



Effective Visible Light Photocatalytic Degradation of Congo Red And Fast Sulphon Black F Using H₂O₂ Sensitized BiVO₄

A.M. Umabala*, P. Suresh and A.V. Prasada Rao

*Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam-530 003, **INDIA**

Email: umabala.au@gmail.com

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ABSTRACT

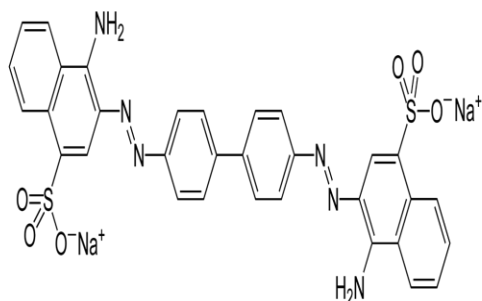
BiVO₄ prepared by solid-state metathesis is used as photocatalyst to degrade 5ppm Congo red and 20ppm Fast sulphon black F dyes in presence of external oxidant H₂O₂. Congo red and Fast sulphon black F got degraded in 90min and 30min respectively under visible light irradiation. BiVO₄ and H₂O₂ exhibited synergetic effect in generating [•]OH free radicals which enhanced the photocatalytic efficiency.

Keywords: Photocatalysis, Congo red, Fast sulphon black F, Bismuth vanadate, Solid-State metathesis.

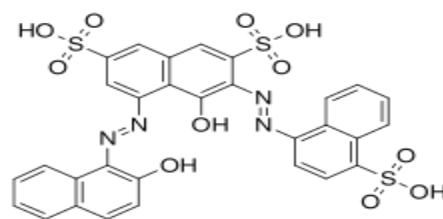
INTRODUCTION

Synthetic dyes are extensively used in textile, paper, cosmetic, pharmaceutical and food industries. Nearly 10-15% of these dyes are discharged in to waste water in the form of unutilized remnant dyes. Since many of the dyes are toxic, less-biodegradable, carcinogenic/mutagenic and impart intense colour to aqueous solutions, their removal from industrial effluents prior to discharge is of prime importance. Though several methods based on physical, chemical, biological, catalytic and electrochemical processes have been proposed for the remediation of hazardous organic pollutants, these techniques suffer from some inherent drawbacks either in the form of generating secondary pollutants by phase transfer or impose cumbersome technology. During the past two decades, a good number of studies are focused on advanced oxidation processes (AOPs) that include U.V, U.V+H₂O₂, Fenton, Photo Fenton and heterogeneous photocatalysis for the non selective remediation of several organic pollutants. Among the AOPs, semiconductor mediated heterogeneous photocatalysis offers a distinct advantage of complete mineralization of pollutant at ambient temperature without formation of any hazardous intermediates. Ease of synthesis, high photo stability, good chemical as well as biological inertness, and good photocatalytic efficiency rendered TiO₂ as the most useful photocatalyst. However, the wide band gap of 3.2 eV associated with TiO₂ restricts its absorption to U.V region, making the process less cost effective. Hence, in order to shift the TiO₂ absorption into visible region, three different approaches are pursued in literature [1] – (i) doping with transition metal atoms, cations and/or anions (ii) coating with a sensitizer and (iii) forming a nano composite. Even though these methods succeeded in shifting the absorption of TiO₂ from U.V to visible region, they showed only a limited range of success in terms of cost effectiveness and ease of synthesis. Consequently, efforts are now focused on ternary metal oxides such as ZnWO₄ [2], BiVO₄ [3, 4], Bi₂MoO₆ [5], Bi₂Mo₃O₁₂ [6, 7], Fe₂Mo₃O₁₂ [8] etc. as alternate photocatalysts.

Congo red, a benzidine based diazo dye is used in textile, printing and dyeing industries. It is toxic and banned in many countries. Its structural stability makes it highly resistant to biodegradation. When released in to environment, the remnant dye causes damage to living organisms by blocking sun light and stopping deoxygenating capacity of water. Removal of such pollutants therefore is a major environmental concern. The aim of the present study is to investigate whether Congo red and Fast sulphon black F can be completely degraded using H₂O₂ sensitized BiVO₄ under visible light irradiation. Chemical structures of Congo red (CR) and Fast sulphon black F (FSB-F) are given below.



Congo red



Fast sulphon black F

MATERIALS AND METHODS

Synthesis of Photocatalyst: BiVO₄ is prepared by room temperature solid-state metathesis synthesis reported elsewhere [4]. Stoichiometric amounts of Bi OCl (Loba Chemie PVT. Ltd) and NaVO₃ (98% HIMEDIA) in the molar ratio of 1:1 are mixed in an agate mortar and ground for 2h in ethanol. After grinding, the mixture is set aside for 12h and washed several times with distilled water to completely remove the bye product Na Cl 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.

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} .

Photocatalytic studies: Photo catalytic activity of BiVO₄ was evaluated in terms of degradation of FSB-F under visible light 100 mg of the catalyst was dispersed in 100mL FSB-F aqueous solution (20 mg L^{-1}) 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 W 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 same procedure has been adopted for (5 mg/L) CR dye. All the experiments were conducted under ambient conditions. 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: 50mg BiVO₄ catalyst is added to 100mL of terphthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution). The solution is stirred for 15min in dark followed by irradiation from 400W metal halide lamp for 30min. The reacted solution was centrifuged and clear

solution is used for photoluminescence measurements using spectrofluorometer (Fluoromax 4) with excitation wavelength of 315nm.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) pattern of the ground mixture of $\text{BiOCl}+\text{NaVO}_3$ after washing is shown in fig. 1. The XRD pattern is in agreement with that of monoclinic BiVO_4 of JCPDS File No. 75-2480. Absence of peaks due to reactants or other Bi-V phases confirms that the sample is phase pure BiVO_4 of monoclinic structure.

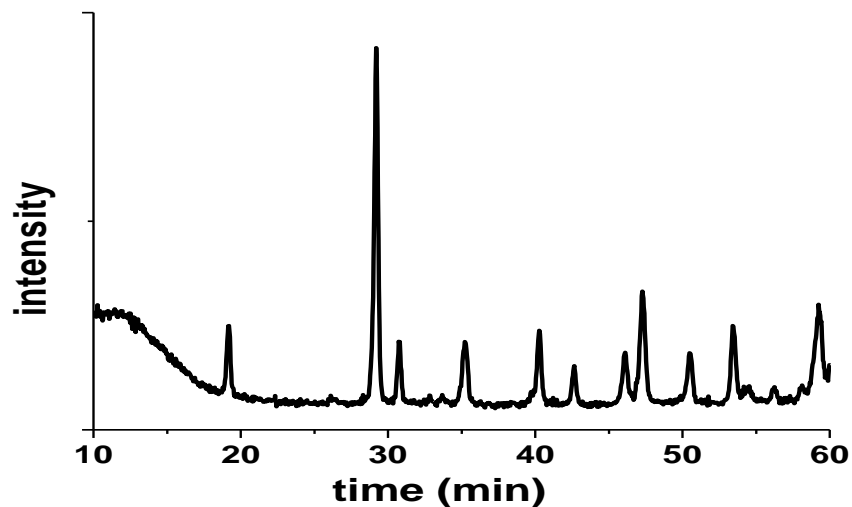


Figure1. X-ray diffraction pattern of $\text{BiOCl}+\text{NaVO}_3$ mixture in 1:1 mole ratio after grinding and washing

Photocatalytic degradation of Congo red has been reported under U.V. irradiation over nano SnO_2 [9], nano TiO_2 [10], ZnO [11], ZrO_2 [12], $\text{TiO}_2/\text{Fe}_3\text{O}_4$ [13], Fe_2O_3 [14], TiO_2 and ZnO [15], anatase TiO_2 [16], $\text{CuInS}_2\text{-ZnO}$ nano composite [17] and TiO_2 P25 [18]. Photodegradation of Congo red has also been reported under visible light irradiation over nanoporous polyoxotungstate – anatase composite [19], nano CdS [20], NiS [21], $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ [6] and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ [8]. Temporal variations of spectral contours for aqueous solution of CR (10ppm), CR (10ppm)+ BiVO_4 , CR+ H_2O_2 , and CR+ BiVO_4 + H_2O_2 as a function of irradiation time are shown in fig. 2. As seen from the figure CR shows a characteristic absorption at $\lambda_{\text{max}}=500\text{nm}$. Progressive exposure of CR aqueous solution to visible light did not show any significant photolysis even up to 180min of irradiation (Fig. 2(a)). Similarly CR solution containing H_2O_2 also did not show considerable photolysis for irradiation up to 180min (Fig. 2(b)). However, CR solution in presence of BiVO_4 showed good photodegradation for irradiation of 120min (Fig. 2(c)). CR aqueous solution containing both BiVO_4 and H_2O_2 showed gradual decrease in absorption intensity as a function of irradiation time and complete decoloration occurred for irradiation of 90min (Fig. 2(d)).

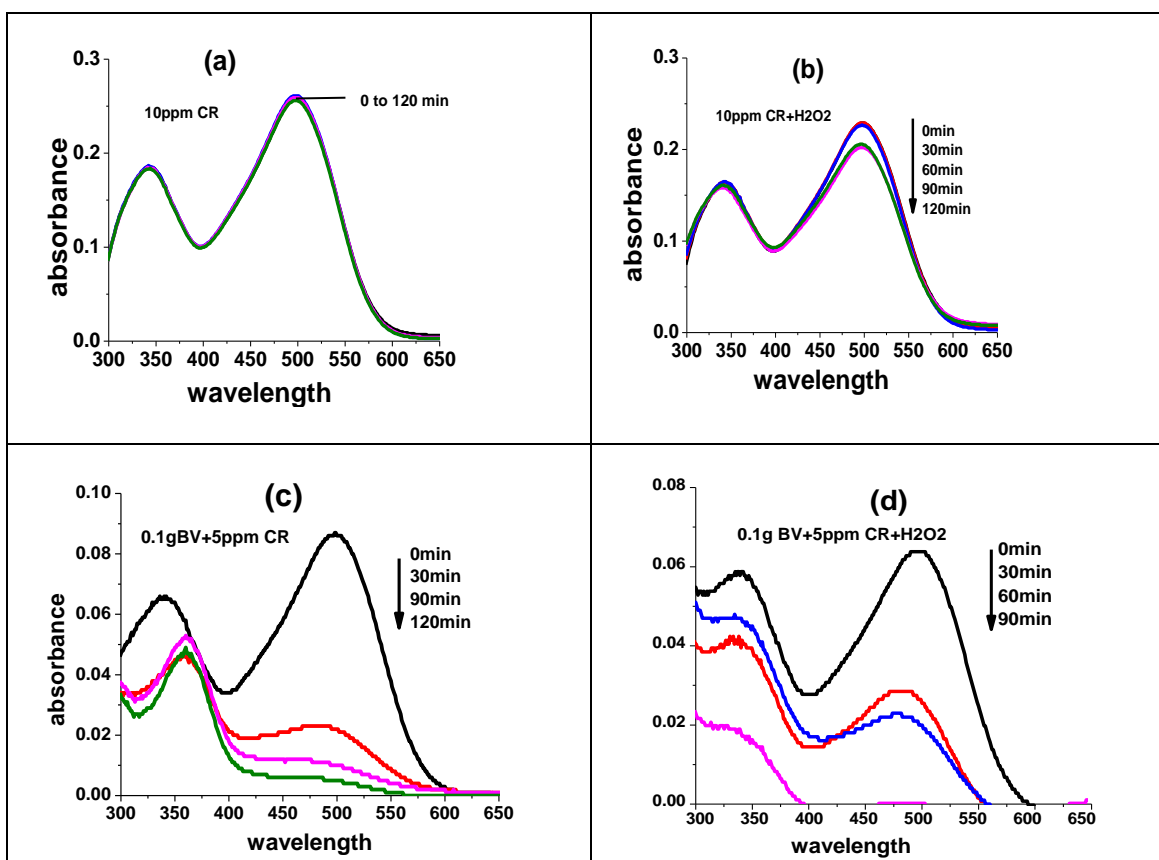
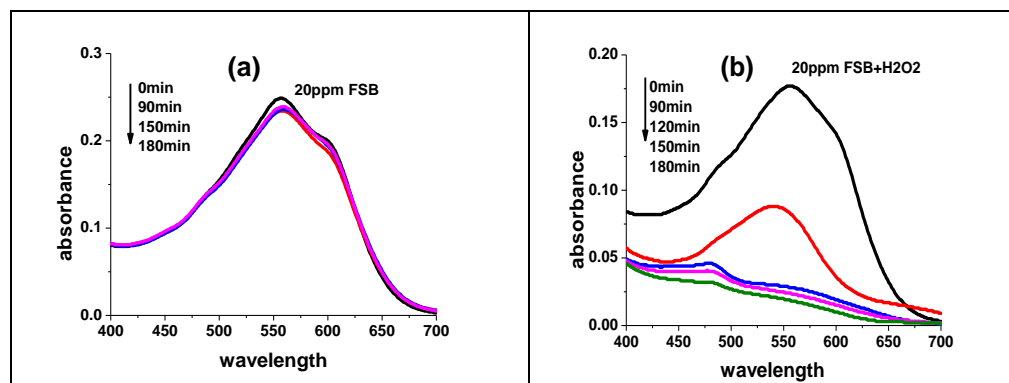


Figure 2. Temporal variations of spectral contours for (a) CR, (b) CR+H₂O₂, (c) CR+BiVO₄ and (d) CR+BiVO₄+H₂O₂ as a function of irradiation time.

Temporal variations of spectral contours for FSB-F, FSB-F+BiVO₄, FSB-F+H₂O₂ and FSB-F+BiVO₄+H₂O₂ as a function of irradiation time are shown in Fig. 3. From the figure, it can be seen that FSB-F has a characteristic absorption at $\lambda_{\text{max}} = 550\text{nm}$ and does not show any photolysis for irradiation up to even 180min (Fig. 3(a)). In presence of BiVO₄, FSB-F shows gradual photodegradation to an extent of 80% for irradiation up to 180min as seen in Fig. 3(b). Presence of H₂O₂ alone also induces photodegradation of FSB-F to an extent of 89% for irradiation of 180min (Fig. 3(c)). Nevertheless, combination of BiVO₄+H₂O₂ shows a synergetic effect and renders rapid photodegradation of FSB-F for 30min of irradiation (Fig. 3(d)).



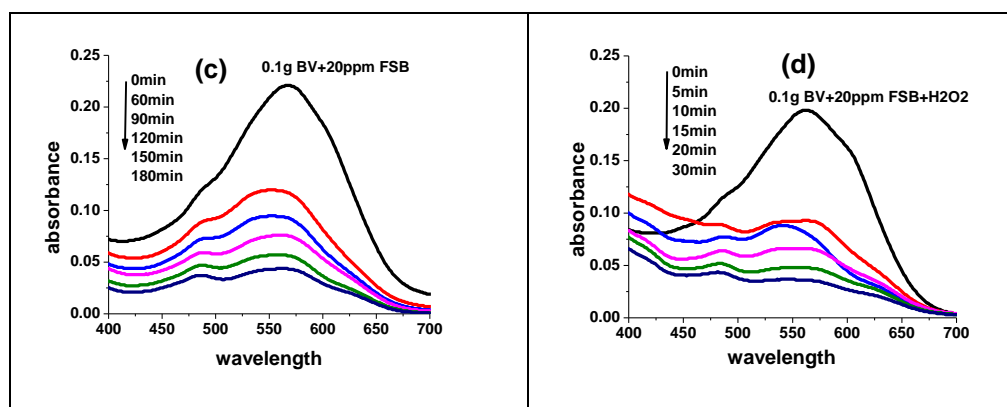


Figure 3. Temporal variations of spectral contours for (a) FSB-F, (b) FSB-F + H₂O₂, (c) FSB-F + BiVO₄, (d) CR + BiVO₄ + H₂O₂ as a function of irradiation time.

Plots of $\ln(C_t/C_0)$ vs time for the degradation of CR and FSB-F under different conditions are shown in fig. 4. Rate constants calculated from respective slopes are given in table 1.

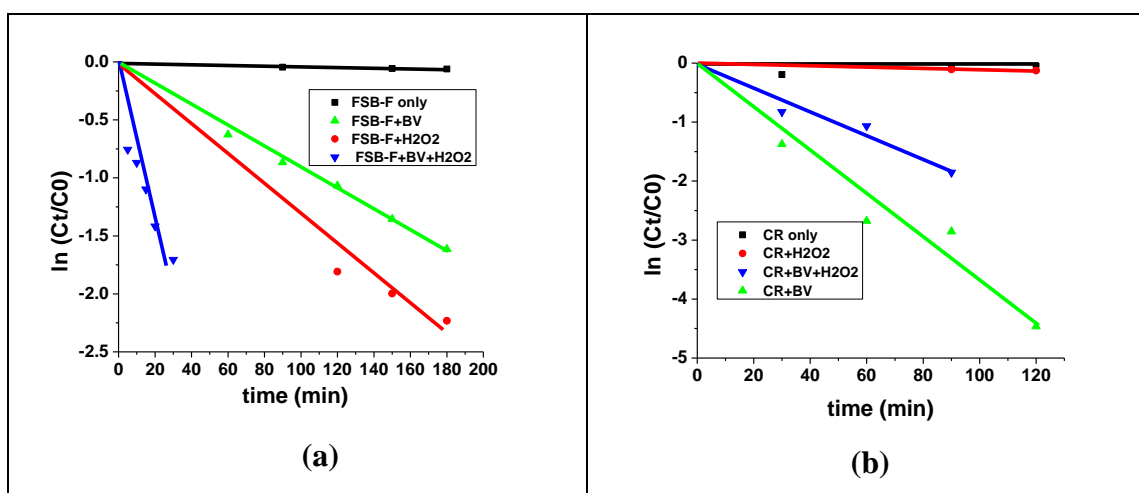
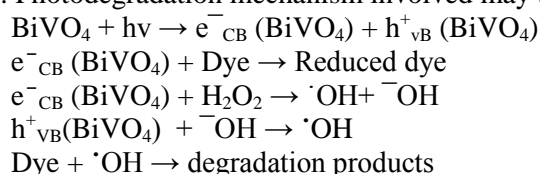


Figure 4. Plot of $\ln(C_t/C_0)$ vs irradiation time for (a) CR, CR + BiVO₄, CR + H₂O₂ and CR + BiVO₄ + H₂O₂ and (b) FSB-F, FSB-F + BiVO₄, FSB-F + H₂O₂ and FSB-F + BiVO₄ + H₂O₂

Table 1. Calculated rate constants for photodegradation of FSB-F, CR with and without catalyst and H₂O₂

photodegradation	Rate constant k (min ⁻¹)
CR + BiVO ₄	3.0 × 10 ⁻⁴
CR + BiVO ₄ + H ₂ O ₂	2.2 × 10 ⁻⁴
FSB-F + BiVO ₄	5.0 × 10 ⁻⁵
FSB-F + H ₂ O ₂	7.0 × 10 ⁻⁵
FSB-F + BiVO ₄ + H ₂ O ₂	2.2 × 10 ⁻³

The above results clearly indicate a beneficial effect of the addition of H₂O₂ on photocatalytic degradation of both Congo red and FSB-F. Photodegradation mechanism involved may be suggested as given below



In order to ascertain the formation of $\cdot\text{OH}$ radicals, Terphthalic acid (TPA) is used as a probe molecule. TPA reacts with $\cdot\text{OH}$ radicals to produce 2-hydroxy Terphthalic acid (TAOH) which is highly fluorescent with wavelength intensity around 419nm. Photoluminescence spectra of the TPA solution containing BiVO_4 with and without H_2O_2 are shown in fig 5. The intense peak at 419nm due to TAOH confirms the formation of $\cdot\text{OH}$ free radicals during irradiation process.

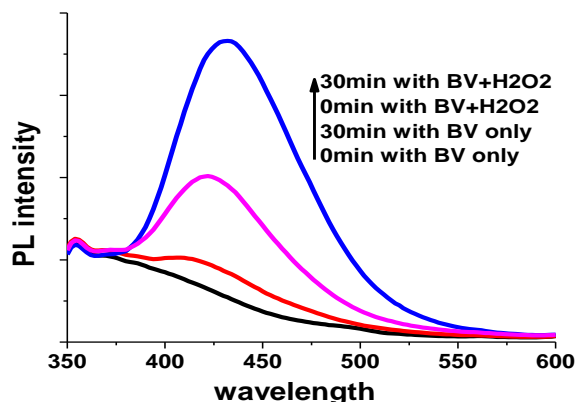


Figure 5. Photoluminescence spectra of TPA solution containing BiVO_4 photocatalyst in presence and in absence of H_2O_2 before and after irradiation for 30min

CONCLUSIONS

Photocatalytic degradation of 5ppm Congo red and 20ppm Fast sulphon black F was achieved in 90min and 30min of visible light irradiation over BiVO_4 in presence of H_2O_2 . Synergetic effect between photocatalyst and H_2O_2 led to generation of more OH free radicals. Consequently, breakdown of molecular frame work of Congo red and Fast sulphon black F occurred rapidly, compared to photodegradation by BiVO_4 alone.

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AUTHORS' ADDRESS

1. **A.M. Umabala**

Department of Inorganic and Analytical Chemistry,
Andhra University, Visakhapatnam-530 003, INDIA.
Email: umabala.au@gmail.com