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RESEARCH ARTICLE

VISIBLE LIGHT ACTIVATED PHOTOCATALYTIC DEGRADATION OF ANILINE USING H_2O_2 SENSITIZED $BiVO_4$

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ABSTRACT

Photocatalytic degradation of aniline is studied over H_2O_2 sensitised monoclinic $BiVO_4$ under visible light irradiation. Combination of $BiVO_4$+H_2O_2 showed a synergetic effect in enhancing the rate of degradation. Formation of more ·OH free radicals during irradiation in presence of H_2O_2 is ascertained by photoluminescence spectra using terpthalic acid as probe molecule.

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INTRODUCTION

Aniline, a common by-product of petroleum, coal and several other chemical industries is used in rubber, polymer, herbicide, fungicide, pharmaceutical and dye industries. Because of its significant solubility in water, aniline occurs as one of the important pollutants in ground water wells as well as in surface waters. Being toxic and recalcitrant in nature aniline is classified as a persistent organic pollutant by the US environmental protection agency. Several methods have been proposed for the treatment of aniline containing effluents. These methods include adsorption (An *et al*., 2010), chemical oxidation (Zhang *et al*., 2010), biological oxidation (Li and Xie, 2007), ozonation (Sauleda and Brillas, 2001), reverse osmosis (Gomez *et al*., 2009), sono degradation (Song *et al*., 2007), catalytic wet air oxidation (Gomesa *et al*., 2008), electro chemical oxidation (Fu *et al*., 2008), photo-Fenton (Fukushima *et al*., 2013), combined photo-Fenton & biological oxidation (Anotai *et al*., 2006) etc. These methods require either disposal of secondary pollutant generated by phase transfer or a control of reaction conditions and operation within a narrow pH range. During the past few decades, considerable attention has been focused on semiconductor mediated heterogeneous photocatalysis for remediation of several toxic organic pollutants. Main advantage of this process is its ability to mineralize hazardous pollutants at ambient temperature under solar radiation avoiding filtration, flocculation and generation of secondary pollutants. TiO_2 has been extensively studied as a useful photocatalyst because it is inexpensive, non-toxic, chemically & biologically inert, photostable and reusable with good efficiency. These advantages are however off set due to its wide band gap of 3.2 eV allowing absorption only in U.V. region below 380nm that lies within 5% of solar radiation. Consequently, a number of strategies have been demonstrated to improve the performance of TiO_2 and enhance the absorption range of TiO_2 in to visible region of solar radiation by suitable doping/codoping with alkali, alkaline earth and transition metal atoms, anions and/or cations, surface sensitization and nano composite formation (Prasada Rao *et al*., 2015). Simultaneous investigations by many researchers on ternary metal oxides as potential visible light responsive photocatalysts led to the development of $ZnWO_4$ (Montini *et al*., 2010), Bi_2MoO_6 (Martínez-de la Cruz and Obregón Alfaro, 2010), Bi_2WO_6 (Yi-Hsien *et al*., 2011), $Bi_2Mo_3O_{12}$ (Suresh *et al*., 2015), $Fe_2Mo_3O_{12}$ (Suresh *et al*., 2014) etc. for the degradation of dyes with different chromophores. Recently, visible light photocatalytic degradation of 2, 4- nitrophenols, nitrobenzene, acetophenone and Brilliant green have been reported from this laboratory using $BiVO_4$ (Umabala, 2015;

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Umabala *et al.*, 2016). Present paper describes photodegradation of aniline over H_2O_2 sensitized $BiVO_4$ under visible light irradiation.

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 bye product NaCl and the residue is dried at 80ºC in an air oven. The dried powder is subjected to phase identification, mcrostructural investigation and photocatalytic studies.

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 (λ= 1.54059 Å), with a scan rate of 2° min^{-1}.

Photocatalytic studies

Photo catalytic activity of $BiVO_4$ was evaluated in terms of degradation of aniline under visible light. 100 mg of the catalyst was dispersed in 100ml aniline aqueous solution (5 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

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

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

Photoluminescence studies

50 mg $BiVO_4$ catalyst is added to the beaker containing 100 ml of terpthalic acid (TPA) solution (0.25 mmol L^{-1} in 1mmol L^{-1} NaOH solution) and 10 µm 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 flourometer (Flouromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

Karunakaran and coworkers (Karunakarn and Senthivelan, 2005) reported photocatalytic oxidation of aniline to azobenzene using CdS under illumination at 254nm. Liu *et al.* (2011) reported degradation of aniline with boron doped goethite under U.V and visible light irradiation. Liao *et al.* (2011) reported photocatalytic degradation of aniline with B-doped MnO under U.V. irradiation for 6h. Guo Lin *et al.* (2014) reported visible light driven photocatalytic degradation of aniline over $NaBiO_3$ at pH= 2. F.A. Aisien and coworkers (2014) reported application of periwinkle shell ash as photocatalyst for the photocatalytic degradation of aniline at pH = 8 under U.V. irradiation with addition of H_2O_2. Anil kumar and Nupar Mathur (2006) studied photodegradation of aniline at the interface of TiO_2 suspension containing carbonate ions under U.V. irradiation and observed that the addition of CO_3^{2-} to Degusa P25 increased the number of active adsorption sites at its surface. Navin San and Zakiye Cinar (2001) reported addition of H_2O_2 increased the photodegradation rate significantly over TiO_2 where as presence of Cu^{2+} showed negative effect. Canle and coworkers (2005) investigated the mechanism of TiO_2- photocatalysed degradation of aniline under U.V. irradiation for 6h and concluded that acid medium inhibited degradation while in alkali medium the degradation was fast and identified nitrobenzene as the main photo product of aniline degradation. Shahrezaei *et al.* (2012) reported 50% photocatalytic degradation of aniline in presence of TiO_2 for 2h of U.V. illumination at pH= 12. Long Wenhua *et al.* (2000) investigated kinetics of photocatalytic degradation of aniline in water over TiO_2 supported on porous nickel and reported 60% degradation for 8h of U.V. irradiation. Hequing Tang *et al.* (2010) reported photoctalytic removal of aniline over TiO_2 at pH=4. According to these investigators, oxidation of aniline occurred for an initial concentration of 0.02mmol/L and when aniline concentration is increased to 0.5mmol/L photocatalytic oxidation of aniline led to formation of azobenzene. Further increase in concentration of aniline to 3mmol/L led to polymerization of aniline. Above reports indicate that most of the studies relating to aniline photo degradation have been done with U.V. irradiation and the irradiation times vary in the range of 4-6 hours.

X-ray diffraction pattern of $BiVO_4$ sample used in this study is shown in Fig. 1. All the observed diffraction peaks could be indexed to monoclinic $BiVO_4$ of JCPDS File No 75-2480. In the absence of any extra peaks due to possible contaminant, the sample under study is ascertained to be phase pure monoclinic $BiVO_4$.

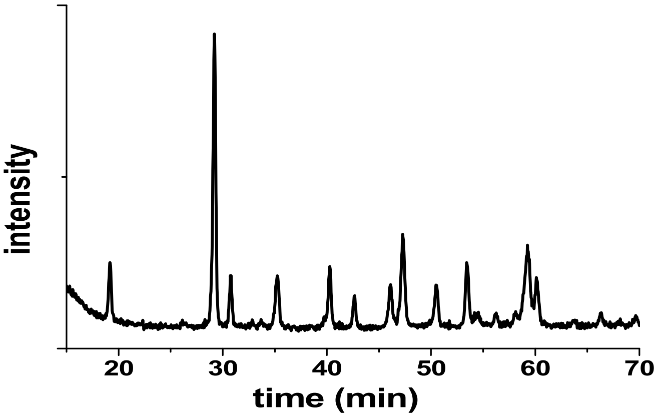

Fig. 1. X-ray diffraction pattern of BiOCl+$NaVO_3$ mixture in 1:1 mole ratio after grinding and washing

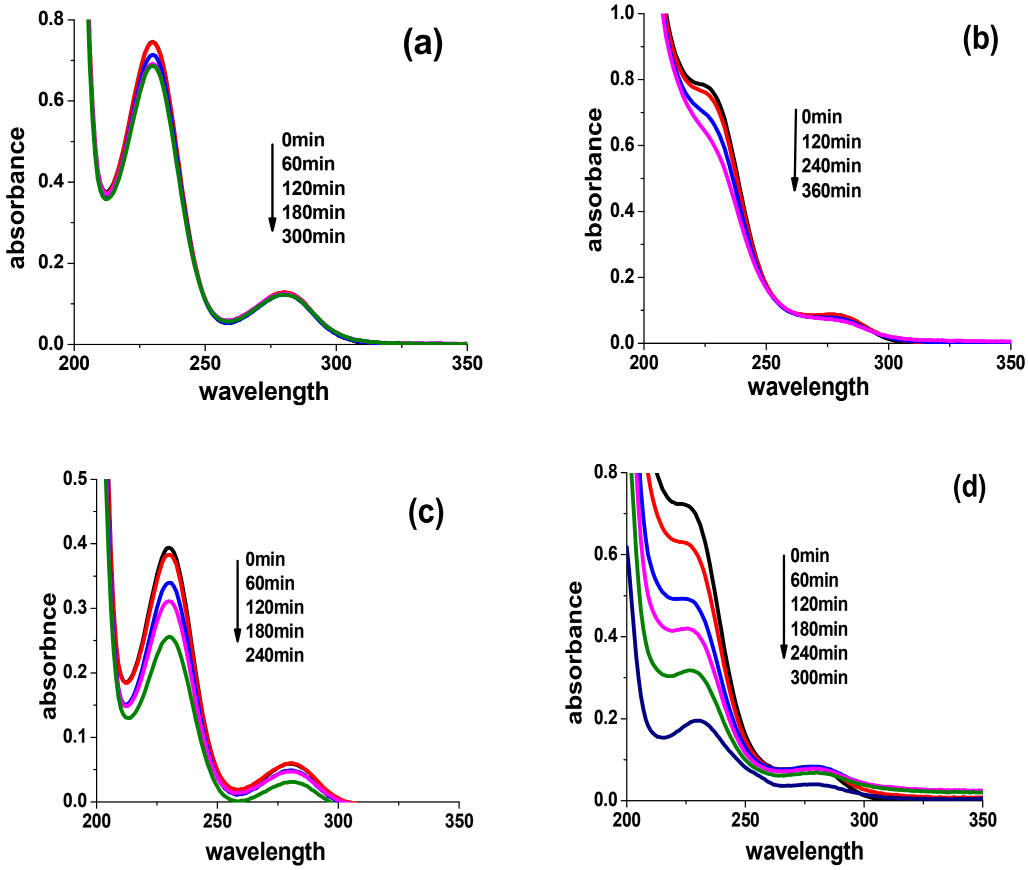

Fig. 2. U.V-visible absorption spectra of (a) aniline, (b) aniline+H_2O_2, (c) aniline+$BiVO_4$, and (d) aniline+$BiVO_4$+H_2O_2 as a function of irradiation time (aniline 5ppm, $BiVO_4$ 100mg, H_2O_2 10 µm)

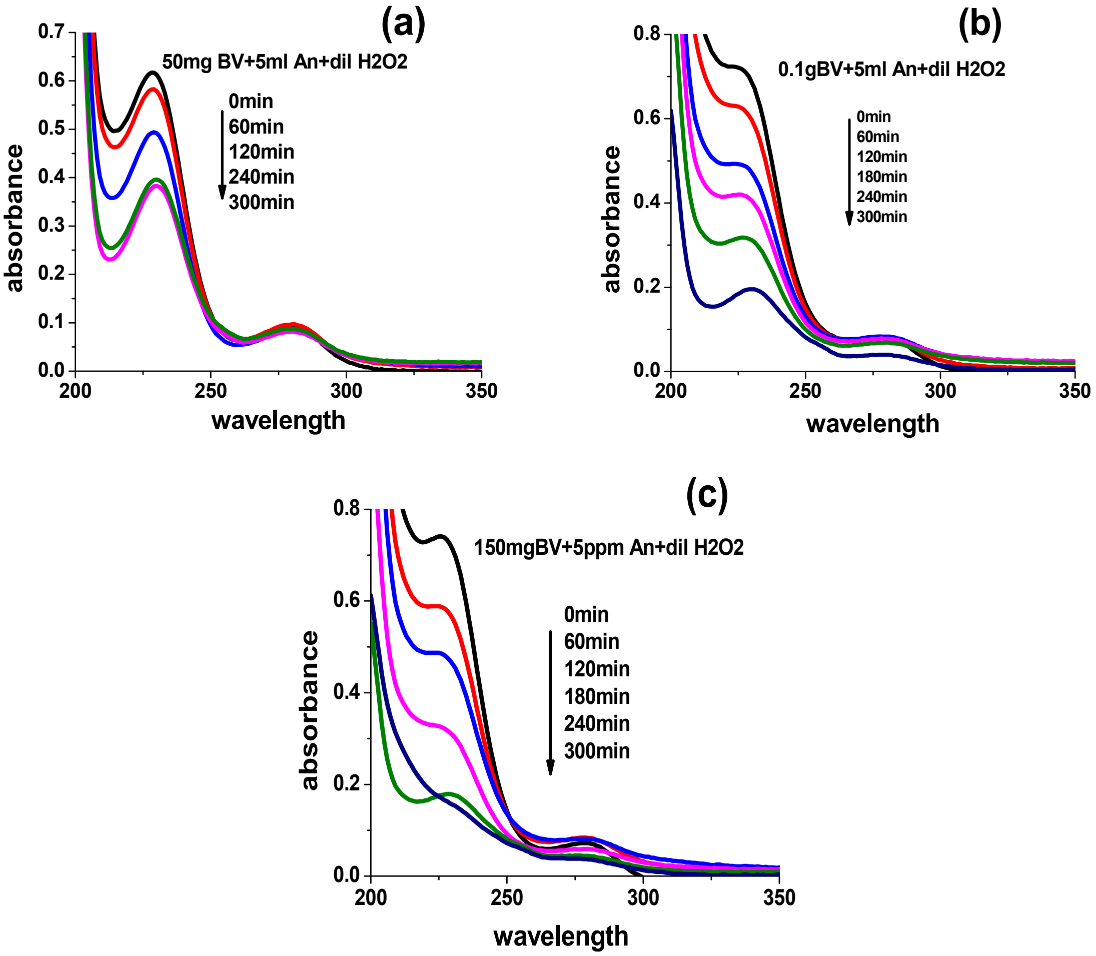

Fig. 3. Variation of spectral intensities for aniline as a function of irradiation time with (a) 50mg, (b) 100mg and (c) 150mg of $BiVO_4$

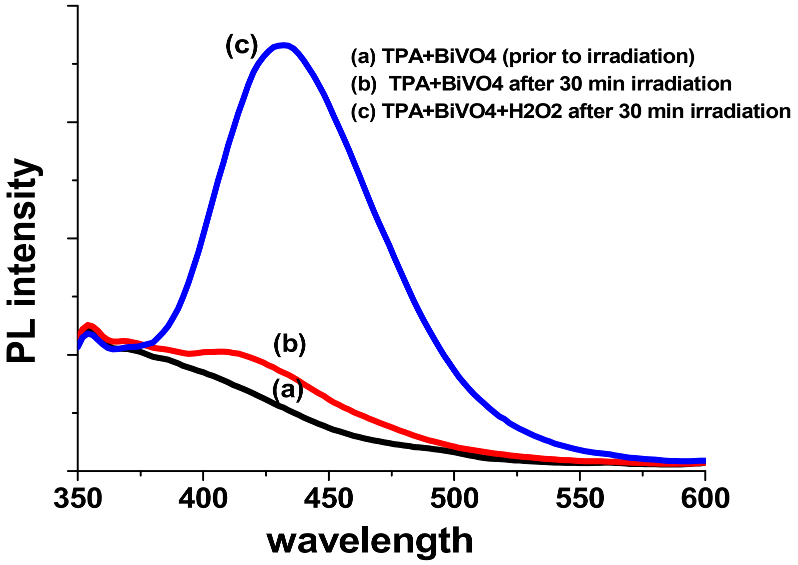

Fig. 4. Photoluminescence spectra of TPA solutions containing $BiVO_4$ in presence and in absence of H_2O_2 before and after irradiation

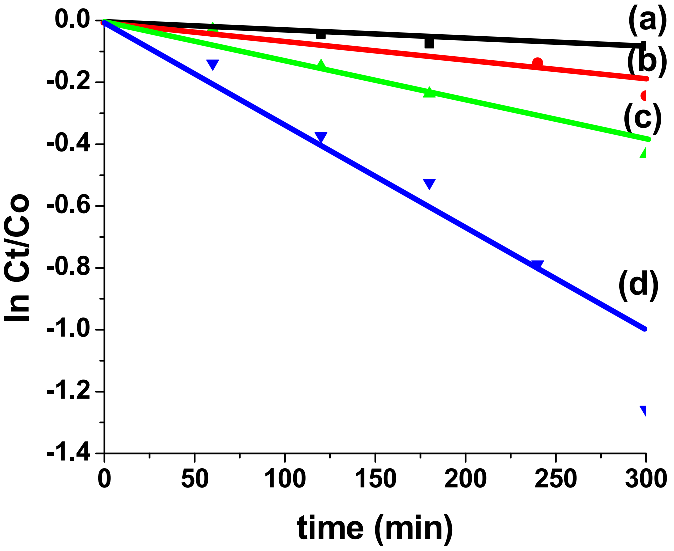

Fig. 5. Plot of ln(Ct/C0) vs irradiation time for (a) aniline, (b) aniline+H_2O_2, (c) aniline +$BiVO_4$ and (d) aniline +$BiVO_4$+H_2O_2

Temporal variation of spectral contours as a function of irradiation time for aniline aqueous solution, aniline+$BiVO_4$, aniline+H_2O_2 and aniline+$BiVO_4$+H_2O_2 are shown in Fig. 2. From the figure it can be seen that aniline exhibits two absorption bands one at 230nm and the other at 280nm attributed to protonated and basic forms of aniline respectively. Further, aniline showed negligible photolysis even for irradiation up to 4h (Fig 2a). Presence of H_2O_2 and $BiVO_4$ alone led to photo degradation of aniline to an extent of 22 and 35% respectively with progressive irradiation up to 5h (Fig 2b and 2c). However, in presence of both $BiVO_4$ and H_2O_2, aniline has undergone photo degradation to a significant extent of nearly 73% (Fig 2d). Since no new absorption peaks are noticed during photo catalytic oxidation, it is presumed that aniline undergoes mineralization directly without forming any detectable intermediates like azobenzene or nitrobenzene. Fig. 3. shows effect of amount catalyst on the photodegradation of aniline. From the figure, it may be observed that 100mg of $BiVO_4$ gives relatively more degradation compared to 50mg. Increase of $BiVO_4$ to 150mg shows the same extent of photodegradation as that for 100mg. Hence, the optimum amount of catalyst in this study seems to be 100mg $BiVO_4$. In view of the observed synergetic effect between $BiVO_4$ and H_2O_2, possible photodegradation mechanism is suggested as follows:

$BiVO_4 + hv \rightarrow e^{-}_{CB} (BiVO_4) + h^{+}_{vB} (BiVO_4)$
$e^{-}_{CB} (BiVO_4) + \text{Dye} \rightarrow \text{Reduced dye}$

$e^{-}_{CB}\,(BiVO_4) + H_2O_2 \rightarrow {}^{\bullet}OH + {}^{-}OH$
$h^{+}_{VB}(BiVO_4)\ + {}^{-}OH \rightarrow {}^{\bullet}OH$
Dye + $^{\bullet}OH$ → degradation products

In order to ascertain generation of $^{\cdot}OH$ radicals during irradiation, Terepthalic acid (TPA) is used as a probe molecule. TPA reacts with $^{\cdot}OH$ radicals to produce 2-hydroxy Terepthalic acid (TAOH) which is highly fluorescent with wavelength intensity around 419nm. Photoluminescence spectra for the solution containing $BiVO_4$ with and without H_2O_2 in presence of Terpthalic acid (TPA) before and after irradiation are shown in Fig 4. The intense peak due to TAOH confirms formation of $^{\cdot}OH$ free radicals during the irradiation process in presence of H_2O_2. In general, photocatalytic degradation reactions are reported to follow pseudo first order kinetics as per Langmuir-Hinshelwood model and a plot of ln C_t/C_o (where C_o and C_t represent concentration of pollutant at time t = t, and t = 0 respectively) versus irradiation time will be a straight line. Fig. 5 shows plot of ln (C_t/C_o) vs t for the photodegradation of aniline aqueous solution, aniline+$BiVO_4$, aniline+H_2O_2 and aniline+$BiVO_4$+H_2O_2. Rate constants calculated from the respective slopes for photocatalytic degradation of aniline+$BiVO_4$ and aniline+$BiVO_4$+H_2O_2 are obtained as 2.0×10^{-4} and 6.0×10^{-4} respectively. The above results indicate that aniline can be photocatalytically degraded to an extent of 75% using H_2O_2 sensitized $BiVO_4$ under visible light in place of energy restrictive U.V radiation without pH adjustment. The process is cost effective, since visible light to an extent of ~ 45% is available from solar radiation.

Conclusion

Monoclinic $BiVO_4$ is used to investigate photocatalytic degradation of aniline in presence of an external oxidant H_2O_2. Photolysis of aniline is negligible but photodegradation of aniline+H_2O_2 and aniline+$BiVO_4$ as a function of irradiation time is 22 and 35% respectively. But in presence of $BiVO_4$+H_2O_2, aniline photodegradation has reached 73% for visible light irradiation of 5h. The synergetic effect is attributed to formation of more $^{\cdot}OH$ free radicals as evidenced by photoluminiscence studies using terpthalic acid as probe molecule.

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