

Visible light assisted photo catalytic degradation of 2, 4-dinitrophenol and 2, 4, 6- trinitrophenol using H₂O₂ sensitized BiVO₄

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Abstract— 2, 4-dinitrophenol and 2, 4, 6- trinitrophenol were successfully photodegraded using visible light active monoclinic BiVO₄ as photocatalyst. 10ppm of dinitrophenol is photodegraded using 50mg BiVO₄ under irradiation for 3h. 10ppm trinitrophenol is photodegraded using 100mg BiVO₄ under irradiation for 3h. Ease of photodegradation of DNP and TNP varied in the order DNP > TNP for the same amount of photocatalyst. Photoluminescence studies confirmed the formation of ·OH free radicals due to irradiation. Synergetic effect is noticed between BiVO₄ and H₂O₂.

Keywords— Photocatalysis, 2, 4- dinitrophenol, 2, 4, 6- trinitrophenol, BiVO₄, Picric acid.

I. INTRODUCTION

Heterogeneous photocatalysis has been widely investigated for the abatement of several toxic organic pollutants because of its ability to completely mineralize hazardous organic contaminants into harmless products at ambient temperature [1]. TiO₂ is used extensively as a photocatalyst because it is inexpensive, easy to synthesize, non-toxic, chemically inert, and highly photostable. But, the wide band gap of TiO₂ restricts its absorption to U.V region with $\lambda < 380\text{nm}$ which require substantial electrical input. Terrestrial solar radiation is composed of 4% U.V radiation, 52% visible light and 44% near infrared light. In order to exploit the large component of solar radiation, it is essential that the photocatalyst needs to be visible light responsive. Different strategies have been demonstrated [2] to extend photo response of TiO₂ into visible light through (i) doping of metal atoms/anions and/or cations, (ii) surface sensitization with dyes, phthalocyanins, porphyrins and (iii) fabrication of nano composites with higher surface to volume ratio. Simultaneous research on ternary metal oxides as potential photocatalysts led to the development of ZnWO₄ [3], CaBi₂O₄ [4], BaBiO₃ [5], BiVO₄ [6], Bi₂WO₆ [7], Bi₂MoO₆ [8], Bi₂Mo₂O₉ [9], Bi₂Mo₃O₁₂ [10], Fe₂Mo₃O₁₂ [11], NaBiO₃ [12], FeV₃O₈ [13] etc. as potential photocatalysts for degradation of dyes and other aromatic pollutants. Majority of these visible light active photocatalysts contain Bi as one of the components. Binary metal oxide systems Bi₂O₃-V₂O₅, Bi₂O₃-MoO₃ and Bi₂O₃-WO₃ form a large group of visible light responsive photocatalysts, probably due to the valance band formed from Bi (6s) and O (2p) orbitals resulting in a smaller band gap [14]. Remediation of several dyes using Bi₂Mo₃O₁₂, xMoO₃ [15-16] and aromatic pollutants such as nitrobenzene [17], 2, and 4- nitrophenols [18], acetophenone [19], and Brilliant green [20] using BiVO₄ have been recently reported from this laboratory.

Nitro aromatic compounds are identified as environmentally hazardous due to their toxicity. Nitrophenols are widely distributed in waste waters, rivers and soil because of their extensive use in manufacturing industries of pesticides, herbicides, dyes, explosives, pharmaceuticals, wood preservatives and photographic developers. 2, 4- dinitrophenol (2, 4-DNP) is a toxic compound used in petrochemical industry as polymerization inhibitor for vinyl aromatics and in agriculture as pesticide. 2, 4-DNP may also be formed as a result of photochemical reaction between benzene and nitrogen monoxide in polluted air. It reacts with alkyl-peroxy radicals in water and has the potential to photolyze. Remediation of 2, 4- DNP has been reported in terms of adsorption [21], biodegradation [22], cavitation [23, 24], anodic oxidation [25], electro chemical [26], Fenton [27], photocatalytic degradation over TiO₂ [28-33], carbon nano tubes/TiO₂ composite [34], Bi₂O₃/Bi₂MoO₆ [35], V₂O₅-ZnO [36], Fe₃O₄/Al₂O₃/TiO₂ nano composite [37], Nitrogen and Indium co-doped mesoporous TiO₂ nano composites [38], Ag⁺ doped BiVO₄ [39], photo and photo-Fenton processes [40] solar Fenton catalytic oxidation using BiFeO₃ [41]. Present paper describes visible light heterogeneous photocatalytic degradation of 2, 4- DNP and 2, 4, 6- trinitrophenol using H₂O₂ sensitised monoclinic BiVO₄.

II. MATERIAL AND METHODS

2.1 Synthesis of Photocatalyst

BiVO_4 is prepared by room temperature solid-state metathesis synthesis reported elsewhere. Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd) and NaVO_3 (98% HIMEDIA) in the molar ratio of 1:1 are mixed in an agate mortar and ground for 2hrs in ethanol. With progressive grinding, the mixture exhibited a canary yellow colour. After 2hrs of grinding, the mixture is washed several times with distilled water to completely remove the by product NaCl and the residue is dried at 80°C in an air oven. The dried powder is subjected to phase identification, microstructural investigation and photocatalytic studies.

2.2 Characterization Techniques

Phase purity of the resultant powder was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} . Microstructural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

2.3 Photocatalytic studies

Photo catalytic activity of BiVO_4 was evaluated in terms of degradation of 2, 4- dinitrophenol and 2, 4, 6- trinitrophenol under visible light. 50 mg of the catalyst was dispersed in 100ml DNP/TNP aqueous solution (10 mg/L) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photo catalyst powder and dye. The suspension was then exposed to 400 wt metal halide lamp; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. The spectra as a function of irradiation time were recorded using UV-Visible spectrophotometer (Schimadzu). The extent of photodegradation was calculated using the following equation

$$\% \text{ Photodegradation} = [(A_0 - A_t) / A_0] \times 100$$

where A_0 and A_t correspond to the initial absorbance and absorbance at time 't' respectively.

2.4 Photoluminescence studies:

50 mg BiVO_4 catalyst is added to the beaker containing 100 ml of terphthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution) and $10 \text{ }\mu\text{m}$ H_2O_2 . The solution is stirred for 15 min in dark followed by irradiation by 400 w metal halide lamp for 30 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectro fluorometer (Fluoromax 4) with the excitation wavelength of 315 nm.

III. RESULTS AND DISCUSSION

BiVO_4 is known to exist in three crystalline modifications- tetragonal Zircon, monoclinic Scheelite and tetragonal Scheelite. Among these three polymorphic forms, only monoclinic BiVO_4 exhibits good catalytic efficiency in the visible region. Fig. 1 shows the XRD pattern of sample prepared in this study by solid- state metathesis reaction between equimolar BiOCl and NaVO_3 . All the observed diffraction peaks could be indexed to monoclinic form of BiVO_4 (JCPDS File NO: 75-2480). Absence of peaks from possible contaminants due to incomplete solid-state reaction or unwashed NaCl confirms the sample as phase pure monoclinic BiVO_4 . Microstructural investigation with SEM revealed particles with no characteristic texture and with size in the μm region (Fig. 2).

Temporal variations of spectral contours as a function of irradiation time for DNP, DNP+ H_2O_2 , DNP+ BiVO_4 and DNP+ BiVO_4 + H_2O_2 are shown in Fig. 3. From the figure, it can be seen that DNP aqueous solution showed only a very small amount of degradation to an extent of 13% photolysis for 4h of irradiation (Fig. 3a). Addition of H_2O_2 caused photodegradation to an extent up to 18% for 4h of irradiation (Fig. 3b). Combination of BiVO_4 +DNP showed photodegradation to an extent of 14% (Fig. 3c). However, when BiVO_4 and H_2O_2 were added to DNP, absorption intensities rapidly decreased with progressive irradiation time and complete photodegradation of DNP is achieved for 3h irradiation (Fig 3d). In the absence of any new peaks arising simultaneously in the U.V.-visible spectral region under study, the complete decrease in absorption intensity is ascribed to oxidative photodegradation of DNP.

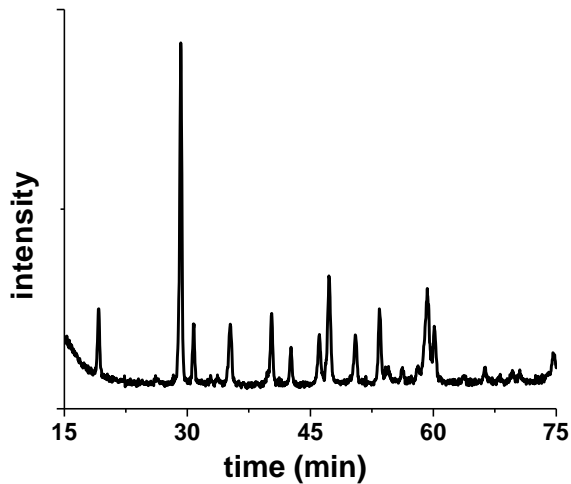


FIG.1. X-RAY DIFFRACTION PATTERN OF BiOCl+NaVO₃ MIXTURE IN 1:1 MOLE RATIO AFTER GRINDING AND WASHING

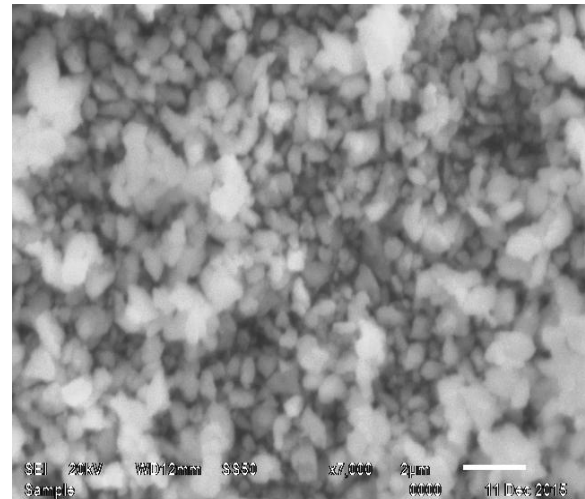


FIG. 2. SEM IMAGE OF BiVO₄ PHOTOCATALYST.

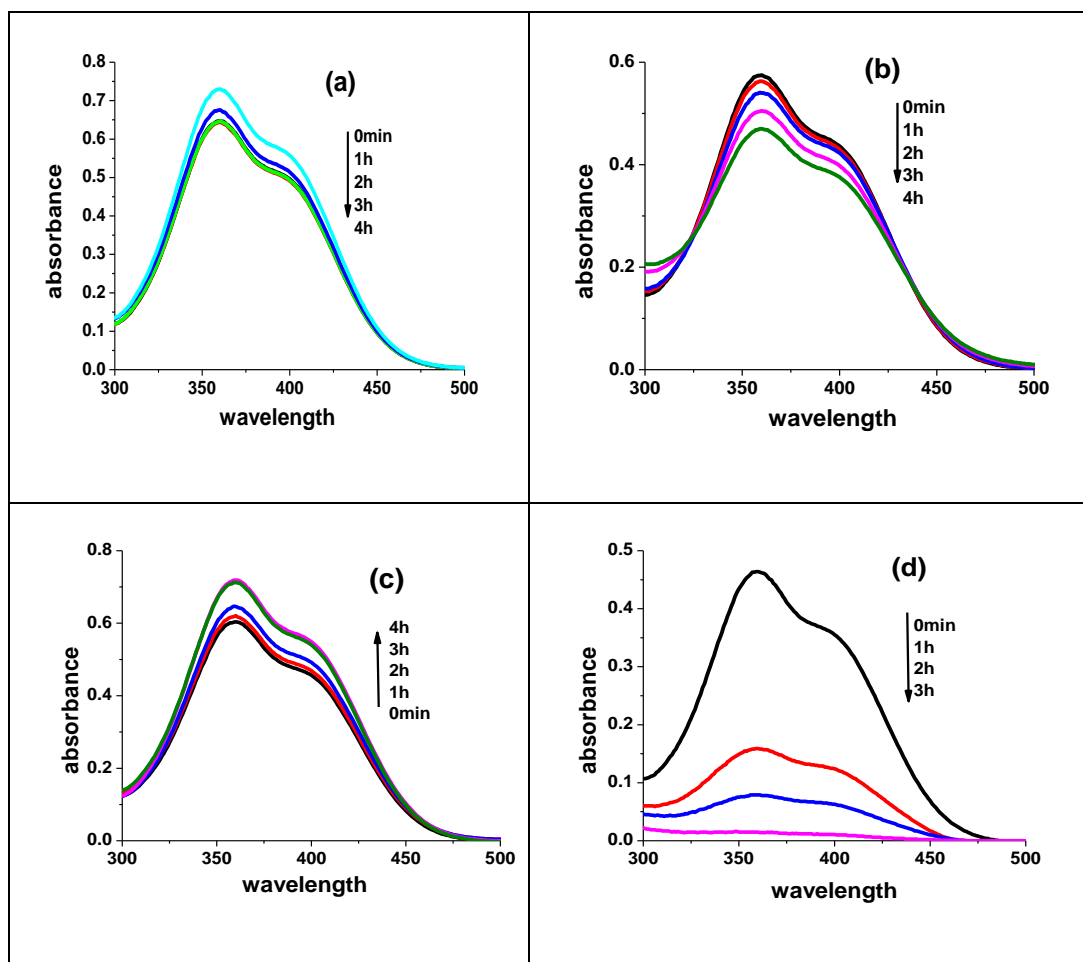


FIG. 3. U.V-VISIBLE ABSORPTION SPECTRA OF (A) DNP, (B) DNP+H₂O₂, (C) DNP+BiVO₄ AND (D) DNP+BiVO₄+H₂O₂ AS A FUNCTION OF IRRADIATION TIME (DNP- 10ppm, BiVO₄ 50mg, H₂O₂-10 μm)

Effect of amount of catalyst on the photodegradation of DNP is studied by using different amounts of BiVO₄ (10, 30, 50 and 100mg) keeping the concentrations of 2, 4-DNP and H₂O₂ unchanged. Time dependent spectra for the photodegradation of DNP with varying BiVO₄ amounts are shown in Fig. 4. With 10mg BiVO₄, photodegradation was found to be slow and

incomplete for irradiation up to 4h. With 30mg BiVO_4 rate of degradation was faster and complete degradation is achieved for 4h of irradiation. For 50mg of BiVO_4 , photodegradation of DNP is complete for 3h of irradiation. For 100mg of BiVO_4 , degradation time is found to increase above 3h. From these results it may be concluded that 50mg BiVO_4 is the optimum amount of photocatalyst to achieve 100% degradation of DNP for irradiation time of 3h.

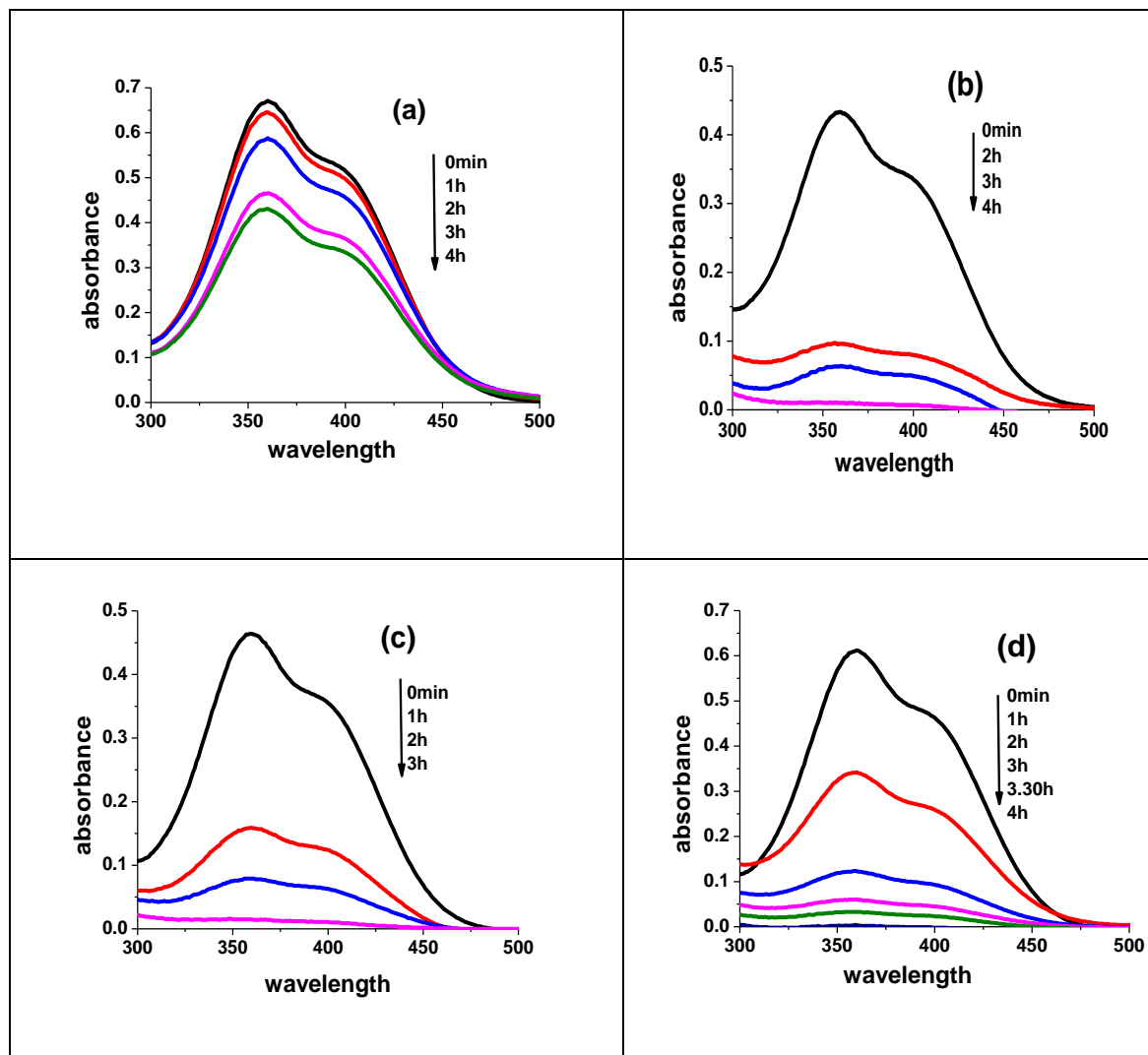


FIG. 4. EFFECT OF AMOUNT OF CATALYST ON THE PHOTOCATALYTIC DEGRADATION OF DNP+ H_2O_2 (a) 10mg, (b) 30mg, (c) 50mg and (d) 100mg

2, 4, 6- trinitrophenol (TNP) also known as picric acid is an explosive under rapid heating. TNP has the potential to be highly mobile and persistent in ground waters and is resistant to hydrolysis, biodegradation and photolysis. Picric acid on contact with skin may result in dermatitis and long exposures lead to skin eruptions and vomiting or nausea. Remediation of picric acid has been reported in terms of photoelectro chemical [42], catalytic [43], catalytic wet air oxidation [44] vacuum U.V radiation [45], Fenton and photo Fenton process [40] and photocatalytic degradation using TiO_2 [46, 47, 28] and multi walled carbon nanotubes supported NiFe_2O_4 [48]. UV-visible absorption spectra of TNP, $\text{TNP}+\text{H}_2\text{O}_2$, $\text{TNP}+\text{BiVO}_4$ and $\text{TNP}+\text{BiVO}_4+\text{H}_2\text{O}_2$ as a function of progressive irradiation are shown in Fig. 5. From the figure 5a, it may be noticed that absorption maximum of TNP is around 350nm and no significant photolysis of TNP is noticeable for irradiation up to 240min. In presence of H_2O_2 , however, TNP showed a photodegradation to an extent of 35% (Fig 5b). In presence of BiVO_4 , TNP showed photodegradation of 4% only. But, in presence of $\text{BiVO}_4+\text{H}_2\text{O}_2$, complete 100% photodegradation of TNP occurred for 4h of irradiation.

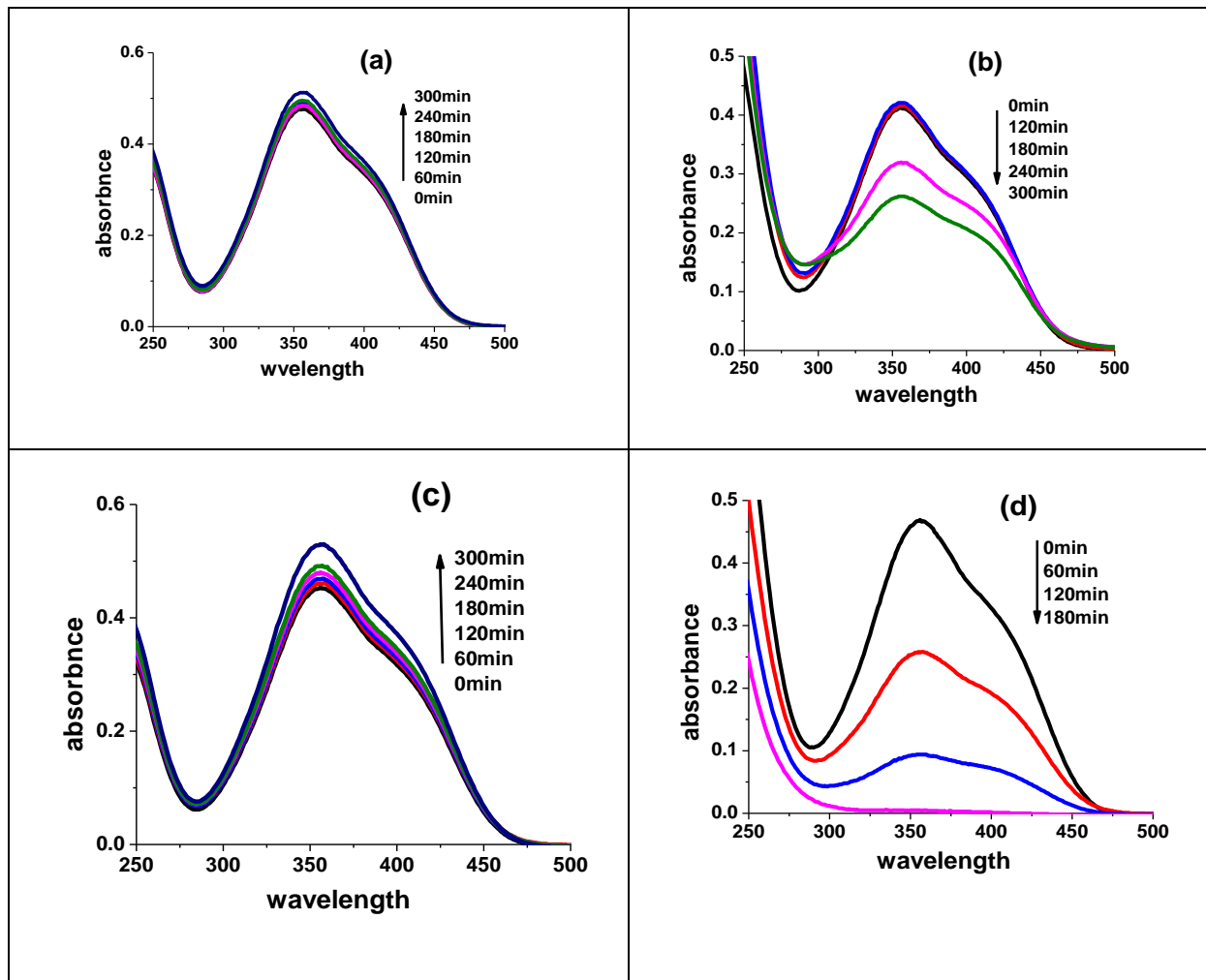


FIG.5. U.V-VISBLE ABSORPTION SPECTRA OF (a) TNP, (b) TNP+H₂O₂, (c) TNP+BiVO₄ and (d) TNP+BiVO₄+H₂O₂ AS A FUNCTION OF IRRADIATION TIME (TNP- 10ppm, BiVO₄ 100mg, H₂O₂ –10 μm)

In order to optimize the amount of catalyst, photodegradation studies have been conducted with varying amounts of BiVO₄ keeping the concentrations of TNP and H₂O₂ constant. Fig. 6 shows the temporal variation of spectral intensities as a function of irradiation time for photodegradation of TNP with 30, 50, and 100mg of photocatalyst. From the spectra recorded, it may be concluded that 100mg is the optimum amount of BiVO₄ for the photodegradation of 10ppm TNP in presence of 10μmoles of H₂O₂.

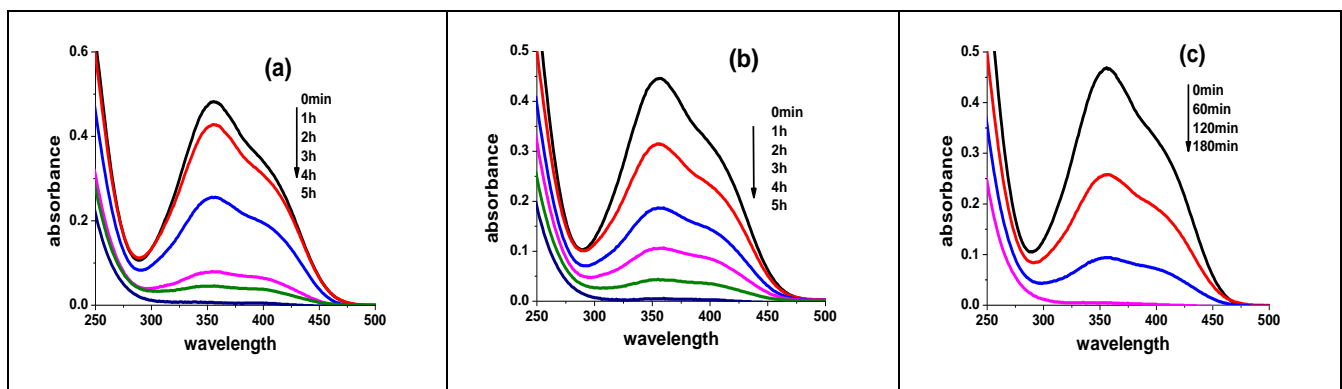
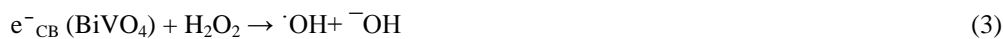
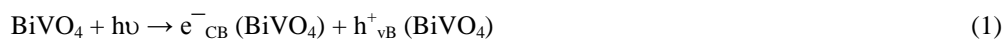


FIG. 6. EFFECT OF AMOUNT OF CATALYST ON THE PHOTOCATALYTIC DEGRADATION OF TNP+H₂O₂ (a) 30mg, (b) 50mg and (c) 100mg

Enhanced degradation of both DNP and TNP in presence of H_2O_2 is ascribed to synergetic effect between $BiVO_4$ and H_2O_2 . Possible photocatalytic mechanism involved is suggested as follows;



Rapid formation of $\cdot OH$ free radicals through steps (iii) and (iv) is the important in accumulation of more $\cdot OH$ free radicals which are used for disintegration of both DNP and TNP. In order to confirm the generation $\cdot OH$ free radicals during irradiation of $BiVO_4$ in presence of H_2O_2 photoluminescence spectroscopy is used with Terphthalic acid (TPA) as a probe molecule. TPA combines preferentially with $\cdot OH$ to form hydroxy terphthalic acid (HTPA) which shows a characteristic luminescence peak at 419nm. Fig. 7 depicts photoluminescence spectra for $BiVO_4$ +TPA with and without H_2O_2 prior to and after irradiation. Intense luminescence peak after irradiation confirms formation of $\cdot OH$ free radicals due to irradiation in presence of H_2O_2 .

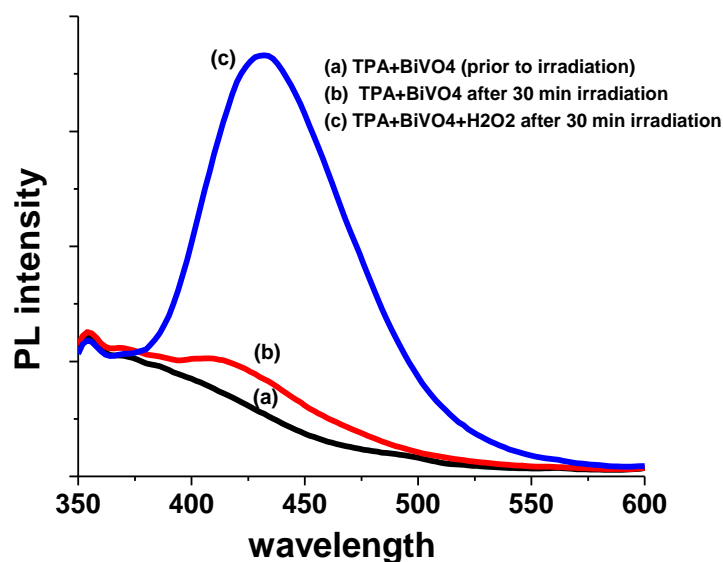


FIGURE 7. PHOTOLUMINESCENCE SPECTRUM OF TPA SOLUTION CONTAINING $BiVO_4$ PHOTOCATALYST IN PRESENCE AND IN ABSENCE OF H_2O_2 BEFORE AND AFTER IRRADIATION FOR 30 MIN

From the above results it may be concluded that both DNP and TNP can be successfully photodegraded under visible light using monoclinic $BiVO_4$ as photocatalyst in presence of external oxidant H_2O_2 . Ease of photodegradation is found to be in the order $DNP > TNP$ for the same amount of photocatalyst.

IV. CONCLUSION

Monoclinic $BiVO_4$ has been found to be a highly useful visible light active photocatalyst to eliminate DNP and TNP in aqueous solutions. Optimum conditions for photodegradation of 10ppm each of DNP and TNP are respectively 50mg and 100mg $BiVO_4$ with 10 μ moles of H_2O_2 . Synergetic effect is observed between $BiVO_4$ and H_2O_2 which led the generation of more $\cdot OH$ free radicals that enhanced the degradation of pollutant. Formation of $\cdot OH$ free radicals is confirmed by photoluminescence spectroscopy using Terphthalic acid.

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