature. A low-cost light simulator was fabricated in which a 500 W halogen lamp was used as the irradiation source and placed 13.6 inches above the reaction system. The temperature of the reaction system was maintained at 20-25 °C. For the photocatalytic test, 100 mL of (10 ppm) dye solution was taken in 250 mL beaker. Then, 0.1 g of as-prepared BiVO₄ photocatalyst was added and stirred for 15 min for adsorption-desorption process. After that, the solution containing beaker was kept in dark for 30 min for adsorption-desorption equilibrium. Before irradiation, absorbance of solution was measured at zero minute. Then irradiation was started. After irradiation, absorbance was measured at every 30 min of time interval at 617 nm using visible spectrophotometer. Each withdrawn solution was centrifuged at 4000 rpm for 20 min and centrifugation was repeated one more time. Air supply was provided to the reaction system as per needed using air pump (Silver Lake, model no. SL-2800). Prior to photocatalysis, a number of observations were made in blank MG solution.

Results and discussion

Phase Analysis by X-ray Diffraction (XRD)

The composition and phase structure of as-prepared BiVO₄ was investigated using XRD measurement. Fig. 2 shows the XRD pattern of as-prepared BiVO₄. Characteristic peaks are observed and were indexed to JCPDS card no. 14-0688.

The major peaks are seen at 30° (121), 33° (040), 40° (211), 49° (116) of 2 θ degrees. It revealed that as-prepared

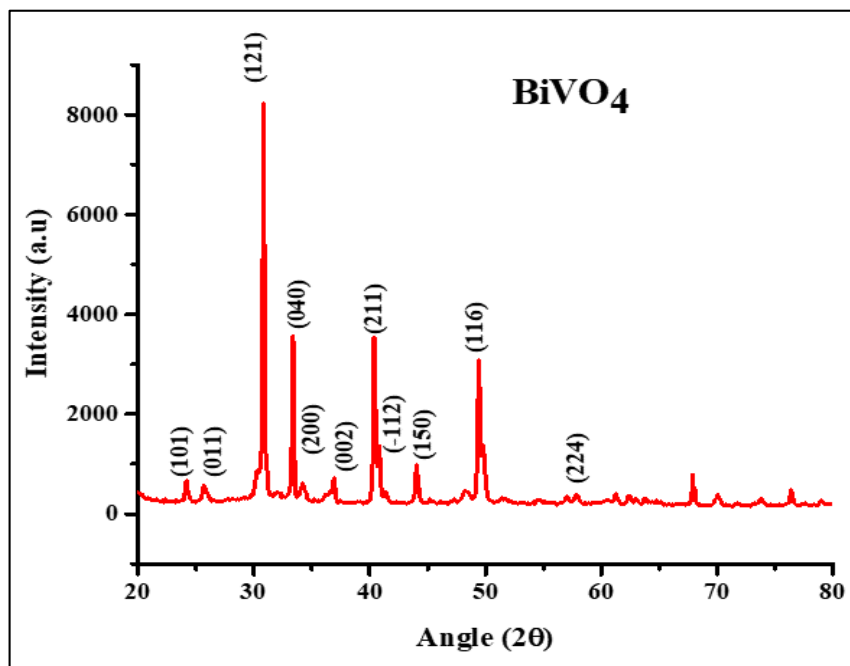


Fig 2: XRD pattern of prepared BiVO₄.

The major peaks are seen at 30° (121), 33° (040), 40° (211), 49° (116) of 2θ degrees. It revealed that as-prepared material is monoclinic crystalline in nature. It is in agreement with literature values [24, 25].

Similarly, the average crystallite size of the material was also calculated using Scherrer's equation (1)

$$D = \frac{K\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

Where K (0.9) is shape factor for spherical particles, λ is wavelength of incident radiation, β is the line width at half-maximum height, θ is Bragg's angle and D is the crystallite size. The crystallite size of the most intense peak was calculated from Scherrer's equation and was found to be 47.22 nm. However, the average crystallite size was found to be 37.76 nm.

Functional Group Analysis by Fourier Transform Infrared Spectroscopy (FTIR)

To identify the functional groups in the as-prepared BiVO₄ sample, FTIR spectra were obtained. Fig. 3 shows the FTIR spectra of as-prepared BiVO₄. A clear band at 833 cm⁻¹ could be seen which is allocated to the symmetric V-O stretch. The band at 669 cm⁻¹ is assigned to the asymmetric stretch of the V-O bonds and that at 681 cm⁻¹ is related to VO₄³⁻. Likewise, the band at 476 cm⁻¹ is assigned to the Bi-O bond stretch. Similarly, the bands 2326 cm⁻¹ and 2348 cm⁻¹ corresponds to the atmospheric CO₂ stretch. The major band observed at 1380 cm⁻¹ is assigned to nitrate from the nitric acid and Bi(NO₃)₃ which was used during preparation. These results are also in agreement with previously reported literatures [24, 26].

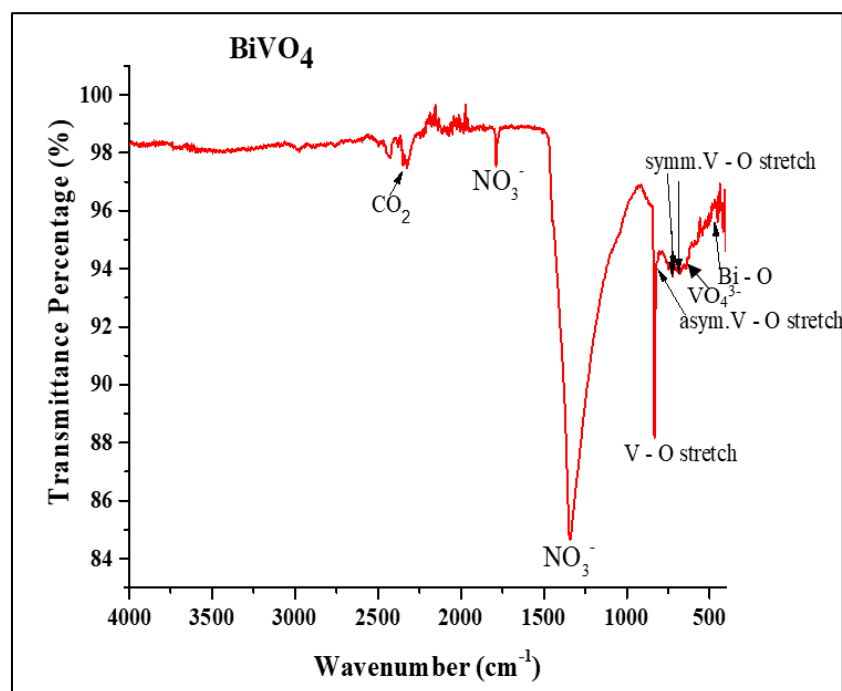


Fig 3: FTIR spectra of as-prepared BiVO₄.

Analysis of morphology based on SEM

Surface morphology of the material and its particle size were studied by scanning electron microscopy.

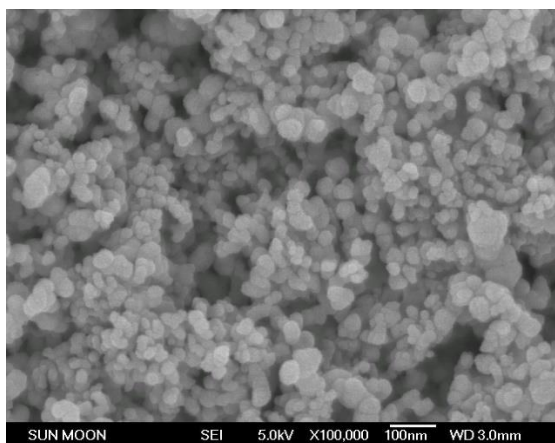


Fig 4: SEM image of prepared BiVO₄.

The SEM image as shown in Fig. 4 shows nanoflakes like particles of various sizes ranging from 20 – 40 nm. The surface of the nanoflakes seems to be smooth and have many microstructures on them. These flakes-like structures are formed by agglomeration of primary structures of smaller dimensions. Such smaller particles formed in basic pH as reported in earlier reports [8, 25].

On the basis of these literatures [8, 25], it was discussed that a significant effect of pH could be seen on the formation of size of particle. If solution pH was low, the concentration of H⁺ was high enough to restrain the hydrolysis of Bi(NO₃)₃ to BiONO₃. Thus, the high concentration of free Bi³⁺ in the reaction system which resulted in the formation of BiVO₄ with large particle size due to its rapid crystal growth. On the other hand, when pH values increased to basic range, relatively lesser amount of free Bi³⁺ existed in the reaction system leading to smaller BiVO₄ nanoparticles which may be due to the fast nucleation and comparatively slow crystal growth rate. Hence, if solution pH was basic and higher sintering temperature was applied, the particles might coalesce and form small flakes like structures.

Elemental analysis by Energy dispersive spectroscopy and Elemental Mapping

The elemental analyses were carried out by energy dispersive spectroscopy (EDS). The EDS spectra was shown in Fig. 5. It

shows that the prepared BiVO₄ consists of Bi, V and O only. The chemical composition shows characteristic X-ray energy level of BiVO₄ materials: bismuth M_α = 1.5 keV, 3,25 keV, 9.5 keV, 11.6 keV, 12 keV and 15.2 keV; vanadium K_α = 0.5 and 5.0 keV and oxygen K_α = 0.5 keV. No other elements were found. The elemental composition is tabulated in Table 1 indicating nearly 50% bismuth, approximately 10% vanadium and 41% oxygen in as prepared BiVO₄.

Table 1: EDS analysis of BiVO₄

Element	Wt%
O	41.06
V	9.69
Bi	49.25

Similarly, EDS layered image of BiVO₄ was also recorded which is shown in Fig. 5(a). It clearly shows the homogeneous distribution of elements throughout the compound. Fig. 5(b) is the separate elemental mapping of each element namely Bi, V and O where one can observe a clear mapping of Bi, V and O respectively.

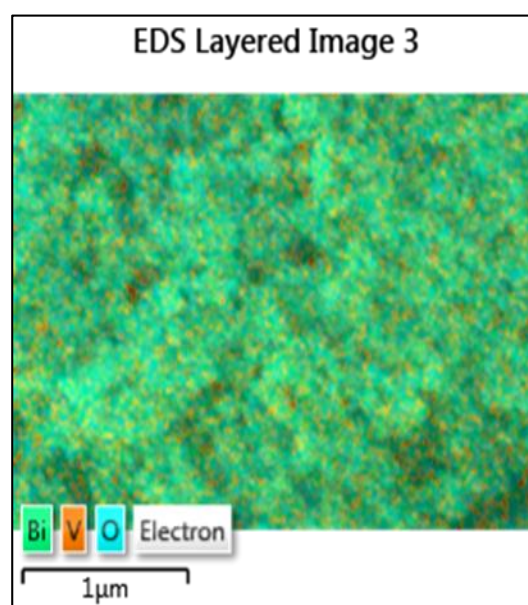


Fig 5(a): EDS layered image of BiVO₄.

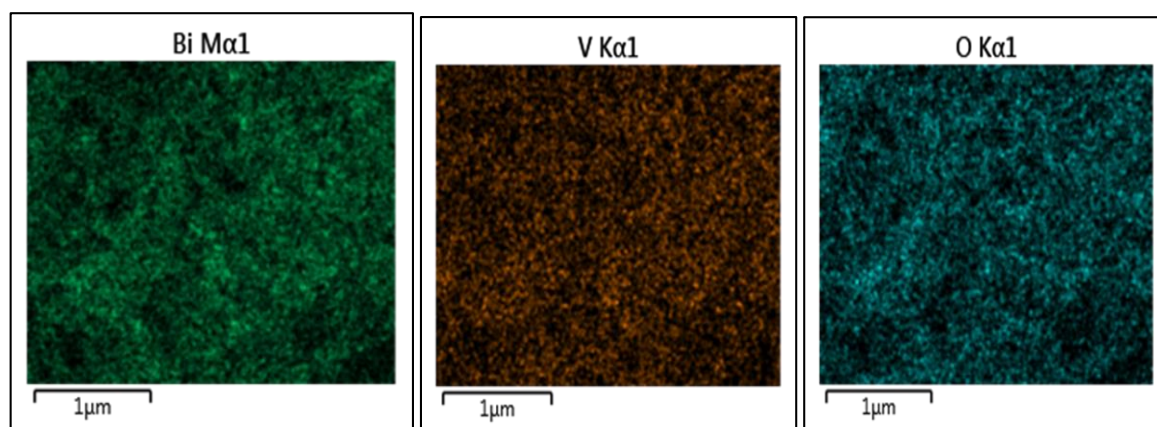


Fig 5(b): Separate Elemental Mapping of Bi, V and O.

Determination of working pH to study the MG degradation

Fig. 6 shows the decolorization of MG at different initial pH carried out in dark in absence of photocatalyst.

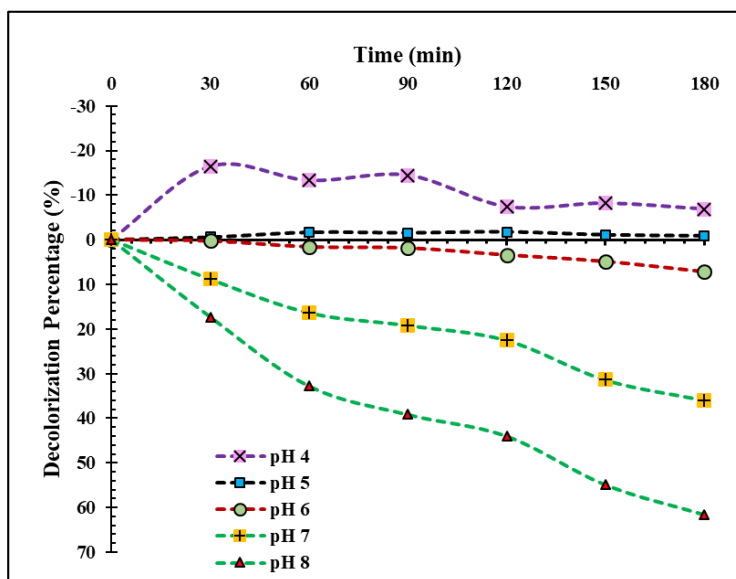


Fig 6: Self-decolorization of MG in different pH.

Fig. 6 shows the curves of decolorization of MG in different pH. At pH 4 and 5, the color intensity increased with time, hence there is no decolorization which might be due to the presence of H^+ ions that inhibit as well as reverse the attack of hydroxide ion (OH^-) on MG molecule to form MG leucocarinol. Hence, all the dye molecules may be changed solely into MG which increases the color intensity with time. However, at pH 6, the color has remained quite constant upto 90 min and then slowly starts to decolorize. At pH 7 and 8, a drastic color change was observed within 60 min. Here ~ 42% of MG has decolorized in 120 min. However, at pH 7 and 8 when left for 18 hrs, the MG solutions were completely decolorized. This might be due to the conversion of MG to leuco forms in basic pH by the attack of OH^- ions which can easily attack the MG molecules to form MG leucocarinol,

hence causing the change in color from blue-green to colorless. The equilibrium pH of all the forms of MG was reported to be at 6.9 in different literatures [17, 27]. In this experiment, the optimum pH chosen was pH 6 so that the degradation of MG can be monitored through spectrophotometry. Some literatures have also been reported on pH 6 [15, 23].

Photolysis of MG

Different conditions were investigated for photolysis of MG maintaining initial pH 6. The conditions maintained are as follows: i) photolysis study in dark ii) photolysis study in dark with air supply iii) photolysis study in lamp light irradiation iv) photolysis study in lamp light with air supply. The results are presented in Fig. 7.

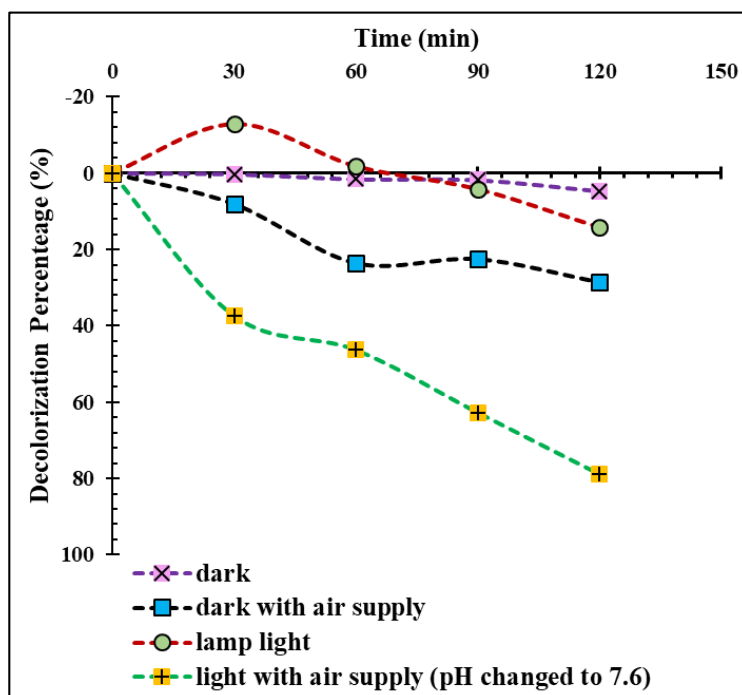


Fig 7: Photolysis of MG in different conditions.

As can be seen in Fig. 7, in the first three conditions, the decolorization was found to be low. The maximum decolorization could be seen when MG solution was irradiated with halogen lamp light along with air bubbling in the reaction system. During the process, the pH of the solution was found to be transformed drastically from pH 6 to pH 7.6 within 120 min. It indicates the formation of leuco-forms of MG which can be due to the formation of OH⁻ ions from interaction of water with O₂ from the air supply. Here, decolorization of the dye was observed rather than degradation. Hence, further experiments were carried out to investigate the degradation process.

Photocatalytic degradation of MG by BiVO₄

To study the photocatalytic degradation of MG, similar four different conditions were tested as in case of decolorization process *viz.* (i) dark (adsorption), (ii) dark with air supply, (iii) under lamp light and (iv) under lamp light with air supply. Here, it was noteworthy that there was no any substantial change in pH during the photocatalysis which indicates the degradation of the dye rather than decolorization. The findings are then presented in Fig. 8.

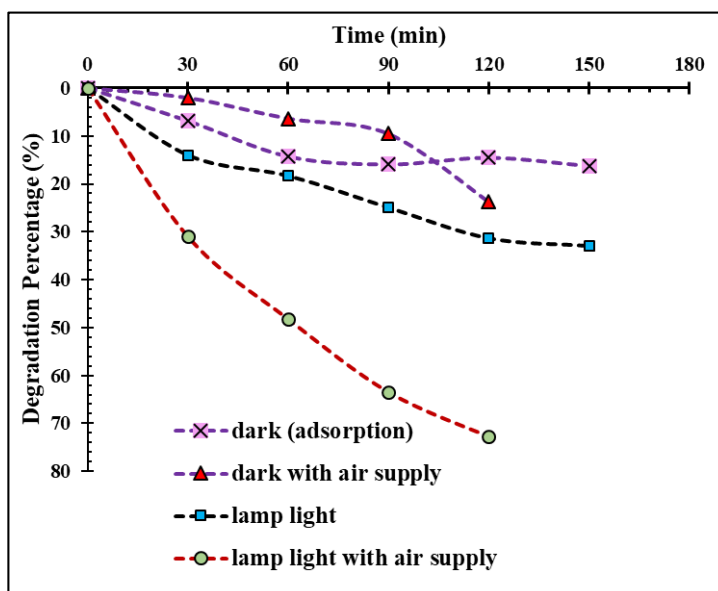


Fig 8: Photocatalytic degradation of MG by BiVO₄ in different conditions.

When the studies were carried out in dark without the air supply, it was found that there was adsorption of the dye particles on to the catalyst particles. In absence of light, there was no activation of catalyst particles for photocatalysis due to the semiconductor nature of the catalyst. In this condition, not even 20% of the dye molecules were adsorbed after 150 min. Upon introduction of air supply in dark, even lesser amount of dye has been degraded till 90 min which is an indication of some degradation. This might again be due to formation of hydroxide ions from air supply which attacked MG molecules to form leucocarbamol. When the dye solution was subjected to irradiation without air supply, it showed a

little degradation (32%) of the dye in 120 min. But when the lamp light and air supply were combined, then maximum degradation 72.73% of MG was observed. This can be attributed to photocatalytic degradation by BiVO₄ along with the synergistic effect of light and air supply which might generate OH[•] radicals, the most possible reactive species.

Effect of dye concentration

Dye concentration of 5 ppm, 10 ppm and 15 ppm were tested for their photodegradation by 0.1 g BiVO₄ in 100 mL dye solution maintaining condition of 500 W halogen lamp irradiation along with air supply.

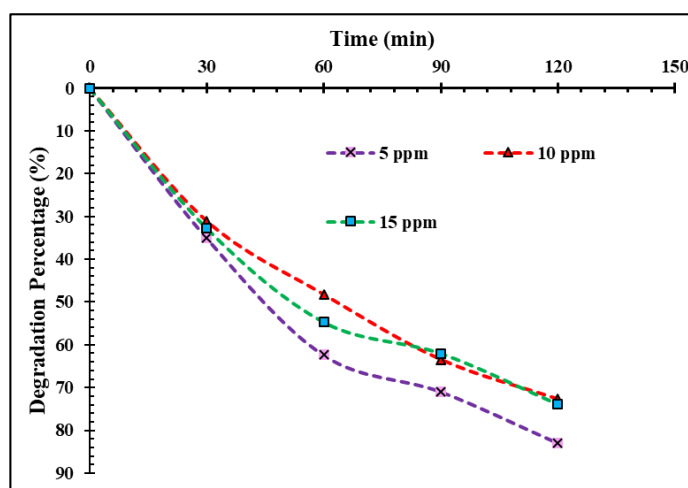


Fig 9: Effect of dye concentration in degradation of MG.

As can be seen in Fig. 9, there is no significant effect of dye concentration during photocatalytic process. Here, similar degradation rates can be observed in all tested concentration. Sharp degradation could be seen within 30 minutes. After 30 min, degradation of 5 ppm solution seems to be smooth compared to 10 ppm and 15 ppm solutions. It may be due to the lesser amount of dye molecules acted upon by larger number of the photocatalyst at an instant. When the dye is in small concentration, dispersion may be easier for the dye molecules over the surface area of the catalyst which can cause faster degradation. However, in 10 and 15 ppm, degradation was found to be almost similar pattern. It may be due to slightly high concentration of dye which resist the penetration of irradiated light to some extent.

Effect of catalyst dose

The catalyst dose of 0.05 g, 0.1 g and 0.2 g were investigated in 100 mL of 10 ppm dye keeping other physical conditions constant as mentioned before.

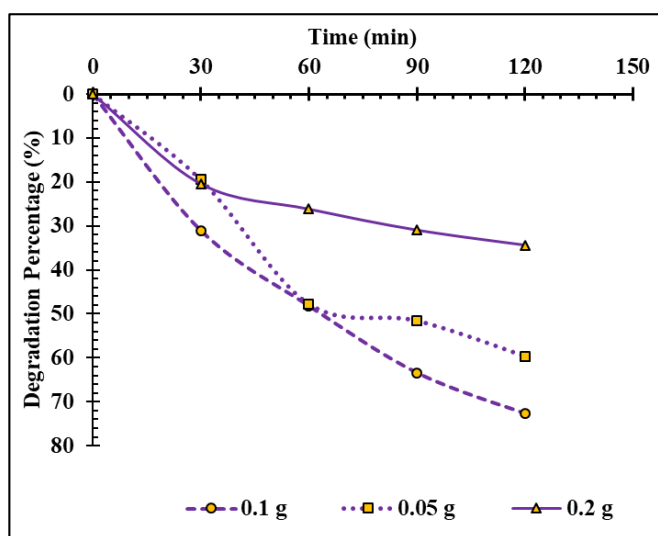


Fig 10: Photocatalytic degradation of MG in different dose of BiVO₄

As can be seen in Fig. 10 that the photodegradation rates of MG in 0.05 g and 0.1 g of catalyst is comparable till 60 min of irradiation. After 60 min, the 0.1 g photocatalyst showed better photocatalysis than 0.05 g dose. It may be due to the increased number of electron-hole pair formation at higher catalyst dose of 0.1 g than 0.05 g catalyst.

However, when the catalyst dose is increased to 0.2 g, there is significant decrease in the photocatalytic activity of the catalyst. Here, high dose may create turbidity in solution system. Such increased turbidity causes scattering of light and reduces the penetration of the irradiated light at the bottom of the solution which leads to lower degradation rate of the dye.

Kinetics

To understand the reaction kinetics of MG degradation quantitatively, the Langmuir-Hinshelwood model expressed by (2) was applied.

$$\ln\left(\frac{C_0}{C}\right) = kt \dots \dots \dots (2)$$

Where C₀, C and k indicate dye concentration at time 0 and t and apparent first-order rate constant, respectively. The reaction rate constant (k) can be determined using the first order linear fit. Fig. 11 shows the photodegradation of MG by

BiVO₄ catalyst followed first order kinetics. The rate constant of the 10 ppm MG photocatalytic degradation by 0.1 g BiVO₄ was calculated to be 0.011 min⁻¹ with R² value of 0.9977. This data justifies the efficient degradation of MG using prepared photocatalyst.

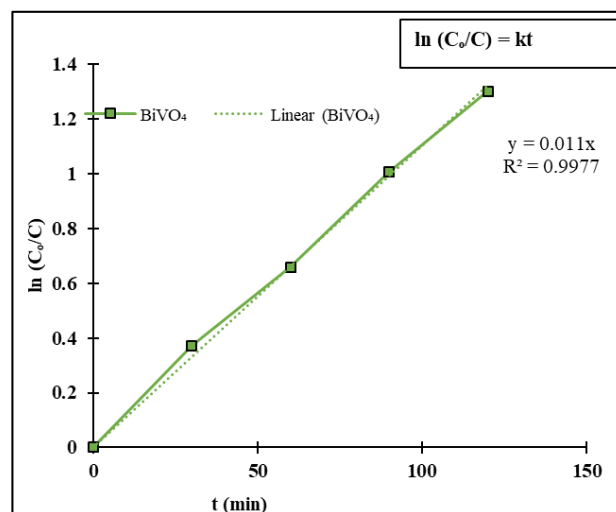


Fig 11: Langmuir- Hinshelwood plot (ln (C₀/C) Vs. irradiation time (t)) for degradation of MG by BiVO₄.

Temporal Spectral Changes

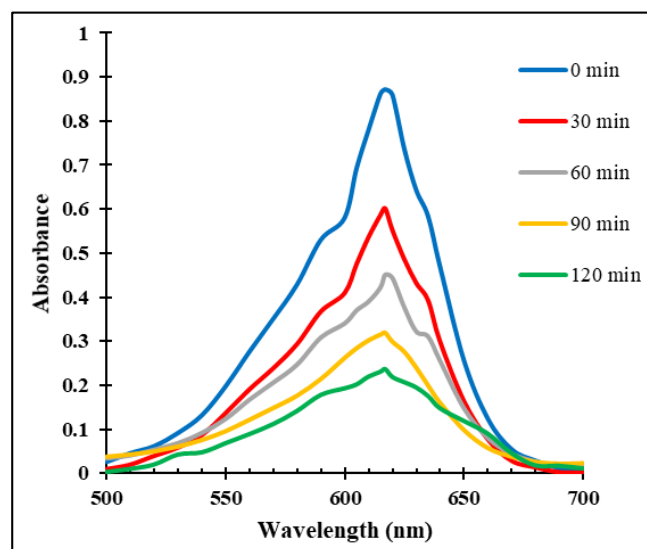
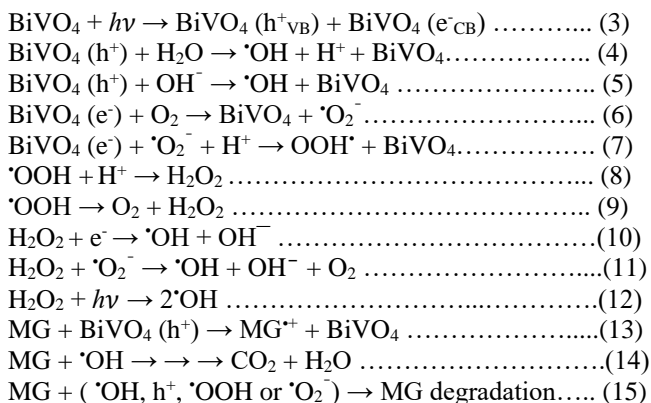


Fig 12: Temporal spectral changes of MG in BiVO₄ nanoparticles under 500 W halogen lamp; experimental conditions being 100 mL 10 ppm MG with 0.1 g BiVO₄.

Fig. 12 represents the temporal evolution of the visible absorption of MG solution in the presence of BiVO₄ under visible irradiation. As can be seen from Fig. 12, the intensity of absorption peaks has decreased with increasing irradiation time. The peaks have broadened with more time while the λ_{max} has remained constant.

Probable mechanism of Photodegradation in BiVO₄

The possible generation of the active photocatalytic species for the degradation of the dyes have been given in previous literatures [9, 28]. Here, the proposed reaction mechanism of the MG degradation was believed to be due to attack of photochemically produced hydroxyl radicals (·OH). In presence of BiVO₄, the generation of hydroxyl radicals may be due to following chain of reactions (3-15) [9, 28];



The reactions (3-15) represent the different pathways of formation of hydroxyl radicals ($\cdot\text{OH}$). When BiVO_4 surface is irradiated with light with energy higher than the band gap BiVO_4 , then the electrons from valence band (VB) shift to conduction band (CB) of BiVO_4 giving rise to electron-hole pairs (e^- - h^+). The holes (h^+) can react directly with water molecules (4) or with the hydroxide ions (OH^-) (5) to give $\cdot\text{OH}$ radicals. The photogenerated electrons in CB can react with O_2 molecules to give superoxide anion ($\cdot\text{O}_2^-$) as in reaction (6). The photogenerated electrons in CB can also react with H^+ to give perhydroxyl radical or hydroperoxyl radical (OOH^\cdot) (7). The perhydroxyl radical can react to give H_2O_2 through various pathways as shown in reaction (8-9). Thus formed H_2O_2 can react with either e^- or $\cdot\text{O}_2^-$ or with photons (10-12) to generate the hydroxyl radicals ($\cdot\text{OH}$). Thus, generated hydroxyl radicals ($\cdot\text{OH}$) can attack the MG molecules to give the degradation products as seen in reaction (14). Meanwhile MG itself can be attacked by the photogenerated holes to give activated MG molecules which can further react to give degradation products which are ultimately basic molecules like H_2O , CO_2 , NH_3 etc. This degradation process can continue with any of the reactive oxygen species ($\cdot\text{OH}$, $\cdot\text{OOH}$ or $\cdot\text{O}_2^-$) as the generated free radicals can easily attack the MG molecules (15).

Conclusion

BiVO_4 nanoflakes can be synthesized in laboratory by co-precipitation method. Monoclinic crystalline phase of BiVO_4 was obtained having spherical nanosize of 20-40 nm. The photocatalytic activity of prepared BiVO_4 showed maximum degradation of malachite green dye in presence of 500W halogen lamp with constant air supply. The optimum catalyst dose was found to be 0.1 g in 100 mL of 10 ppm MG dye solution.

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