



Photocatalytic Degradation of Amaranth Dye Using Bismuth Vanadate-Nickel Sulfide Composite

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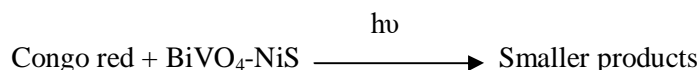
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ABSTRACT

The photocatalytic activity of $\text{BiVO}_4\text{-NiS}$ composite on photodegradation of amaranth has been studied. As-prepared photocatalyst was used for degradation of Amaranth in visible light. The characterization of composite was done on the basis of XRD, EDX and FESEM data. The progress of photodegradation reaction was monitored by spectrophotometer at definite time intervals. The effect of various parameters such as pH, concentration of dye, amount of composite and light intensity was observed to achieve optimum rate of photodegradation. It was observed that bismuth vanadate - nickel sulfide composite has the highest catalytic activity in almost neutral medium. A tentative mechanism for the reaction has been proposed.

Graphical Abstract:



Keywords: Photodegradation, Nanocomposites, Amaranth dye, XRD.

INTRODUCTION

Li *et al.*, [1] designed and synthesized highly efficient nanostructured photocatalysts NiS/BiVO_4 (NiS/BVO). It was observed that coupling p-type NiS nanoparticles on n-type decahedral nanostructured BVO cannot increase the specific surface area, but it can increase the harvesting of light, photocurrent response, and separation and transfer of the photo-generated electron-holes. It was reported that 0.7 molar ratio of NiS/BVO exhibited the highest photocatalytic capability (95.6 %) within 90 min on irradiation, and highest degradation rate (1.7970 h^{-1}), which was almost 16 and 33 times higher than pure BVO (15.8 %, 0.1134 h^{-1}) and NiS (7.9 %, 0.0543 h^{-1}). It was also revealed that NiS/BVO exhibited photocatalytic stability for five repetitive cycles. Zhang *et al.*, [2] synthesized ternary $\text{BiVO}_4\text{/NiS/Au}$ nanocomposites via simple two-step hydrothermal and photo-reduction methods. They used electron collector property of Au and advantages of p-n junction between NiS and BiVO_4 , so that as-prepared $\text{BiVO}_4\text{/NiS/Au}$ composites can exhibit significant improvement in degradation of tetracycline (TC) compared to pure BiVO_4 photocatalyst or binary composites ($\text{BiVO}_4\text{/NiS}$ or $\text{BiVO}_4\text{/Au}$). It was revealed that photodegradation efficiency of the ternary

BiVO₄/NiS/Au composites in degradation of tetracycline was 4.25 times higher as compared to BiVO₄.

She *et al.*, [3] effectively loaded NiS and CoS nanospheres on BiVO₄ thin films to afford NiS/BiVO₄ and CoS/BiVO₄ composites. It was reported that formation of the composites can effectively prevent the recombination of holes and electrons. As a result, NiS/BiVO₄ and CoS/BiVO₄ can give photocurrent of 2.1 and 2.7 mA cm⁻² under light respectively, which was about 1.75 and 2.25 times higher than that of BiVO₄ (1.2 mA cm⁻²). It was revealed that hydrogen production using NiS/BiVO₄ and CoS/BiVO₄ photoanodes was also found to be 4.7 and 7.3 times higher as compared to BiVO₄ photoanode, respectively. Zheng *et al.*, [4] constructed BiVO₄-modified hexagonal MoO₃ (BiVO₄/MoO₃) composites and used for solar-light induced photodegradation of tetracycline hydrochloride using a chemical precipitation route. It was found that removal efficiency of tetracycline over BiVO₄/MoO₃ was affected by pH, BiVO₄ content, and inorganic ions. It was observed that adsorption-photocatalytic efficiency of 3-BiVO₄/MoO₃ with a BiVO₄ (4.25%) (190 mg L⁻¹) was 97.66% within 160 min, and decreased to 91.35% on using for five cycles. It was revealed that tight junction interface between BiVO₄ and MoO₃ enhanced the visible-light response and the transfer and separation of photoinduced electron-hole pairs resulting in increased photocatalytic degradation.

Hu *et al.*, [5] reported the synthesis of m-BiVO₄ (rod-like structures). The photocatalytic activities of as-synthesized rod-like BiVO₄ were evaluated on the photodegradation of rhodamine B (RhB) and orange IV (OG-IV) dye under natural sunlight irradiation. The effects of different variable were investigated, such as calcination temperature, catalyst dosage, and initial concentration of RhB or OG-IV on the photocatalytic degradation efficiency. It was also found that the as-prepared BiVO₄ photocatalysts exhibited excellent repeatability and stability. Peng *et al.*, [6] constructed a fibrous BiVO₄/Bi₂S₃/MoS₂ heterojunction through electrospinning and hydrothermal processes. The Bi₂S₃ was formed during hydrothermal synthesis of MoS₂ on to structure of BiVO₄ fibers (porous). It was reported that BiVO₄/Bi₂S₃/MoS₂ (BBM) heterojunction was organized with MoS₂ nanosheets (several layers in thickness) which encapsulated both; Bi₂S₃ nanorod (about 40 nm in diameter) and fibrous BiVO₄ template. It was revealed that BiVO₄/Bi₂S₃/MoS₂ heterojunction exhibited enhancement of visible light absorption (500–800 nm). The optimized BBM-2 sample presented higher photodegradation efficiency as compared to pure BiVO₄ fibers in 2 h in presence of visible light irradiation.

Prabhavathy and Arivuoli, [7] prepared silver and lanthanum co-doped BiVO₄ photocatalysts via hydrothermal method. They used as-prepared photocatalysts for photocatalytic degradation of xylenol orange (XyO) and rhodamine B (Rh-B). It was reported that pinecone-shaped Ag/La-BiVO₄ particles exhibited increased photocatalytic activity, may be due to its porous structure, narrow bandgap energy, and strong visible light absorption. It was observed that doped materials showed higher degradation efficiency of 93 and 95% for XyO and Rh-B respectively. Wang *et al.*, [8] prepared porous structure of BiVO₄-C nanocomposite via hydrothermal approach. Here, lignin not only controlled the growth of BiVO₄ effectively but it also carbonized to form a porous structure of biochar-based photocatalyst. It was revealed that BiVO₄-C nanocomposites have increased photocatalytic activity and it was attributed to charge migration and departure of electron-hole pairs. Hemmatpour *et al.*, [9] prepared coupled CdS/BiVO₄ catalyst via mechanical mixing of the as-synthesized CdS and BiVO₄ NPs. It was reported that average crystallite sizes for CdS, BiVO₄, and CdS/BiVO₄ were 5.8, 34.9, and 37.3 nm, respectively. The bandgap energies were 1.99, 2.24, and 2.17 eV, respectively for CdS, BiVO₄, and CdS/BiVO₄. The highest photocatalytic activity of such coupled system was observed in the photodegradation of eriochrome black T on keeping moles of the BiVO₄ component 3–4 times greater than CdS. Zhao *et al.*, [10] prepared ternary magnetic photocatalyst BiVO₄/Fe₃O₄/reduced graphene oxide (BiVO₄/Fe₃O₄/rGO) through hydrothermal method. It was reported that BiVO₄/Fe₃O₄ with 0.5 wt% of rGO (BiVO₄/Fe₃O₄/0.5% rGO) exhibited highest activity, which can degrade more than 99% rhodamine B (RhB) in 2 h on solar light radiation. It was reported that hole (h⁺) and superoxide radical (O₂^{•-}) were responsible species for degradation of

RhB over BiVO₄/Fe₃O₄/rGO in presence of light. The reusability of this composite was tested up to five successive runs. The BiVO₄/Fe₃O₄/rGO composite can be easily separated, retaining high photocatalytic activity.

Sunidhi and Singh, [11] synthesized TiO₂/BiOI nano-composite and used for removal of amaranth. They assessed catalytic activity of as-prepared TiO₂/BiOI nano-composite for the degradation of amaranth under solar light. It was reported that about 91% degradation of amaranth dye could be achieved at pH 6, with catalyst dose 25 mg L⁻¹, and dye concentration of 10 mg L⁻¹ in 40 min. Shahmoradi *et al.*, [12] prepared *in situ* modified tungsten doped TiO₂ hybrid nanoparticles. They used n-butylamine and tungsten oxide as surface modifier and dopant, respectively. It was revealed that photodegradation of brilliant blue FCF and amaranth dyes exhibited a higher efficiency for modified tungsten doped TiO₂ hybrid nanoparticles as compared to reagent grade TiO₂.

Leeladevi *et al.*, [13] fabricated SmVO₄/g-C₃N₄ (SM/CN) nanocomposite via hydrothermal route without using any surfactants or template. They evaluated photocatalytic activity of as-synthesized SM/CN nanocomposite for the degradation of chloramphenicol (CP) and amaranth dye in aqueous solution under visible light. It was also revealed that the SM/CN nanocatalyst exhibited excellent photocatalytic activity towards the degradation of CP and amaranth with 94.35 and 99.11% efficiency, respectively. The highest photocatalytic activity of SM/CN nanocatalyst was attributed to the separation of photoinduced charge carrier's electrons and holes. Roşu *et al.*, [14] prepared ternary nanocomposites containing silver, TiO₂ and graphene and used as photocatalysts for degradation of amaranth under UV and natural light. It was observed that graphene/TiO₂-Ag nanocomposites had highest photocatalytic activity for amaranth degradation of under UV and solar irradiation. It could achieve about 85.3–98% of dye degradation in the first 2 h. The highest degradation of amaranth was obtained with the reduced graphene/TiO₂-Ag catalyst (up to 99.9%). Karkmaz *et al.*, [15] investigated photocatalytic degradation of amaranth in an irradiated titanium dioxide aqueous suspension. It was reported that TiO₂/UV-based photocatalysis can fully oxidize the dye, with a complete mineralization. It was also revealed that central –N=N– azo group was 100% transformed into nitrogen.

MATERIALS AND METHODS

Synthesis of Bismuth vanadate: Bismuth vanadate has been prepared by the method used by J. Panwar *et al.*, [16].

Preparation of composite: Bismuth vanadate and nickel sulphide were mixed in 1:1 ratio and grinded with a pestle and motor.

Amaranth: Amaranth dye was used as a model system to investigate the photocatalytic degradation by BiVO₄-NiS composite. Amaranth is an azo dye. Molecular formula of amaranth is C₂₀H₁₁N₂Na₃O₁₀S₃, and its molar mass is 604.47 g mol⁻¹.

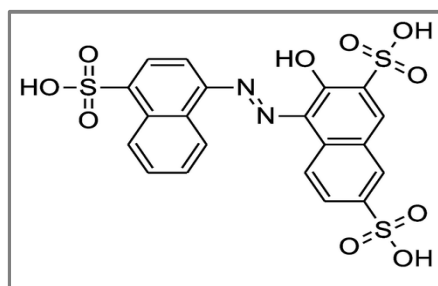


Figure 1. Structure of Amaranth dye

Characterization of composite

Energy dispersive X-ray (EDX) Analysis: EDS detects X-ray emitted from the sample during bombardment by electron beam to characterize the elemental composition. It is based on an interaction of source of X-ray excitation and sample. The results are reported in the [table 1](#) and presented in [figure 2](#).

Table 1. EDX data of BiVO₄-NiS composite

Element	Norm. C (wt. %)	Atom. C (at. %)
Bismuth	78.96	47.62
Vanadium	20.73	51.29
Sulfur	0.24	0.93
Nickel	0.08	0.16
Total	100.00	100.00

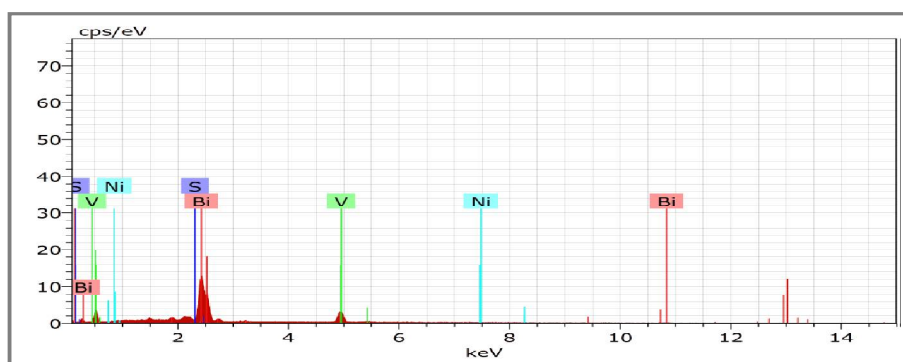


Figure 2. EDX of composite.

X-Ray diffraction (XRD) Analysis: XRD is a method to determine crystallinity of a compound. The crystal size of the composite was determined by the X-ray Diffractometer system XPERT-PRO using CuK α radiation ($\lambda = 1.54060$ nm) in the 2θ scanning ranges from 20° to 80° with a scan rate at 10 min.⁻¹ The applied voltage and current were 45 kV and 40 mA, respectively. The powder XRD pattern of BiVO₄-NiS is given in [Figure 3](#).

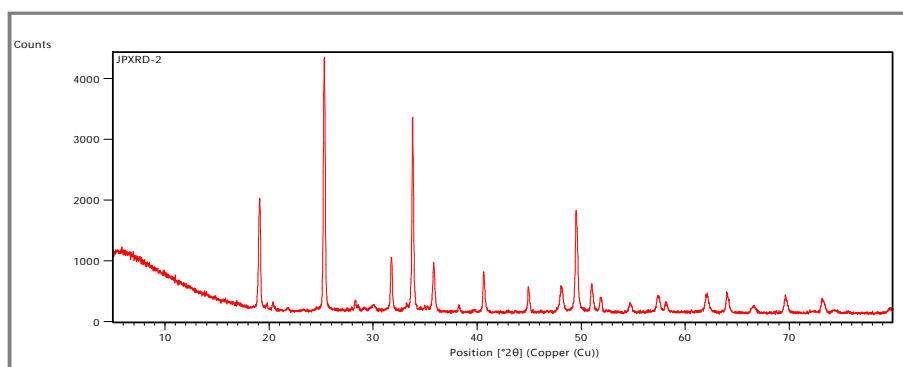


Figure 3. XRD of composite.

The average crystalline size of as-prepared composite was found to be 25.32 nm for BiVO₄-NiS composite, which is in nanometric range.

Field Emission Scanning Electron Microscopy (FESEM) Analysis: The FESEM analysis of the photocatalyst showed the morphology of BiVO₄-NiS nanoparticles ([Figure 4](#)), which shows the existence of almost flower like crystal structure (nanoflowers).



Figure 4. FESEM of composite.

Experimental: The absorbance of amaranth solution was determined by spectrophotometer (Systronics Model 106) (λ_{max} 520 nm) at various time intervals. It was observed that the absorbance of the solution decreases with increasing time of exposure, which indicates that the concentration of amaranth dye decreases with increasing time.

The data for a typical run are presented in table 2 and graphically presented in figure 5. The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

Table 2. A typical run

[Amaranth] = 6.00×10^{-5} M pH = 7.5
Composite = 0.10 g Light Intensity = 60.0 mWcm^{-2}

Time (min)	Absorbance (A)	1 + log A
0.00	1.02	1.008
10.0	0.93	0.968
20.0	0.86	0.934
30.0	0.83	0.919
40.0	0.76	0.880
50.0	0.72	0.857
60.0	0.67	0.826
70.0	0.63	0.799
80.0	0.60	0.778
90.0	0.56	0.748
100.0	0.52	0.716
110.0	0.48	0.681

Rate constant (k) = $1.11 \times 10^{-4} \text{ s}^{-1}$

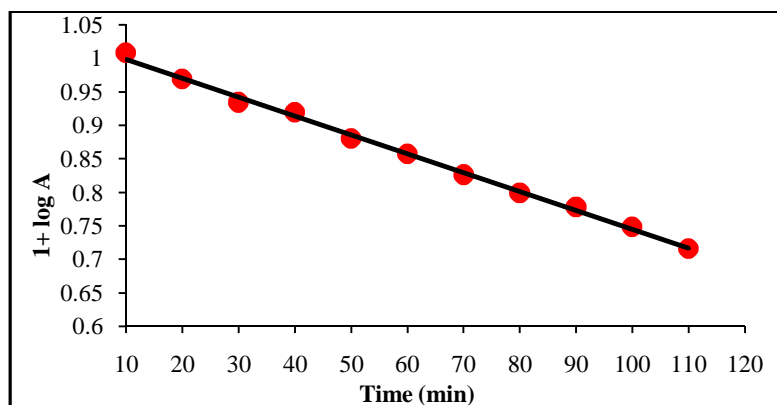


Figure 5. A typical run.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on photocatalytic degradation was investigated in the range 5.0- 9.0. The results are reported in [figure 6](#).

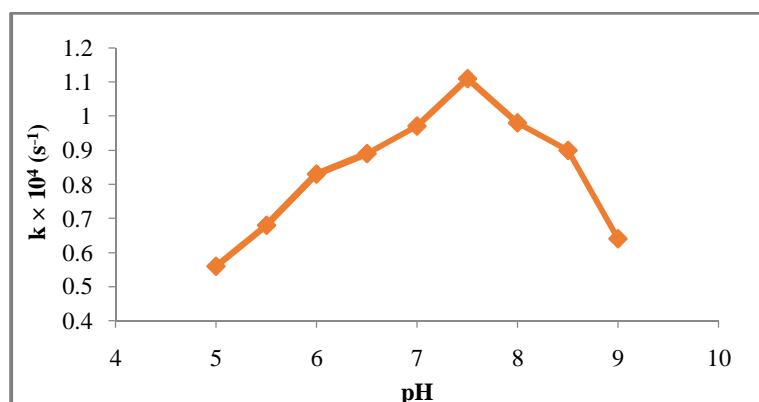


Figure 6. Effect of pH.

It is clear from the data that the degradation rate of amaranth increases with increasing pH of solution upto 7.5 and above this value of pH, the rate of photocatalytic degradation started decreasing. It may be explained on the basis that at low pH, the anionic dye was attracted by positively charged surface of photocatalyst, but further increase in pH above 7.5, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that amaranth does not remain in its cationic form and will not experience a force of attraction with negatively charged surface of the semiconductor due to adsorption of more OH^- ions on the surface of photocatalyst.

Effect of dye concentration: The effect of dye concentration on the rate of reaction was also observed by using different concentrations of the amaranth solution. The results are represented graphically in [figure 7](#).

It was observed that the rate of photocatalytic degradation increases with increasing concentration of the dye upto 6.00×10^{-5} M. It may be due to fact that as the dye was increased, more dye molecules were available for excitation and consecutive degradation. Hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye started acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface; thus, a decrease in the rate of photocatalytic degradation was observed.

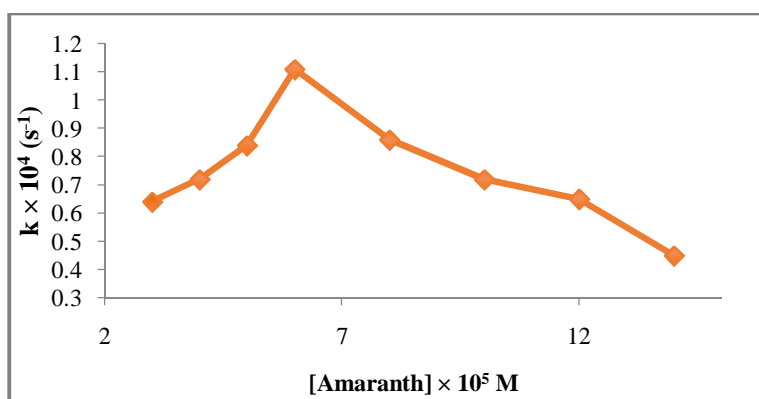


Figure 7. Effect of dye concentration.

Effect of amount of photocatalyst: The effect of amount of photocatalyst on the rate of photocatalytic degradation of amaranth was also observed. The results are graphically presented in figure 8.

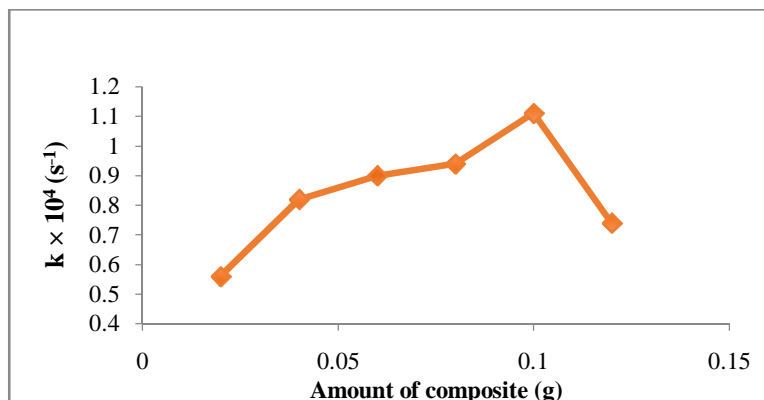


Figure 8. Effect of amount of composite.

It was observed that the rate of reaction increases with increase in the amount of semiconductor up to 0.10 g but beyond 0.10 g, the rate of reaction decreases. This may be due to the fact that as the amount of photocatalyst was increased in the initial state, the exposed surface area of the semiconductor also increases but after this limiting value (0.10 g), any increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the semiconductor layer. This was also confirmed by using reaction vessels of different dimensions.

Effect of light intensity: The effect of light intensity on the rate of degradation Amaranth was also observed. The results are reported figure 9.

The data indicated that the degradation was enhanced as the intensity of light was increased, because any increase in the light intensity increases the number of photons striking per unit time per unit area of the composite. The reaction rate shows a declining behavior above 60.0 mW cm^{-2} , may be due to some thermal side reactions.

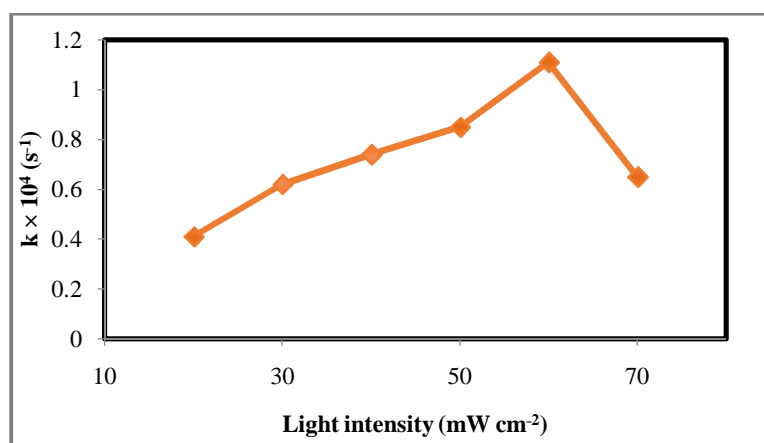
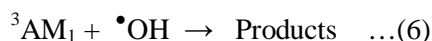
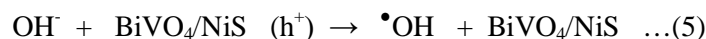
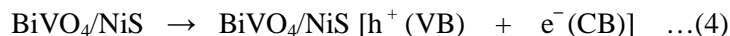


Figure 9. Effect of light intensity.

Mechanism of Amaranth degradation: On the basis of our experimental observations, a tentative mechanism for photocatalytic degradation of Amaranth may be proposed as –



When the solution of Amaranth was exposed to light in presence of BiVO₄/NiS composite, the dye molecules are excited to first excited singlet state. Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). On the other hand, the BiVO₄/NiS composite also absorbs photons and as a result electron-hole pair is generated. The OH⁻ will react with hole of the semiconductor to generate •OH radicals and these radicals will convert the dye molecules into smaller products, which are harmless. The participation of •OH radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of some hydroxyl radical scavengers like 2-propanol, where the rate of degradation was drastically reduced.

APPLICATION

The composite of BiVO₄-NiS can be used successfully for the degradation of various organic pollutants like organic dyes, pesticides, nitro compounds, pharmacuticles, etc.

CONCLUSION

The BiVO₄-NiS composite can successfully degrade amaranth into smaller harmless products. The optimum conditions were achieved as : pH = 7.5, concentration of dye = 6.00 × 10⁻⁵ M, amount of composite = 0.10 g and light intensity = 60.0 mW cm⁻².

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