Effective visible light photodegradation of ortho and para- nitrophenols using $BiVO_4$

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***Abstract*— T Photocatalytic degradation of ortho- and para nitrophenols was investigated over $BiVO_4$ under visible light irradiation. $BiVO_4$ degraded ortho nitrophenol completely in 210 min. Rate of degradation enhanced in presence of H_2O_2 and complete degradation was achievd in 120min. Unlike ortho nitrophenol, para nitrophenol showed less photolysis and complete degradation of para nitrophenol was achieved for 120min of irradiation in presence of $BiVO_4$ and H_2O_2.**

***Index Terms*—A2-nitrophenol, 4-nitrophenol, $BiVO_4$, photocatalytic degradation.**

I. Introduction

Phenols and phenolic compounds are common pollutants of aquatic systems. For instance, nitro phenols are common compounds detected in agricultural waste. Similarly, para nitro phenol used in the synthesis of dyes, pharmaceuticals, pesticides, herbicides and explosives is a common constituent in the effluents from industries involved in manufacturing these chemicals. Besides being carcinogenic and mutagenic, para nitro phenol is toxic even to plants, animals and microorganisms. Though different methods have been employed for the remediation of phenols in terms of solvent extraction, adsorption, membrane separation and chlorination, these methods have some inherent drawbacks as they generate secondary pollution due to phase transfer of pollutants. During the last two decades, attention has been focused on the semiconductor mediated heterogeneous photocatalysis for remediation of nitro phenols using different advanced oxidation processes as discussed in different reviews [1-4].

Giuseppe Marci et al [5] reported degradation of 4-nitro phenol (4-NP) using polycrystalline ZnO/TiO_2 under U.V irradiation for 150min and continuous oxygen bubling. Di Paola et al [6] studied photocatalytic activity of TiO_2 impregnated with various transition metal ions for 4-NP degradation using 150min of U.V. irradiation. Kashif Naeem and Feng Ouyang [7] reported 35% photocatalytic degradation of 4-NP under U.V irradiation for 120min over TiO_2 dispersed on active carbon, ZSM-5, SiO_2 and rice husk. Lixia Yang et al [8] reported degradation of 4-NP over Cu deposited on TiO_2 heterojunction in 250min under solar light. Hasan Ilyas et al [9] reported 80% degradation of 4-NP over Ag-TiO_2 particles under U.V irradiation for 60min. Wan-Jun Sun et al [10] reported 90% degradation of 4-NP under visible light over Cu porphyrin-TiO_2 +H_2O_2. Rahmatollah Rahimi and co workers [11] studied photodegradation of 4-NP over N, S codoped TiO_2 under visible light irradiation for 180min. Hond Ben Ybt Suida and Bassem Jamoussi [12] reported 98% degradation of 4-NP over TiO_2-Zinc pthallocyanin under solar light and oxygen bubling for 60min. Lu Pan et al [13] reported 90% degradation of 4-NP in 180min over $CuCr_2O_4$ and H_2O_2 under visible light irradiation. Safa et al [14] reported 98% degradation of 4-NP in 180min over ZnO-nano flowers under U.V irradiation. Shafiqual Islam et al [15] reported 90% degradation of 4-NP in 120min over TiO_2+H_2O_2 under U.V irradiation and observed that addition of Cu^{2+} enhances the percent degradation but excess of Cu^{2+} decreases the degradation. Sugiyama et al [16] reported that the degradation capability of ZnO particles towards 4-NP under solar radiation was superior to U.V light irradiation. Zhigang Xiong and coworkers [17] reported 90 to 100% degradation of 4-NP in 300min over Au and Pt-TiO_2 composites under visible light. Si Zhan Wu and coworkers [18] reported 90% degradation of 4-NP in 360min over graphitic carbon-nitride (g-C_3N_4). Hong Xu GuO et al [19] reported 90% degradation of 4-NP over $Zn_3(VO_4)_2$ under visible light. Radwa Elsalamony and Dalia Abd El- Hafiza [20] reported degradation of 4-NP in 150min over Cu-TiO_2 under U.V irradiation. Nguyen Quang Long et al [21] reported degradation of 4-NP over Fe_3O_4 –N-doped TiO_2 under visible light with continuous air bubbling. Hyun-Gyu Lee et al [22] reported degradation of 4-NP under visible light using TiO_2-graphene-palladium nanowires. Khadija Eddanani et al [23] reported degradation of 4-NP over $Li_{0.5}M_{0.5}Ti_2(PO_4)_3$ (M=Ni, Co and Mn) + H_2O_2 under visible light. Jing Zhang et al [24] reported 80% degradation of 4-NP in 180min over TiO_2-Sn-Porphyrin nanoparticles under visible light irradiation. Suranjan Sikdar, and Coworkers [25] studied degradation of 4-NP over $M_xNb_xTi_{1-2x}O_{2+x/2}$ M=Cr, Fe; X=0.01-0.2) under U.V irradiation. To our knowledge, so far there are no studies reported on photocatalytic degradation of nitro phenols using $BiVO_4$ although $BiVO_4$ is reported to be an excellent visible light responding photocatalyst for the degradation of several dyes [26].

In view of the above, the present work is under taken to investigate the degradation of ortho nitrophenol and para nitrophenols using $BiVO_4$ as photocatalyst in presence of an external oxidant H_2O_2 under visible light irradiation without any air/oxygen bubbling.

II. MATERIALS AND METHODS

A. Synthesis

Monoclinic $BiVO_4$ is synthesized using room temperature solid-state metathesis reported elsewhere [27] from this laboratory. A.R.grade $BiCl_3$ (Loba) was used as precursor along with Na_3VO_4 (Aldrich). Stoichiometric quantities of reactants in 1:1 molar ratio were weighed and ground thoroughly in an agate mortar for 2hrs in presence of ethanol. The mixture immediately turned to canary yellow in colour. The homogenized mixture was washed with distilled water to

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remove NaCl bye product and dried at room temperature. The dried sample was used for phase identification and catalytic studies.

B. Characterizations

Phase identification of the sample was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-Kα radiation (λ= 1.54059 Å), over a range of $10^o \leq 2\theta \leq 80^o$ with a scan rate of 2^o min^{-1}.

C. Photocatalytic studies

Photo catalytic activity of $BiVO_4$ was evaluated in terms of degradation of ortho and para nitro phenols under visble ight. 10 mg of the catalyst powder was added into 100ml 2-NP/4-NP aqueous solution (10 mg/L). Before irradiation, the above suspension was magnetically stirred for 30 minutes. The suspension was then exposed to 400 W metal halide lamp; 5ml aliquots were pipetted at periodic time intervals. Progress of decolorization was followed by recording the corresponding absorption spectrum. All the experiments were conducted under ambient conditions. Percent degradation of dye was computed using the relation

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

where A_0 and A_t are respectively initial absorbance and absorbance at time't'

III. RESULTS AND DISCUSSION

$BiVO_4$ has been reported to exist in three polymorphic modifications namely Tetragonal zircon, Monoclinic scheelite and Tetragonal scheelite. Of these three crystalline modifications, only the monoclinic form of $BiVO_4$ exhibits visible light induced photocatalytic activity. Fig. 1 depicts X-ray diffraction (XRD) pattern of $BiVO_4$ sample prepared by solid-state metathesis reaction. All peaks in the XRD pattern could be assigned to monoclinic $BiVO_4$ of JCPDS File NO 83-1698. Absence of peaks due to any contaminant suggests that the sample obtained is phase pure $BiVO_4$ of monoclinic structure.

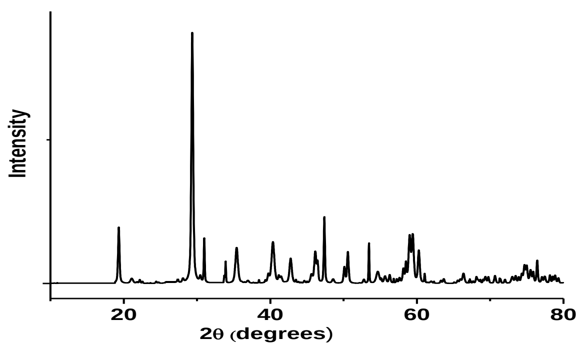

Fig. 1. X-ray diffraction pattern of resultant ground mixture of reactants after washing

In the degradation of dyes with different chromophores, three different approaches were proposed in literature to enhance the photocatalytic quantum efficiency of $BiVO_4$. These are (i) synthesis of phase pure monoclinic $BiVO_4$ crystalline modification (ii) preparing high surface area $BiVO_4$ through high energy facets and (iii) formation of special architecture composites such as Bi_2O_3-$BiVO_4$, Bi_2S_3-$BiVO_4$, Fe_2O_3-$BiVO_4$ etc. Since synthesis of nano $BiVO_4$ with high surface area or with special architecture is not cost effective and not viable for large scale industrial applications, addition of external oxidant H_2O_2 is taken up in this study to enhance the photocatalytic efficiency of m-$BiVO_4$ because addition of H_2O_2 has been reported to be beneficial in degradation of several dyes over different photocatalysts [28].

Reports on photocatalytic degradation of ortho nitrophenol (2-NP) are somewhat limited as compared to that of 4-NP. Di Paola et al [29] reported photocatalytic degradation of 2-NP over TiO_2 under U.V irradiation for 240min. Priya and Giridhar [30] reported degradation of 2-NP over TiO_2 under U.V irradiation for 150min. Asha and Sharma [31] reported degradation of 2-NP over Ag-TiO_2 under U.V. irradiation for 360min of irradiation. Jingtao Dai et al [32] reported degradation of 2-NP over TiO_2 nanoparticles synthesized by hydrothermal method using ionic liquids. Aslam et al [33] reported enhanced photocatalytic activity of V_2O_5-ZnO composites for the mineralization of 2-NP for 150min of irradiation under sun light. Temporal variation of spectral contours for 2-NP, 2-NP+H_2O_2, 2-NP+$BiVO_4$ and 2-NP+$BiVO_4$+H_2O_2 as a function of irradiation time are shown in Fig 2.

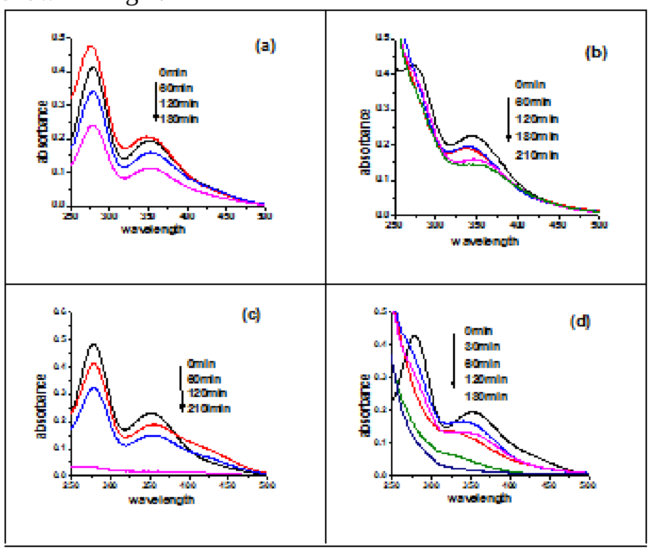

Fig 2. Temporal variations of spectral contours for (a) 2-NP, (b) 2-NP+H_2O_2, (c) 2-NP+$BiVO_4$, and (d) 2-NP+$BiVO_4$+H_2O_2 as a function of irradiation time.

From the spectra it can be seen that 2-NP exhibits two absorption peaks at λ= 275 and 350nm and undergoes slow photodegradation to an extent of ~42% for irradiation of 180min (Fig 2(a)). In presence of H_2O_2, 2-NP shows photodegradation to an extent of ~36% for irradiation of 210min (Fig 2(b)). However, in presence of $BiVO_4$ the intensities of both peaks become zero indicating complete degradation (Fig 2(c)) for 210min of irradiation. The rate of photodegradation of 2-NP is found to be expedited in presence of H_2O_2 since 100% degradation is achieved in 180 min (Fig 2(d)). Fig. 3 shows variation of spectral intensities of 2-NP as a function of irradiation time for 20, 30 and 50mg of catalyst. From the figure it can be seen that 20mg of $BiVO_4$ is the optimum amount of catalyst required for complete degradation in 120min.

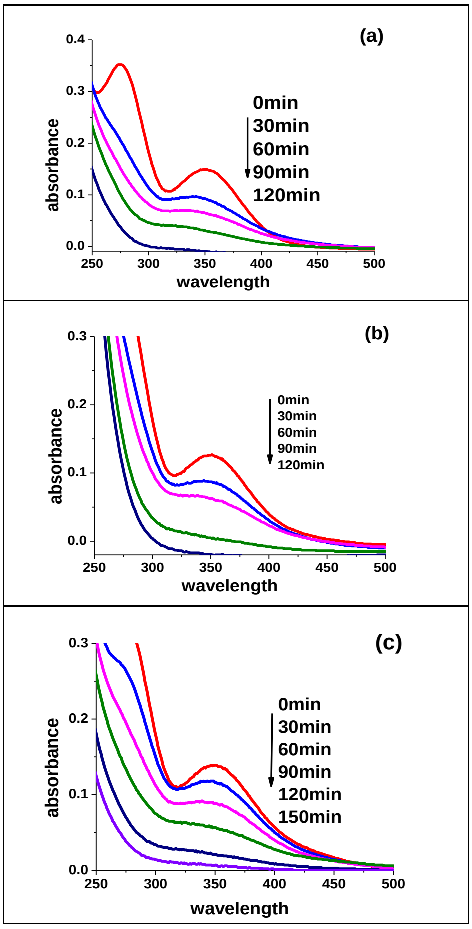

Fig. 3. Temporal variation of spectral changes of 2-NP with (a) 20mg, (b) 30mg and (c) 50mg of photocatalyst in presence of H_2O_2 as a function of irradiation time

The above data clearly indicates that 2-NP can be successfully degraded over $BiVO_4$ in presence of H_2O_2. Fig. 4 depicts temporal variation of spectral contours for 4-NP, 4-NP+H_2O_2, 4-NP+$BiVO_4$ and 4-NP+$BiVO_4$+H_2O_2 as a function of irradiation time.

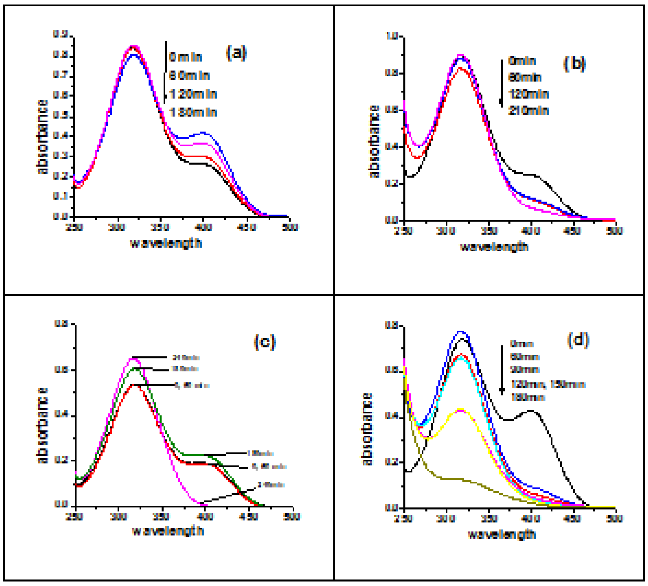

Fig 4. Temporal variation of spectral contours for (a) 4-NP, (b) 4-NP + H_2O_2, (c) 4-NP + $BiVO_4$, and (d) 4-NP + $BiVO_4$ + H_2O_2 as a function of irradiation time.

The spectra in Fig 4 (a) indicates characteristic absorption for 4-NP at 310 along with a shoulder at 400 nm. From the figure it can be seen that both 4-NP and 4-NP+H_2O_2 undergo very less photodegradation with progressive irradiation up to 210min (Fig 4 a and b). In contrast to 2-NP, degradation of 4-NP in presence of only $BiVO_4$ is not observed (Fig.4(c)). However, in presence of H_2O_2 and $BiVO_4$, intensities of both peaks decrease to zero indicating near complete degradation of 4-NP for 150min of irradiation (Fig 4(d)). Fig. 5 depicts variation of spectral intensities as a function of irradiation time for 4-NP with 20, 30 and 50mg of photocatalyst keeping the concentrations of 4-NP as well as H_2O_2 unchanged.

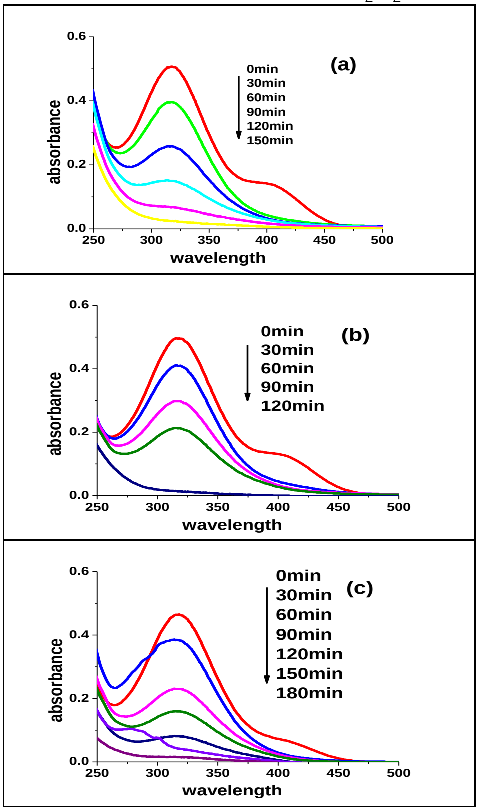

Fig. 5. Temporal variation of spectral changes of 4-NP for (a) 20mg, (b) 30mg and (c) 50mg of photocatalyst in presence of H_2O_2 as a function of irradiation time

From the figure it can be seen that 30mg of $BiVO_4$ is the optimum amount of catalyst required for irradiation of 120min. Based on the experimental data, the photocatalytic degradation mechanism in presence of H_2O_2 can be given as follows.

$BiVO_4 + h\nu \rightarrow e^{-}_{CB} (BiVO_4) + h^{+}_{VB} (BiVO_4)$

$e^{-}_{CB} (BiVO_4) + H_2O_2 \rightarrow {}^{\cdot}OH + {}^{-}OH$

$h^{+}_{VB}(BiVO_4) + {}^{-}OH \rightarrow {}^{\cdot}OH$

2-NP/4-NP + $^{\cdot}OH$ → degradation products

The above results show that $BiVO_4$ can be used as a successful photocatalyst for complete degradation of both ortho and para-nitrophenol in the visible region in presence of H_2O_2 without any O_2 or air bubbling.

CONCLUSIONS

Complete photocatalytic degradation of ortho and para nitrophenols was successfully achieved by photocatalysis over $BiVO_4$ in presence of H_2O_2 under visible light irradiation. $BiVO_4$ effected photocatalytic degradation of ortho nitrophenol even in the absence of H_2O_2 and the degradation rate increased in presence of H_2O_2. $BiVO_4$ degraded para nitrophenol completely only in presence of H_2O_2.

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