Poll Res. 42 (3) : 361-366 (2023)
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ISSN 0257–8050
DOI No.: http://doi.org/10.53550/PR.2023.v42i03.009

PHOTODEGRADATION STUDY OF EVANS BLUE IN PRESENCE OF $BIVO_4$/MWCNTS

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(Received 10 March, 2023; Accepted 15 May, 2023)

ABSTRACT

The $BiVO_4$ was synthesized by sol-gel and $BiVO_4$/MWCNTs by mechano chemical method and characterized by XRD, EDX, and FESEM. The photocatalytic degradation of Evans blue has been studied under visible light in the presence of $BiVO_4$/MWCNTs composite. The effect of various parameters such as pH, the concentration of dye, amount of composite, and light intensity on the rate of degradation was also studied. It was observed that $BiVO_4$/MWCNTs have the highest catalytic activity in basic medium. A tentative mechanism for the degradation has been proposed.

KEY WORDS : Photodegradation, Bismuth vanadate, Photocatalytic, MWCNTs, Evans blue.

INTRODUCTION

Natural resources are becoming polluted as a result of human activities and rapid industrialization. Polluted water may have adverse effects on animals, plant life and humans. Effluents from dyes and textile industries make them polluted, when mixed in water sources. Despite regulatory measures, restricting industrial and agricultural operations from throwing pollutants into lakes, streams, and rivers. Around 1.1 trillion m^3 of wastewater is still disposed in waterways around the world, and this amount continues to grow (Sharma and Chaudhary, 2015; Incera *et al.,* 2017 and Verma *et al.,* 2022). Many communities and researchers are working to increase water conservation and also looking for alternate resources to remediate the existing water shortages. Use of recycled and treated water for uses such as irrigation, or byindustries is one of the options that has helped significantly in water supplies. Several technologies such as membrane processes (nanofiltration, reverse osmosis), advanced oxidation processes (H_2O_2, O_3, etc.), desalination,ect. are used to treat water in wastewater treatment plants (Ghernaout, 2018; Chong *et al.,* 2010; Tsolaki and Diamadopoulos, 2010 and Pendergast and Hoek, 2011). Recently, carbon based adsorption technology emerged with a great potential for wastewater treatment for removal of several contaminants present in water. Unlike several other porous adsorbents, CNTs possess large surface area, and well developed mesopores, which contribute to its removal capacities (Upadhyayula *et al*., 2009; Gangu *et al*., 2019 and Aslam *et al.,* 2021).

Adarsha *et al.* (2022) synthesised nanostructured calcium ferrite ($CaFe_2O_4$) particles via solution combustion method and used it for photocatalytic degradation of Evans blue. They observed that at optimum parameters as-synthesised calcium ferrite exhibited adsorption degradation capacity as 42.42 mgg^{-1} at optimum parameters. They revealed that catalyst can be reused for almost five times without any major loss in its activity.

Paliwal *et al.* (2017) synthesized cobalt doped bismuth ferrite to enhance the photocatalytic activity of bismuth ferrite and used it for photocatalytic degradation of Evans blue. They observed that doping of bismuth ferrite by cobalt increases the rate of photocatalytic degradation. Kumar *et al.* (2021) have synthesized a nano-spherical shaped reduced graphene oxide NS-rGO decorated with modified tin and sodium-doped titanium oxide nanocomposite. They used as-synthesised composites as an efficient photocatalyst for degradation of Evans blue. They revealed that graphene oxide decorated with sodium displayed higher photocatalytic activity as compared to tin decorated graphene oxide.

Ananda *et al.* (2022) prepared MgO nanoparticles via green synthesis with different fuel ratios using the *Phyllanthus emblica* aqueous fruit juice (Indian gooseberry). They used as-synthesised nanoparticles for photocatalytic degradation of Evans blue. They observed that 90% of dye was removed from the wastewater on using MgO nanoparticles.

Magnetic nanocrystalline $ZnFe_2O_4$ was successfully synthesized by Vergis *et al.* (2019) using oxalyldihydrazine as fuel via combustion route. They studied the adsorption capacity of as–synthesised nanospinel $ZnFe_2O_4$ for the removal of Evans blue. They observed that $ZnFe_2O_4$ nanoparticles showed good adsorptive capacity upto 46 mgg^{-1} of the adsorbent. It was revealed that this adsorption follows pseudo–second order kinetics and intraparticle diffusion was the rate determining step. It was also reported that this adsorption process is exothermic in nature and involved physisorption.

Zolfaghari *et al.* (2021) prepared iron, sulfur and poly(ethylene glycol) doped TiO_2 nanoparticles and used these in photodegradation of the methylene blue and Evans blue. They observed that as-synthesised nanostructured photocatalysts shows significant photocatalytic activity for the degradation of both these dyes in water in presence of visible light.

EXPERIMENTAL

Materials

Bismuth nitrate, citric acid, nitric acid, and ammonia were used in synthesis of bismuth vanadate and then it was mixed with MWCNTs. All chemicals used were of analytical grade and used without further purification. Evans blue was purchased from Himedia. The dye solutions were prepared in double distilled water.

Synthesis of Composite

The $BiVO_4$NPs were synthesized by sol-gel method using Bi $(NO_3)_3{\cdot}5H_2O$, NH_4VO_3, HNO_3, NH_4OH, and CH_3COOH as the starting materials. In the typical synthesis, the stoichiometric amount of the starting precursors such as Bi $(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 were dissolved in 50 ml of double distilled water, separately. The above two solutions were mixed together. Additionally, 100 ml of ethanol was added drop wise into the solution, stirrered and heated at 70 °C. A yellow sol was formed. The acetic acid (1M) was added to make 50 mL stock solution. The solution was maintained at 100 °C for a few hrs. Then gel was collected and calcined at 600 °C in the furnace. The monoclinic $BiVO_4$/MWCNTs sample was formed.Nanocomposite of bismuth vanadate and MWCNT was prepared using mechano-chemical method by 1:1 ratio of bismuth vanidate and MWCNT powder.

Characterization of Composite

EDS Analysis

Energy-dispersive X-ray spectroscopy (EDS) detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the sample. It is based on an interaction of source of X-ray excitation and sample. Energy dispersive X-ray spectroscopy data revealed the presence of 61.51, 21.71, 29.75, and 27.96% of bismuth, vanadium, oxygen, and carbon, respectively (Fig. 1). It indicates that there was no impurity in the sample and it contains only these elements.

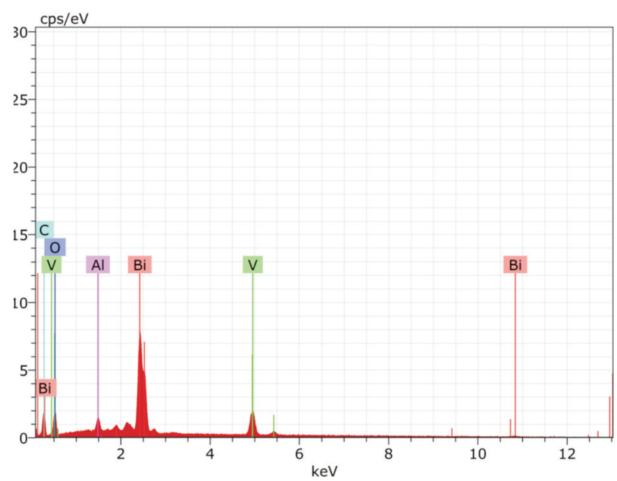


Fig. 1. EDS of $BiVO_4$/MWCNTs Composite

XRD Analysis

The pattern of X-ray diffraction was recorded for $BiVO_4$/MWCNTs with the help of XRD instrument (Pan Analytical X Pert Pro.). The X–ray diffraction data were used to calculate particle size of $BiVO_4$/MWCNTs using Debye-Scherrer formula and it was found to be 74.43nm (Fig. 2).

FESEM Analysis

The morphology of particles was examined using

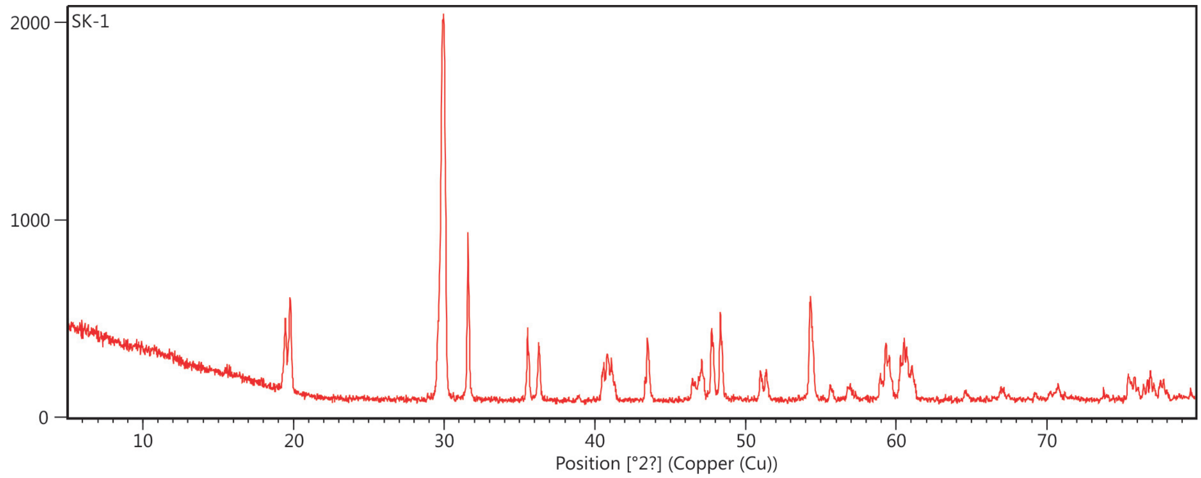
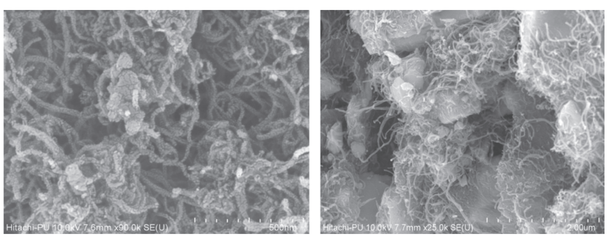


Fig. 2. XRD graph of $BiVO_4$/MWCNTs

Field Emission Electron Microscopy (Hitachi PU). The FESEM images of the composite are reported in Fig. 3. Thi clearly indicates carbon nanotubes and bismuth vanadate.



(a) (b)

Fig. 3. FESEM image of $BiVO_4$/MWCNTs

RESULTS AND DISCUSSION

A stock solution of Evans blue (1.0×10^{-3} M) was prepared by dissolving 0.096 g of dye in 100 ml double distilled water. This stock solution was further diluted. The photocatalytic degradation of Evans blue was studied after addition of 0.08 g of $BiVO_4$/MWCNTs in 50.0 ml dye solution (1.0×10^{-5} M). The reaction mixture was exposed to visible light with a 200 W tungsten lamp. Absorbance of solution (A) was measured with the help of a spectrophotometer (Systronics Model 106) at λ_{max}= 630 nm at several time intervals. The intensity of light was varied by changing the distance between the light source and surface of composite. 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 Evans blue was photocatalytic in nature. This degradation was also carried out with $BiVO_4$/MWCNTs for comparison.

A graph was plotted between log 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–

$$k = 2.303 \times \text{slope} \qquad \ldots(1)$$

The results of typical run for the photocatalytic degradation of Evans blue using $BiVO_4$/MWCNTs as composite has been reported in Table 1 and graphically presented in Fig. 4, having all the parameters constant.

Table 1. A typical run

pH = 7.5 [Evans Blue] = 1.0×10^{-5}M

Amount of composite=0.08 g Light Intensity =60.0 mWcm^{-2}

Time (min.)	Absorbance(A)	1+ log A
0.0	0.867	0.9380
10.0	0.595	0.7745
20.0	0.465	0.6675
30.0	0.395	0.5966
40.0	0.315	0.4983
50.0	0.251	0.3997
60.0	0.165	0.2175

Rate constant (k) = $4.61 \times 10^{-4}s^{-1}$

pH VARIATION

The effect of pH was investigated by varying the initial pH of solution from 5.0 – 9.0. The results are represented graphically in Fig. 5. It was found that degradation increases with pH up to 7.5with an increase in pH and then it decreases on increasing pH above 7.5. An electron from conduction band is

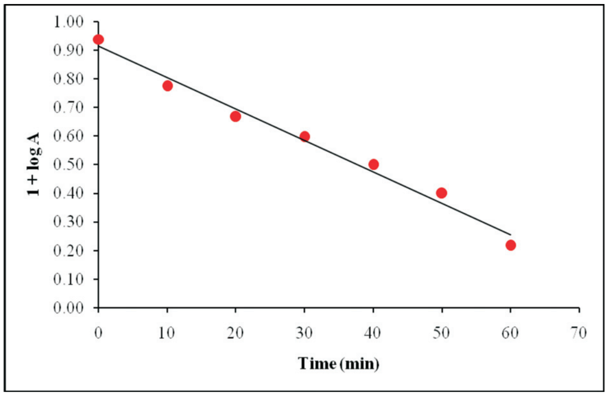


Fig. 4. A typical run

removed by dissolved oxygen to generate $O_2^{\bullet-}$ anion radical. 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 photocatalytic degradation at higher pH may be due to the fact that cationic toluidine blue will become neutral and it does not face any attrection/repulsion with negatively charged surface of the composite due to adsorption of $^{-}$—OH ions.

[Evans Blue] = 1.0 ×10^{-5}M Amountofcomposite=0.08 g
Light Intensity =60.0 mWcm^{-2}

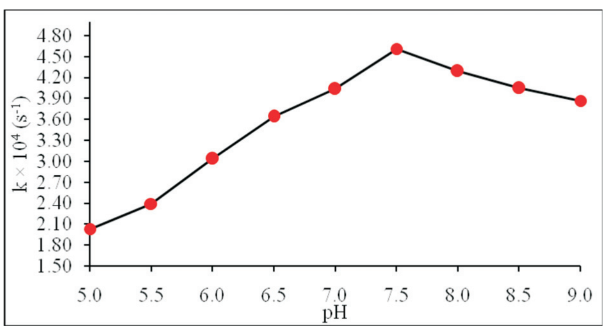


Fig. 5. Effect of pH

Concentration Variation

The effect of variation of concentration of Evans blue has been observed in the range from 0.2 ×10^{-5} M –1.8 ×10^{-5} M for $BiVO_4$/MWCNTs. The results are reported in Fig 6. It has been observed that rate of degradation increases with increasing concentration of dye but it decreases after attaining optimum condition at 1.0 ×10^{-5} M. On increasing the concentration of dye, the degradation rate increases due to availability of more molecules for excitation and energy transfer but after a certain concentration, the rate of photocatalytic degradation was observed to decrease. This may be due to accumulation of excessive molecules acting as an internal filter, which do not allow incident light to reach the composite and thus, resulted in a decrease in rate of degradation on further increasein the concentration of Evans blue.

pH = 7.5 Amount of composite=0.08 g
Light Intensity =60.0 mWcm^{-2}

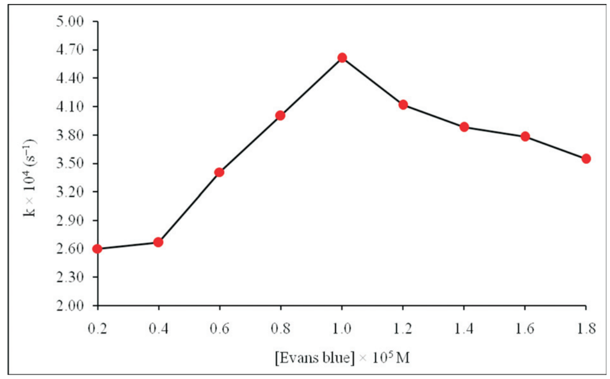


Fig. 6. Effect of dye concentration

Amount of Composite Variation

The effect of variation in dosages of composite on dye degradation was investigated in the range of 0.02–0.14 g. The results are summarized in Fig 7. It was observed that rate of degradation increases on increasing the amount of composite, but up to a certain amount of composite for $BiVO_4$/MWCNTs (0.08 g). After this point, the rate of reaction decreases on increasing the amount of composite further. It may be explained on the basis that as amount of composite was increased, the exposed surface area of composite will also increase. As a result, the rise in the rate of reaction has been observed, but on increasing the amount of composite, there is no increase in exposed surface area of composite. 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 = 7.5 [Evans Blue] = 1.0 ×10^{-5}M
Light Intensity =60.0 mWcm^{-2}

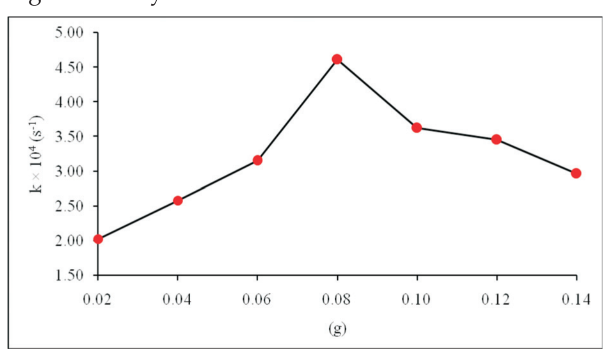


Fig. 7. Effect of amount Variation

Light IntensityVariation

The effect of light intensity on rate of degradation of dye was also investigated by changing the light intensity from 20.0–70.0 $mWcm^{-2}$. The observations are reported in Fig 8. The data indicate that the rate of reaction increases with increasing light intensity and maximum rate was found at 60.0 $mWcm^{-2}$. 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 composite will also increase, resulting in higher rate of degradation. Any further increase in the light intensity may initiate some side thermal reactions and therefore, higher intensities of light are avoided.

pH = 7.5 [Evans Blue] = 1.0×10^{-5}M
Amount of composite=0.08 g

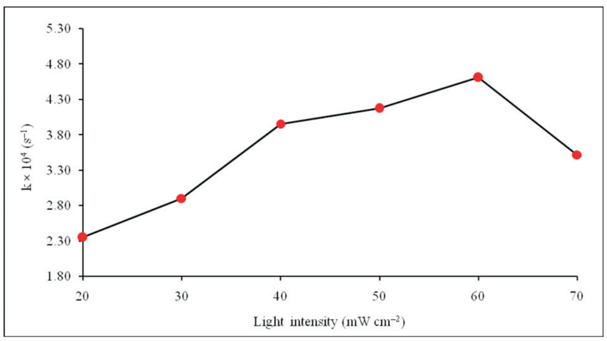


Fig. 8. Effect of light intensity variation

Mechanism

The hydroxyl ($^{\bullet}OH$) radicals were not found to act as an active oxidising species in the present investigation as confirmed by using hydroxyl radical scavenger (2–propanol), where the rate of degradation was not decreased appreciably. On the basis of the observations, a tentative mechanism for photocatalytic degradation of Evans blue (EB) has been proposed as –

$^1EB_0 \xrightarrow{} hv\ ^1EB_1$ .. (2)

$^1EB_1 \xrightarrow{} {}^{ISC3}EB_1$ .. (3)

$BiVO_4$/MWCNTs (comp.) $\longrightarrow$ Comp. [h^+ (VB) + e^- (CB)] .. (4)

O_2 (Dissolved Oxygen) + $e^- \longrightarrow O_2\bullet^-$ .. (5)

In basic medium-

$^3EB_1 + O_2\bullet^- \longrightarrow$ LeucoEB .. (6)

LeucoEB $\longrightarrow$ Products .. (7)

Evans blue 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 composite $BiVO_4$/MWCNTs (comp.) also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. The dissolved oxygen accepts are electron from conduction band and it is converted to superoxide radical anion, which converts the EB in to its leuco from. Aleuco form is unstable and it degrades to smaller almost harmless products.

CONCLUSION

The $BiVO_4$ and $BiVO_4$/MWCNTs samples have been synthesized by sol-gel and mechenochemical methods, respectively. The structure and morphology of composite samples were characterised by FESEM, XRD and EDX. The experimental results showed that degradation efficiency of EB was affected by various working parameters like pH (7.5), concentration (1.0×10^{-5}M), dose of composite (0.08g) and light intensity (60.0 $mWcm^{-2}$) where, rate constant in presence of $BiVO_4$/ MWCNTs at optimum condition was $4.61\times 10^{-5}\ s^{-1}$. Photocatalytic degradation has emerged as a promising technology for waste water 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 methods of wastewater treatment.

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