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**VISIBLE LIGHT PHOTOCATALYTIC DEGRADATION OF ACETOPHENONE USING
H₂O₂ SENSITISED BiVO₄**

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Abstract

Photocatalytic degradation of acetophenone has been investigated over BiVO₄ under visible light irradiation. Presence of H₂O₂ enhanced the rate of degradation of acetophenone by lowering the degradation time from 5h to 3h. On the other hand, presence of K₂S₂O₈ did not show any beneficial effect. Formation of ·OH free radicals in the case of BiVO₄+H₂O₂ is confirmed by photoluminescence studies using terephthalic acid.

Keywords: BiVO₄, Photocatalytic degradation, acetophenone, K₂S₂O₈.

Introduction

Remediation of toxic organic pollutants from industrial waste water effluents has become a prime concern because the continuous contamination of aquatic sources is posing a serious threat to human health and ecosystem as well. Though several methods such as adsorption, filtration, biosorption, ion-exchange, chlorination, ozonation, reverse osmosis, electro catalysis etc. were proposed from time to time for the removal of hazardous pollutants prior to their discharge, none of these methods is completely satisfactory due to some inherent defect in each technique. In recent times, there is a growing interest in advanced oxidation process based on semiconductor mediated heterogeneous photocatalysis for non-selective degradation of several organic pollutants such as dyes, phenolic compounds, pharmaceutical compounds and pesticides [1-4]. The distinct advantages of this process are - complete mineralization of pollutant without formation of hazardous intermediates, processing at ambient conditions of temperature and, utilization of near UV/solar radiation that makes it a cost effective green technology. Among the various semiconductor binary metal oxide photocatalysts investigated, TiO₂ is considered to be highly useful due to its ease of synthesis, high chemical and biological inertness, high

oxidizing capacity, high photostability and good photocatalytic quantum efficiency. However, the wide band gap associated with TiO₂ precludes absorption in the visible region of solar radiation above 380nm. Several efforts in terms of doping, addition of sensitizer and nano composite formation by coupling with other materials have been attempted to render TiO₂ into a visible light absorptive photocatalyst. Alternately, attention has also been focused on exploring several ternary metal oxides such as ZnWO₄ [5], BiVO₄ [6], Bi₂WO₆ [7], Bi₂MoO₆ [8], Bi₂Mo₃O₁₂ [9], Fe₂Mo₃O₁₂ [10], Bi₄Ti₃O₁₂ [11] to effect photocatalytic oxidative degradation under visible light as discussed in the review [12].

Photocatalytic degradation of acetophenone over transition metal ion impregnated mesoporous TiO₂ was investigated by Rajesh and co workers [13] who concluded that both Ag and Ni ions enhanced degradation from 89% to 100% under U.V irradiation for 240min. Praveen and co workers [14] studied the effect of anions on the photocatalytic activity of Fe(III) salts impregnated TiO₂ towards photodegradation of acetophenone under U.V irradiation. Rajesh et al. [15] studied photodegradation of acetophenone over anatase

and rutile separately under U.V irradiation and concluded that higher photocatalytic activity was obtained with anatase phase compared to rutile. Ehsan Amereh and Shahrara Afshar [16] reported photocatalytic degradation of acetophenone by nano-TiO₂ powder supported on NaX zeolite under U.V irradiation for 210min. Liwsirisaeang et al [17] reported photodegradation of acetophenone over TiO₂ powders and obtained only incomplete degradation even after 4h of U.V irradiation. Photocatalytic reduction of acetophenone under U.V and visible light using TiO₂ and Pd-TiO₂ was reported by Molinari and co workers [18]. Photodegradation of acetophenone using coumarine dye sensitized TiO₂ under visible light irradiation was reported by Shigeru Kohtani et al [19]. From the above literature survey, it appears that photocatalytic degradation of acetophenone has so far been studied only with TiO₂ under U.V irradiation. Recently photocatalytic degradation of 2, 4 - nitrophenols and nitrobenzene has been reported from this laboratory using H₂O₂ sensitised BiVO₄ under visible light irradiation [20-21]. In view of this, the present work is under taken to investigate the photocatalytic degradation of acetophenone under visible light irradiation using BiVO₄ in presence of two different external oxidants H₂O₂ and K₂S₂O₈.

Materials and Methods

Synthesis of Photocatalyst:

BiVO₄ is prepared by room temperature solid-state metathesis synthesis reported elsewhere [21]. Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd) and NaVO₃ (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 developed a canary yellow colour slowly. After 2hrs of grinding, the mixture is set aside for a few hours and then 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.

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 radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} . FT-IR data has been obtained with Shimadzu IR prestige -21.

Photocatalytic studies:

Photo catalytic activity of BiVO₄ is evaluated in terms of degradation of acetophenone under visible light. 100 mg of the catalyst is dispersed in 100ml acetophenone 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 acetophenone solution. 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 spectrum as a function of irradiation time is recorded using UV-Visible spectrophotometer (Shimadzu). All the experiments are conducted under ambient conditions. The extent of photodegradation is 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.

Results and Discussion

BiVO₄ has been reported to exist in three polymorphic modifications- tetragonal Zircon, monoclinic Scheelite and tetragonal Scheelite. Even though the coordination around Bi and V is the same in all three phases, only BiVO₄ of monoclinic structure exhibits visible light photocatalytic activity. Fig. 1 depicts X-ray diffraction pattern of the prepared sample. All the diffraction peaks observed could be indexed to monoclinic BiVO₄ of JCPDS file No 75-2480. As there are no extra peaks due to any contaminant the sample is ascertained to be phase pure monoclinic BiVO₄.

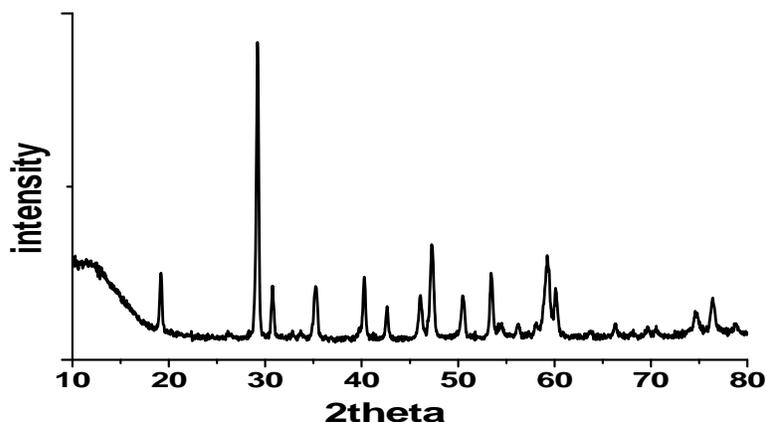


Fig. 1. X-ray diffraction pattern of BiOCl+NaVO₃ mixture in 1:1 mole ratio after grinding and washing

Fig. 2 shows the FTIR spectrum for the same sample in the range 500-4000 cm^{-1} . The spectrum obtained is in good agreement with earlier reports [22-23]. The FTIR spectrum shows one highly intense band at 726 cm^{-1} with a shoulder at 822 cm^{-1} and two other broad peaks of relatively low intensity, one at 3420 cm^{-1} and the other at 1620 cm^{-1} . The intense band at 726 cm^{-1}

is assigned to characteristic $\nu_{\text{V-O}}$ asymmetric stretching in while the shoulder at 822 cm^{-1} is ascribed to $\nu_{\text{V-O}}$ symmetric stretching. The other two broad peaks of less intensity are respectively assigned to O-H stretching and O-H bending modes of adsorbed moisture on the sample.

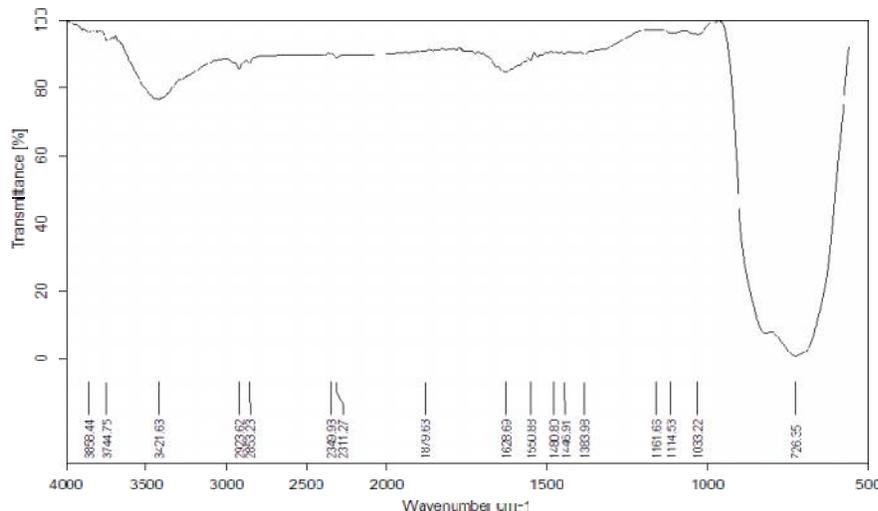


Fig. 2. FTIR spectrum of BiVO_4

Temporal variation of spectral contours as a function of irradiation time for acetophenone aqueous solution, acetophenone + H_2O_2 , acetophenone + BiVO_4 and acetophenone + BiVO_4 + H_2O_2 are shown in Fig. 3. From the figure, it can be seen that acetophenone exhibits a characteristic absorption at $\lambda_{\text{max}}=240\text{nm}$ and shows complete degradation due to photolysis under irradiation for 7h (Fig. 3 a). In presence of H_2O_2 ,

complete photolysis of acetophenone occurred in 5h (Fig. 3 b). Similarly in Presence of BiVO_4 , progressive lowering in intensity till complete degradation is observed for 5h of irradiation (Fig. 3 c). But, in presence of BiVO_4 and H_2O_2 , the absorption intensity completely vanished for 3h of irradiation indicating a synergetic effect between H_2O_2 and BiVO_4

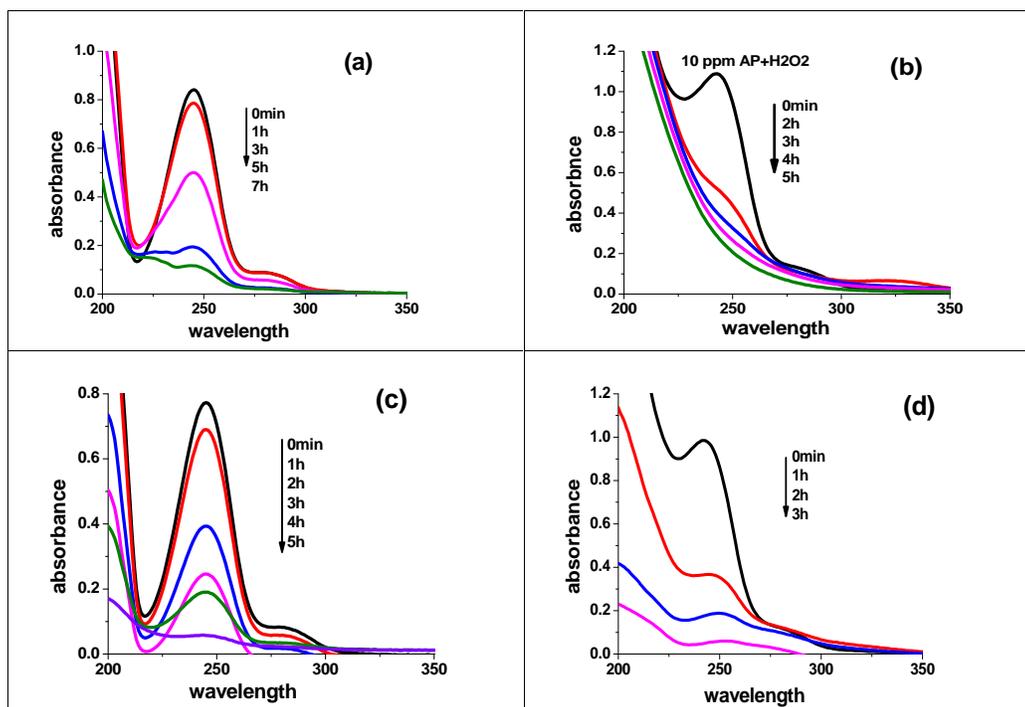


Fig. 3. Temporal variation of spectral contours of (a) acetophenone aqueous solution (10ppm), (b) acetophenone + H_2O_2 , (c) acetophenone + BiVO_4 and (d) acetophenone + BiVO_4 + H_2O_2 as a function of irradiation time

Several investigators reported $K_2S_2O_8$ also as an external oxidant besides H_2O_2 for the photocatalytic degradation of dyes and pesticides over TiO_2 . Since H_2O_2 itself is causing photolysis of acetophenone, photodegradation is investigated over $BiVO_4$ with $K_2S_2O_8$ as an external oxidant in place of H_2O_2 . Fig. 4 shows time dependent variation of spectral intensities as a function of irradiation time for acetophenone+ $BiVO_4$ with 10, 30 and 50mg of $K_2S_2O_8$. In the case of 10mg and 30mg of $K_2S_2O_8$, the absorption intensity decreased steadily with progressive irradiation up to 5h indicating a total degradation to an extent of 80% (Fig. 4 (a) and 4 (b))

the same as without $K_2S_2O_8$ (Fig. 3 a). Nevertheless, when the amount of $K_2S_2O_8$ is increased to 50mg, the absorption intensity initially increased for 1h irradiation and subsequently got lowered for 2, 3 and 4hr of irradiation, and resulted in lesser photodegradation (Fig. 4 (c)) as compared to those with 10 and 30mg $K_2S_2O_8$. Increase in the amount of oxidant over an optimum value is reported to be detrimental in many cases because it generates scavengers for free radicals as a result of which the extent of degradation will be constrained. These results indicate that addition of $K_2S_2O_8$ is not beneficial in the photodegradation of acetophenone over $BiVO_4$.

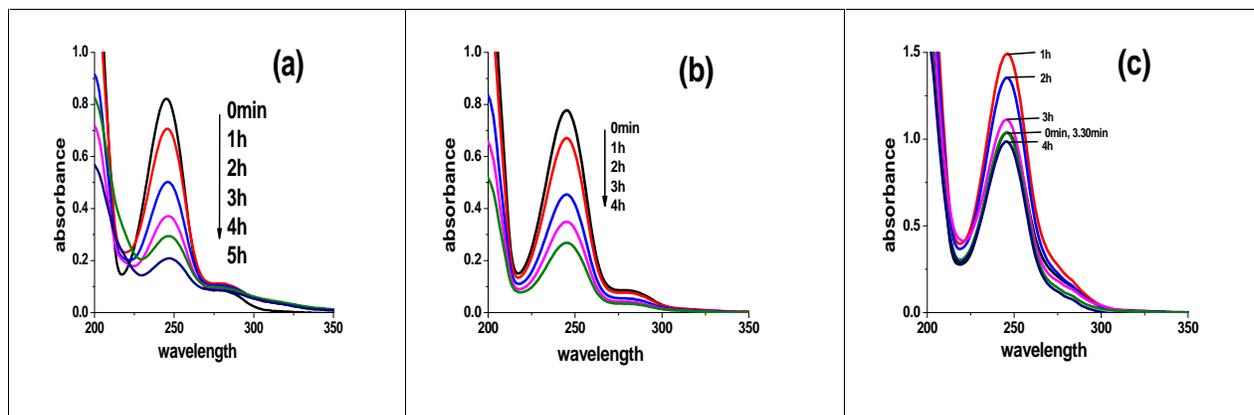


Fig. 4 Variation of spectral intensities as a function of irradiation time for aqueous solution of acetophenone with (a) 10mg, (b) 30mg and (c) 50mg of $K_2S_2O_8$ in presence of $BiVO_4$.

Since acetophenone is successfully photodegraded over $BiVO_4$ under visible light irradiation in presence of H_2O_2 , in order to assess whether $\cdot OH$ free radicals are taking part in the photocatalytic degradation, mannitol is added to acetophenone+ $BiVO_4$ + H_2O_2 solution and time dependent spectra of this mixture solution are recorded as a function of irradiation time which are shown in Fig. 5

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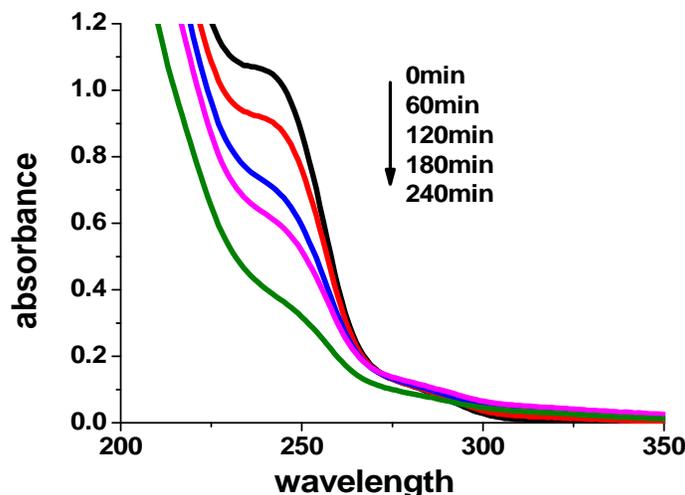
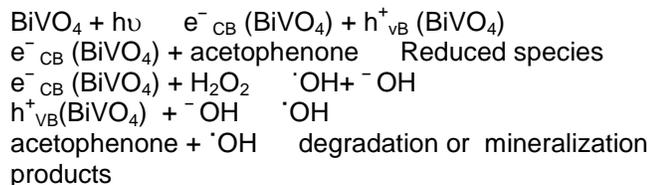


Fig. 5. Effect of mannitol on photodegradation of acetophenone+ $BiVO_4$ + H_2O_2

From the figure, it can be seen that the degradation is slowed down in presence of mannitol and is incomplete even after 4h of irradiation. Since mannitol functions as a scavenger for $\cdot\text{OH}$ free radicals, the degradation is constrained in presence of mannitol. Based on this, the possible mechanism for the photodegradation may be suggested as follows.



Photocatalytic degradation is usually described by pseudo first order kinetics of Langmuir - Hinshelwood model according to which

$$\ln C_t = -kt + \ln C_0$$

where C_0 and C_t refer to initial concentration and concentration at time 't'. Plot of $\ln C_t/C_0$ vs time for the degradation of acetophenone under different conditions are shown in Fig. 6. Rate constants calculated from the respective slopes are given in table 1.

Table 1. Calculated rate constants for photodegradation of acetophenone with H_2O_2 , BiVO_4 and $\text{BiVO}_4+\text{H}_2\text{O}_2$

Photodegradation of	Rate constant $K (\text{h}^{-1})$
Acetophenone	7.4×10^{-4}
Acetophenone+ H_2O_2	9.8×10^{-4}
Acetophenone+ BiVO_4	1.4×10^{-3}
Acetophenone+ $\text{BiVO}_4+\text{H}_2\text{O}_2$	5.4×10^{-3}

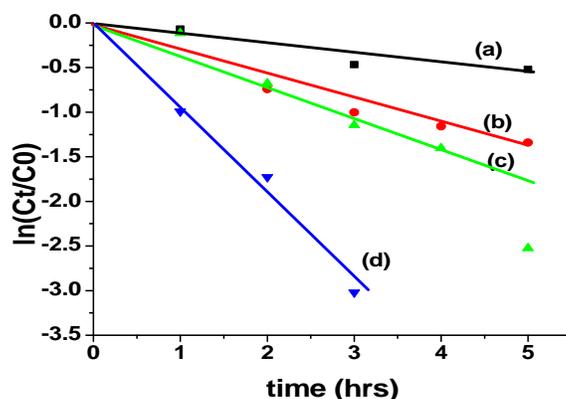


Fig. 6. Plot of $\ln(C_t/C_0)$ vs irradiation time for (a) acetophenone, (b) acetophenone + BiVO_4 , (c) acetophenone + H_2O_2 and (d) acetophenone + BiVO_4 + H_2O_2

Conclusions

XRD and FTIR studies indicated formation of phase pure monoclinic BiVO_4 . Photodegradation of acetophenone due only to photolysis occurred in 7h. Photocatalytic degradation over BiVO_4 under visible light occurred for 5h of irradiation. Addition of H_2O_2 enhanced the photodegradation by further lowering the degradation time to 3h. No such beneficial effect was observed with $\text{K}_2\text{S}_2\text{O}_8$ in the photodegradation of acetophenone. Presence of $\cdot\text{OH}$ free radical formation is ascertained by scavenging effect due to mannitol and by photoluminescence spectroscopy using terephthalic acid as probe molecule.

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