

**Visible-light-induced degradation of Rhodamine-B and Methylene Blue by combustion synthesized ZnWO₄****P. Suresh^{*}, U. Sujana Kumari and A. V. Prasada Rao**^{*}Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam, 530003, **INDIA**Email: sureshp12345@gmail.comReceived on 31st October and finalized on 04th November 2013**ABSTRACT**

Phase pure monoclinic ZnWO₄ has been prepared by glycine combustion method at 400^oC. The calcined powder showed a band gap of 3.2eV as calculated from UVDRS. SEM studies revealed particle size in the sub micro meter region with lot of aggregation. ZnWO₄ powder prepared by this method showed photocatalytic degradation to an extent of 80% for 5ppm Rhodamine B in 100ml aqueous solution and 96% for 5ppm Methylene Blue in 100ml aqueous solution under visible light irradiation from 400 W high pressure mercury vapour lamp for 120 min and 90 min respectively. Initial pH prior to exposure is found to effect the degradation of both Rh-B and MB to a significant extent.

Keywords: ZnWO₄, Visible light degradation, Rhodamine-B, Methylene Blue, Combustion synthesis.**INTRODUCTION**

Semiconductor metal oxides such as TiO₂, WO₃, CeO₂, ZnO and mixed metal oxides like LaFeO₃, SrTiO₃, NaTaO₃, BiVO₄, Bi₂WO₆ have been found to be highly useful for photocatalytic degradation of organic pollutants in waste water as well as for photochemical decomposition of water. Among the various metal oxides, TiO₂ is studied extensively because of its high photocatalytic activity, high chemical stability, low photo corrosion and low cost. Nevertheless, since the absorption of TiO₂ lies predominantly in the UV region, search for newer non TiO₂ based visible light activated photocatalysts is still actively pursued. Recently, some tungstates have been reported to show good photocatalytic activity for mineralisation of organic pollutants under U.V radiation and of the various bivalent transition metal tungstates studied, ZnWO₄ has been reported to be promising [1].

ZnWO₄ crystallises in monoclinic wolframite structure, with C_{2h} point group symmetry, P2/c space group and consists of infinite zigzag chains of either edge-sharing ZnO₆ or WO₆ octahedra parallel to [0 0 1]. Preparation of ZnWO₄ has been reported by many investigators in terms of solid-state synthesis [2], sol-gel [3-4], hydrothermal [5-9], decomposition of polymeric complex [10], coprecipitation [11] solid-state metathesis [12] and ethylene glycol combustion methods [13]. Enhancement of photocatalytic performance of ZnWO₄, through fabrication of thin films, nanorods, nanoparticles (doped with F, Cl, Eu, Cd, Ag) and formation of hetero junctions/composites with g-C₃N₄, graphite, BiOI, Bi₂WO₆ and ZnO have also been reported in literature [14-22]. Survey of existing literature on the use of ZnWO₄ as photocatalyst for

degradation of Methylene Blue, Rhodamine B, phenol, 4-chlorophenol, salicylic acid, Acetaldehyde and Methyl orange indicated that (i) except for one report on methylene blue [1] all other studies made use of U.V irradiation around 254 nm (ii) effect of pH on photocatalytic activity was not investigated and (iii) no degradation studies were reported on glycine combustion synthesized ZnWO_4 . In view of above, the present study is undertaken to assess the visible light activity of combustion synthesised ZnWO_4 for photocatalytic degradation of Rhodamine B and Methylene blue under two different pH conditions.

MATERIALS AND METHODS

Synthesis of Catalyst: Zinc tungstate is prepared by solution combustion synthesis. 4 mmol of $\text{Zn}(\text{NO}_3)_2$, 4mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and appropriate amount of glycine to maintain oxidant/fuel ratio 1:1 were dissolved separately in 30ml portions of deionised water. All the three solutions were mixed and stirred for half an hour on a magnetic stirrer and the resulting precursor suspension was heated on a hot plate at 110°C under stirring until the solution becomes viscous and evolution of large amounts of brown fumes is intensified. The resultant mass was ground for 10 minutes and calcined at 400°C for 4hrs followed by washing with distilled water until it is free from sodium. The calcined and washed powder was used for phase identification.

Characterization Techniques: Phase purity of the calcined and washed powder was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), over the range of $10\text{-}80^\circ$ with a scan rate of 2° min^{-1} . Diffuse reflectance UV-visible spectrum (UVDRS) of the sample was measured for the dry pressed disk samples using Shimadzu UV-visible spectrophotometer (UV-3600) between 200 to 800 nm range. Spectral grade BaSO_4 was taken as reference for the reflectance spectra. Microstructural investigations of the samples were performed on the powders of the samples using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

Photocatalytic activity: Photocatalytic activity of ZnWO_4 was evaluated in terms of degradation of Rhodamine B (RhB) and Methylene Blue (MB) under visible light emanating from 400 W high power mercury vapour lamp as a light source for irradiation. UV radiation below 350nm is eliminated by surrounding the sample with a water jacket. 100 mg of ZnWO_4 was added into 100ml RhB solution (5 mg L^{-1}) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye. The suspension was then exposed to light emanating from the source, 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron millipore filters to remove the photocatalyst powder. Progress of decolorization was followed by determination of residual concentration of the indicator by recording the corresponding absorption spectrum. The same procedure has been adopted for MB indicator. All the experiments were conducted under ambient conditions.

RESULTS AND DISCUSSION

XRD pattern of the resultant powder from combustion of aqueous metal nitrates and glycine mixture preheated at 110°C followed by calcination at 400°C for 4 hrs is shown in fig.1(a). All peaks in XRD pattern could be indexed to monoclinic wolframite ZnWO_4 of JCPDS file no: 85-0251. Absence of extra peaks indicates that the sample obtained is phase pure without any traceable impurity. It is further characterised by FTIR spectroscopy. All the observed peaks in the FTIR spectra shown in fig.1(b) are in good agreement with earlier reports [11]. Peaks at 833 cm^{-1} and 870 cm^{-1} are ascribed to stretching mode of W-O in WO_6 octahedra. Peaks at 532 and 620 cm^{-1} are due to symmetric vibrations of bridged oxygen atoms of Zn-O-W. The absorption bands at 430 and 465 cm^{-1} are due to symmetric and asymmetric deformation modes of W-O bonds and Zn-O bonds in WO_6 and ZnO_6 octahedra respectively. Other peaks at 3600 and 1660 cm^{-1} are due to H-stretching vibrations of ethyl alcohol and HOH bending mode of

vibrations. Microstructure of ZnWO_4 powder is investigated by SEM and the SEM images are shown in fig.2(a)

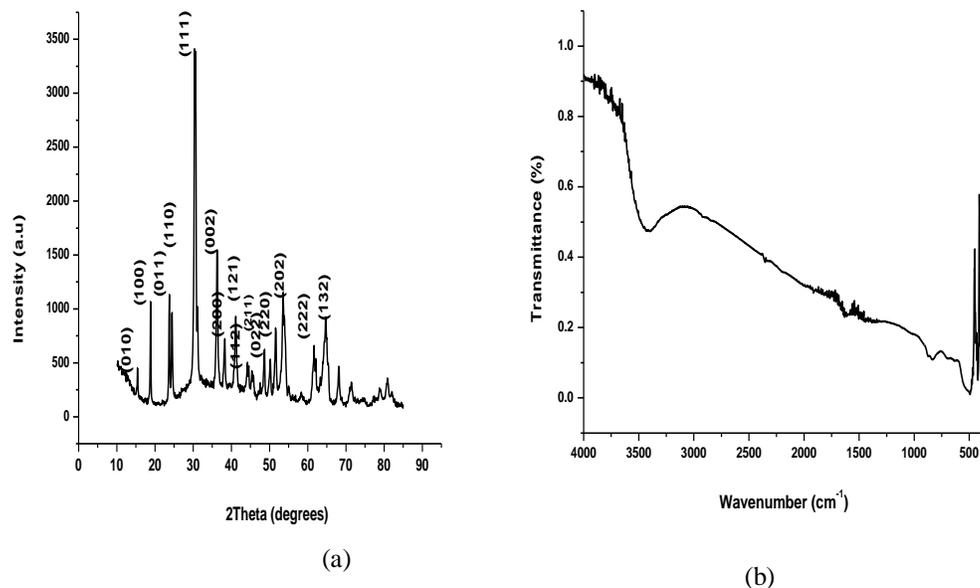


Fig. 1(a) XRD pattern of resultant powder from combustion followed by calcination at 400°C for 4hrs (b) FTIR spectra of ZnWO_4 calcined powder.

Photo absorptive ability of the sample is assessed by UV-DRS shown in fig.2(b) which shows an absorption edge in the region close to 400 nm from which the estimated band gap for the synthesized ZnWO_4 powder is calculated to be 3.2ev. A band gap of 3.9 - 4.4 ev was reported for ZnWO_4 single crystals, while for nano structured powders a direct band gap of 3.31 ev and an indirect band gap of 3.8 ev were reported [9].

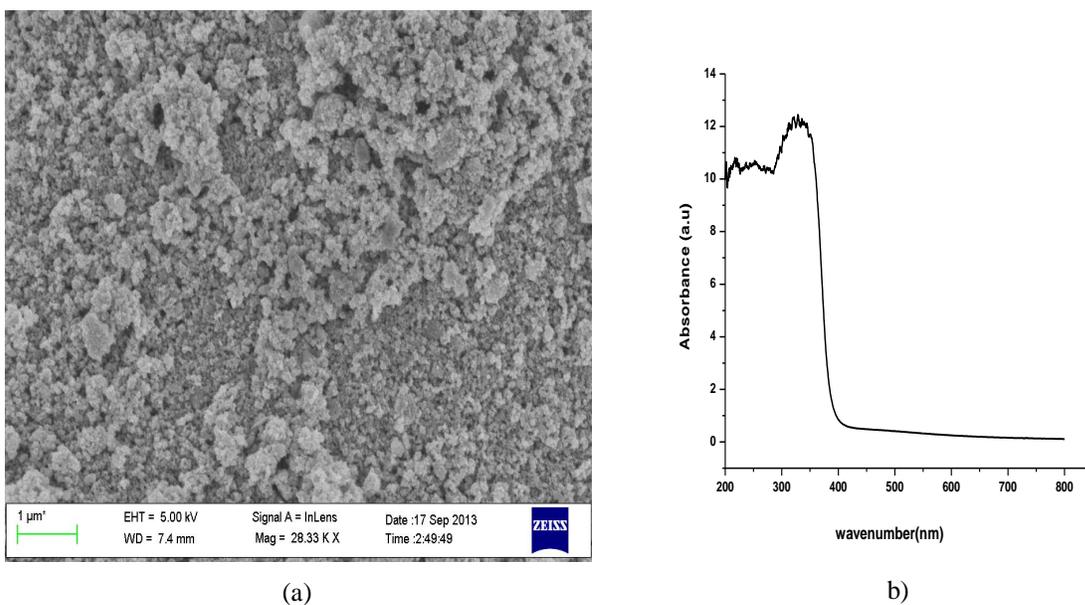


Fig. 2 (a) SEM image of ZnWO_4 (b) UV-vis diffuse reflectance spectrum of ZnWO_4 powder.

Decolorization of Rh-B and MB were used as model reactions to evaluate the photocatalytic activity of ZnWO_4 at different pH values of 8.0 and 10.0, initially adjusted by addition of NaOH prior to light exposure. Temporal evolution of spectral changes during photodegradation of Rh-B as a function of exposure time for different initially adjusted pH values of 8.0 and 10.0 are shown in Fig.3. Aqueous solution of pure Rh-B gives a major absorption band at 553 nm and visible light irradiation on Rh-B aqueous solution containing dispersed ZnWO_4 caused an apparent change in the magnitude of absorbance both with exposure time and pH.

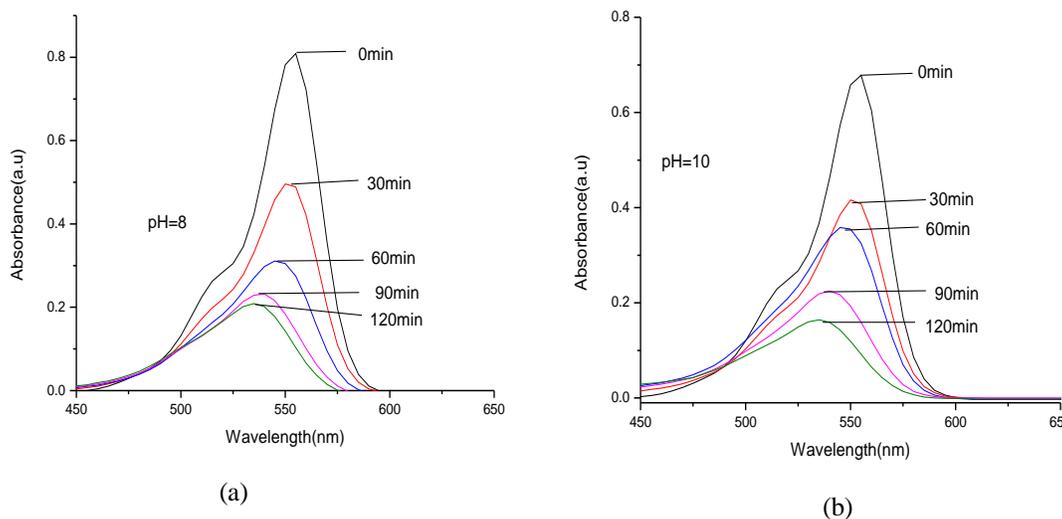


Fig 3. Temporal evolution of spectral changes of Rh-B solution containing ZnWO_4 as a function of exposure time for (a) pH=8.0 and (b) pH=10.0

From fig.3, it can be seen that the absorbance due to Rh-B decreases with increase in irradiation time and maximum degradation upto 80% could be obtained for Rh-B solution adjusted to initial pH=10 for an exposure time of 120 min. The decrease in absorption at 553nm clearly indicates that the chromophoric structure of Rh-B was decomposed and the hypsochromic shift was attributed to the stepwise deethylation of the $\text{N,N}'$ -diethylammonium groups in the Rh-B structure [11]. According to plane wave DFT calculations for ZnWO_4 , [23] it is claimed that the highest occupied band consisted of only oxygen 2p orbitals and the lowest unoccupied band is comprised mainly of tungsten 5d orbitals. Under such conditions, the photoelectrons in the excited states of the dye due to absorption are supposed to be injected to the W 5d orbitals of ZnWO_4 and they will be responsible for formation of O_2^- and mineralisation of dye occurs due to the reaction of O_2^- with the Rh-B. However, in the present study, there is no evidence for photo sensitization process and photocatalytic step alone seems to be predominant as shown in fig. 4 for the plots of C/C_0 vs time of exposure for the Rh-B aqueous solution with and without the photocatalyst for pH= 8.0 and pH = 10.

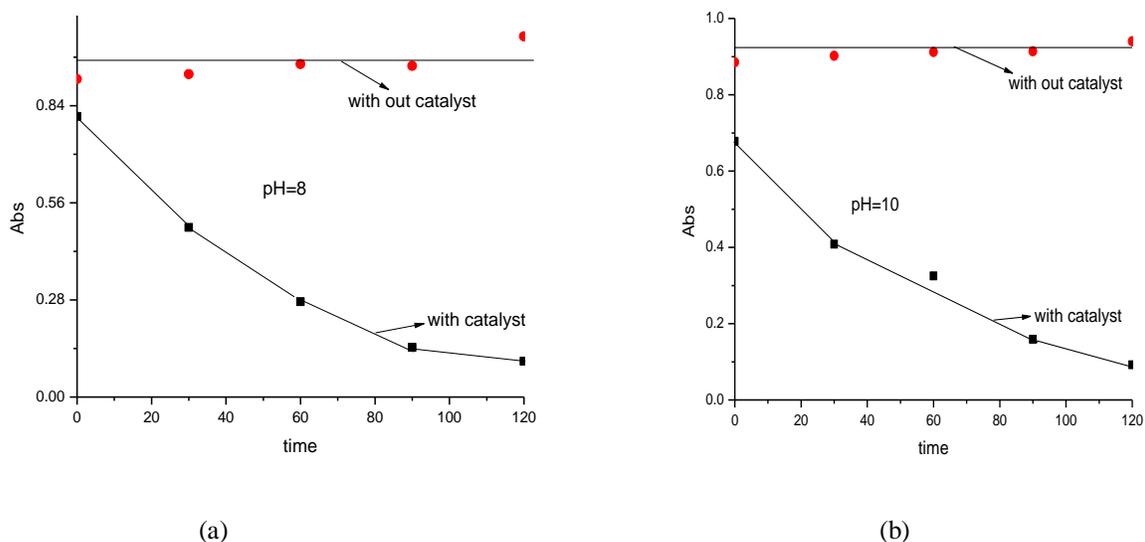


Fig 4. Variation of absorbance at 553 nm due to Rh-B solution with $ZnWO_4$ and without $ZnWO_4$ versus exposure time for (a) pH=8.0 and (b) pH=10.0.

Temporal changes of spectral behaviour for MB aqueous solution containing $ZnWO_4$ powder as a function exposure time are depicted in fig.5. According to Fu et al [25] $ZnWO_4$ displayed relatively high photocatalytic activity for degradation of MB under U.V irradiation ($\lambda > 290$ nm), and showed no activity for irradiation above 420 nm. Tiziano Montini et al [1] reported that $ZnWO_4$ showed degradation of about 95% for the decomposition of MB for irradiation in the range of 300-800nm after 120 minutes of exposure. In the present study 96% MB was observed to degrade for an exposure time of 90 min at pH=10. Fig.6 shows the plot of absorbance as a function of exposure time for MB with and without $ZnWO_4$. From the graph it is evident that photosensitization and photocatalysis both occur simultaneously but photocatalysis predominates photosensitisation process.

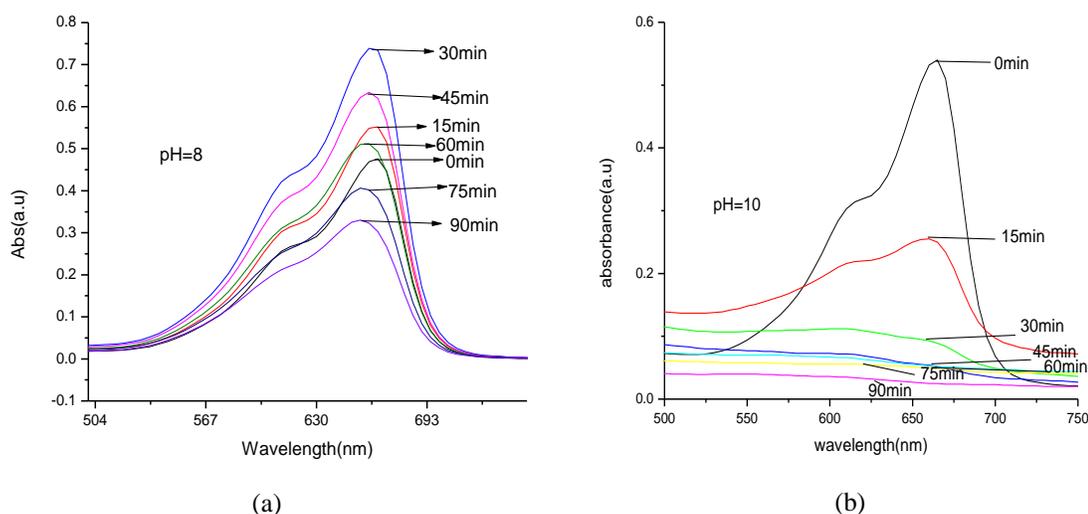


Fig 5. Temporal evolution of spectral changes of MB containing $ZnWO_4$ as a function of exposure time at different pH values (a) 8.0 (b) 10.0

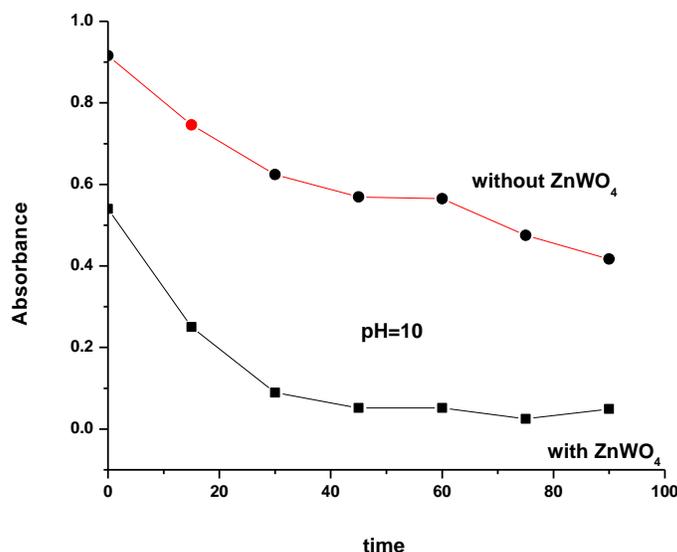


Fig 6. Variation of absorbance of MB with and without ZnWO₄ at pH=10

In the present study ZnWO₄ powder prepared by combustion method showed better visible light induced degradation for both Rh-B and MB compared to earlier reports in literature. Since photocatalytic activity depends on surface area, crystallite size, dispersion and crystallinity, the enhanced photocatalytic activity observed in this study is attributed to formation of more crystalline ZnWO₄ obtained by glycine combustion method.

APPLICATIONS

The present study is useful to assess the visible light activity of combustion synthesised ZnWO₄ for photocatalytic degradation of Rh-B and MB under different pH conditions.

CONCLUSIONS

Phase pure ZnWO₄ of monoclinic structure has been prepared by glycine combustion method at 400⁰C. Both XRD pattern and FTIR spectrum of ZnWO₄ powder agreed well with literature reports. The obtained ZnWO₄ powder showed considerable absorption in the region between 350-400 nm as evident from UV Visible - DRS studies. Photocatalytic activity of ZnWO₄ powder under visible light irradiation was evaluated in terms of the degradation of Rh-B and MB as model reactions at different pH exact to 8 and 10. Approximately 80% of Rh-B degraded after 120 min of exposure and 96% of MB in 90 minutes. The enhanced visible light photocatalytic activity of ZnWO₄ was attributed to the particle size.

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