



Factors Effecting Visible Light Photocatalytic Degradation of Rhodamine-B using $ZnWO_4$ Synthesized by Combustion Method

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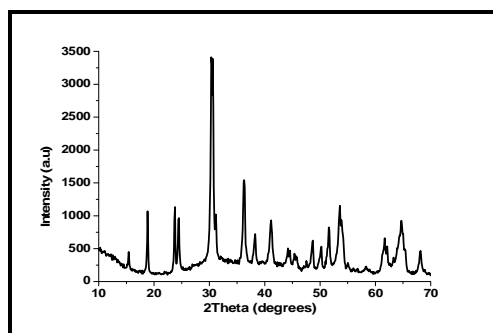
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ABSTRACT

$ZnWO_4$ photocatalyst was synthesized with the help of combustion method by taking $Zn(NO_3)_2$, $Na_2WO_4 \cdot 2H_2O$ are taken as oxidant and glycine as fuel. The photocatalyst was calcined at $400^\circ C$ for 4 h. After calcinations, resulting product was characterized by X-ray diffraction study (XRD), Scanning Electron Microscopy (SEM) and UV-visible diffuse reflectance spectra (UV-DRS) to get information about phase purity, morphology and activity of photocatalyst under UV or visible light respectively. The obtained phase pure monoclinic $ZnWO_4$ photocatalyst was used to degrade Rhodamine-B under visible light irradiation by using 400 W metal halide lamp as visible light source.

Graphical Abstract



XRD pattern of resultant powder from combustion followed by calcinations at $400^\circ C$ for 4h

Keywords: Combustion method, $ZnWO_4$, Rhodamine-B, X-ray Diffraction, Photocatalytic degradation.

INTRODUCTION

Waste waters from various industries, factories, laboratories, etc. are creates serious problems to the environment. The discharged wastes containing dyes are carcinogenic, mutagenic, less biodegradable and hugely colored there by it reduce the penetration of sun light in to aquatic system hence it effects the aquatic life and human beings [1]. Hence it needs to removal of dyes from effluents obtained from

the above said industries. Though several methods such as adsorption, ultrafiltration, reverse osmosis, ion exchange, biosorption, chlorination and ozonation were proposed for remediation of industrial waste waters, these processes have their own advantages and disadvantages. For instance, adsorption, filtration, ion-exchange and biosorption result in transfer of pollutant from one phase to another and lead to more serious secondary pollution, where as chlorination and ozonation are not cost effective. So, in addition to conventional primary and secondary treatment processes, scientific community has been in the search for complete degradation methods of toxic pollutants into environmentally benign and non-hazardous products [2]. To overcome these problems an alternate method heterogeneous photocatalytic degradation processed under visible light irradiation with the help of metal oxides such as TiO_2 [3], ZnO [4], SnO_2 [5], CeO_2 [6], Bi_2O_3 [7], Cu_2O [8] etc. and mixed metal oxides such as ZnWO_4 [9], $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ [10], $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ [11], BiVO_4 [12], LaVO_4 [13], CuBi_2O_4 [14], Bi_2WO_6 and Bi_2MoO_6 [15].

Photocatalysis may be termed as a photoinduced reaction which is accelerated by the presence of a catalyst [16]. Every semiconducting material either TiO_2 -based or non- TiO_2 based having corresponding band gap energy i.e energy gap between valance band and conduction band. Hence, photocatalysts in this process were activated by absorption of energy from sun light or visible light produced through other sources such as metal halide lamp, xenon lamp or mercury lamp. The absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band to the conduction band, thus generating a hole (h^+) in the valence band and electron (e^-) in the conduction band. Figure 1 depicts schematic representation of heterogeneous photocatalytic degradation process.

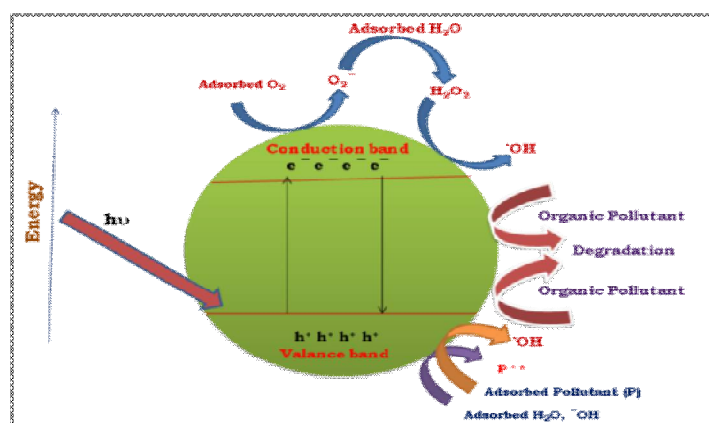


Figure 1. Schematic representation of redox reactions of a dye in presence of a photocatalyst under UV/visible light irradiation.

MATERIALS AND METHODS

Synthesis of ZnWO_4 Photocatalyst: 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 30 mL portions of deionized 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 min and calcined at 400°C for 4 h 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 ranges. Spectral grade BaSO₄ 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 ZnWO₄ was evaluated in terms of degradation of Rhodamine-B (Rh-B) by changing the Amount of catalyst, pH of the solution and dye concentration under visible light irradiation with the help of 400 W metal halide lamps. UV radiation below 350 nm is eliminated by surrounding the sample with a water jacket. 100 mg of ZnWO₄ was added into 100 mL Rh-B 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, 5 mL 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.

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 h is shown in fig. 2(a). All peaks in XRD pattern could be indexed to monoclinic wolframite ZnWO₄ of JCPDS file no: 85-0251. It is further characterized by FTIR spectroscopy. All the observed peaks in the FTIR spectra shown in fig. 2(b) are in good agreement with earlier reports [17]. Peaks at 833 cm⁻¹ and 870 cm⁻¹ are ascribed to stretching mode of W-O in WO₆ octahedral. 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 WO₆ and ZnO₆ octahedral respectively. Other peaks at 3600 and 1660 cm⁻¹ are due to H-stretching vibrations of ethyl alcohol and HOH bending mode of vibrations.

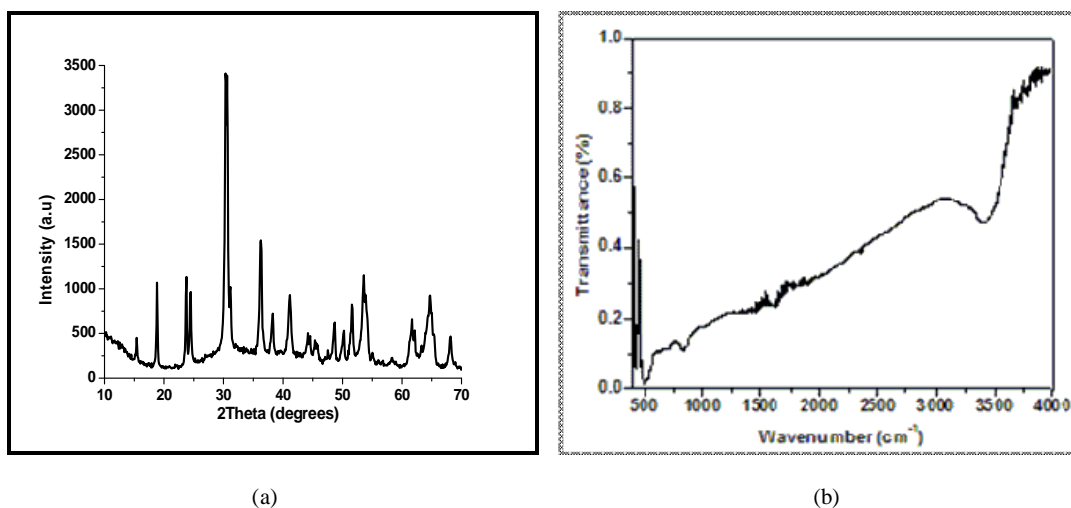


Figure 2. (a) XRD pattern of resultant powder from combustion followed by calcinations at 400°C for 4h
(b) FTIR spectra of ZnWO₄ calcined powder.

Microstructure of ZnWO₄ powder is investigated by SEM and the SEM images are shown in fig.3(a) Photoabsorptive ability of the sample is assessed by UV-DRS shown in fig.3(b) which shows an absorption edge in the region close to 400 nm from which the estimated band gap for the synthesized ZnWO₄ powder is calculated to be 3.2eV.

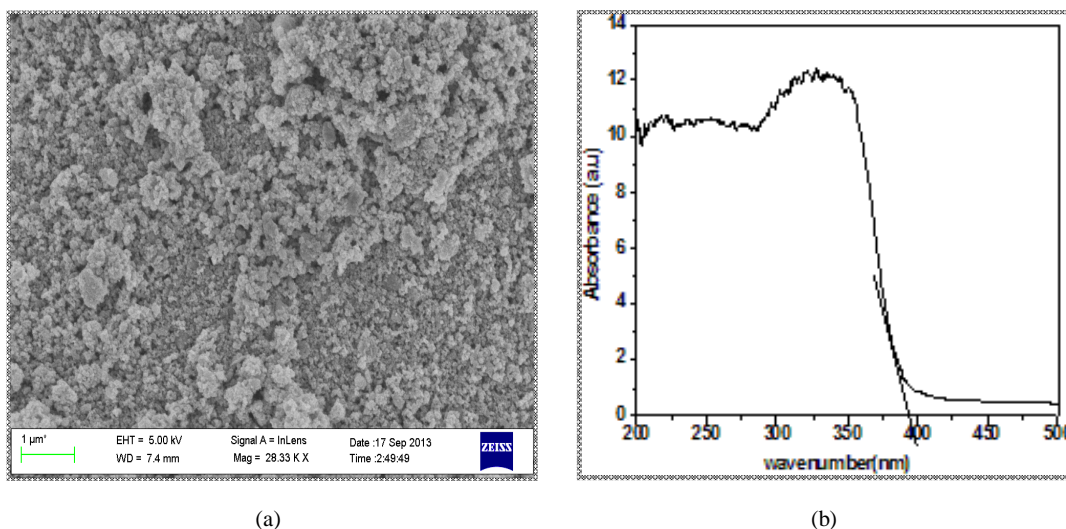


Figure 3. (a) SEM image of ZnWO₄ (b) UV-Vis diffuse reflectance spectrum of ZnWO₄ powder.

Factors affecting the rate of photocatalytic degradation of dyes: The oxidation rates and efficiency of the photocatalytic system are highly dependent on a number of operational parameters that govern the photodegradation of the organic molecule [18-22]. Several study have been reported the significance of operational parameter.

Effect of pH of the dye solution: In the photocatalytic degradation of dyes, effect of pH plays vital role. Figure 4 depicts change in absorption with time at different initial pH of the solution i.e. 3, 5, 8 and 10. From the figure, the rate of photodegradation of Rh-B dye with ZnWO₄ is more at pH=10.

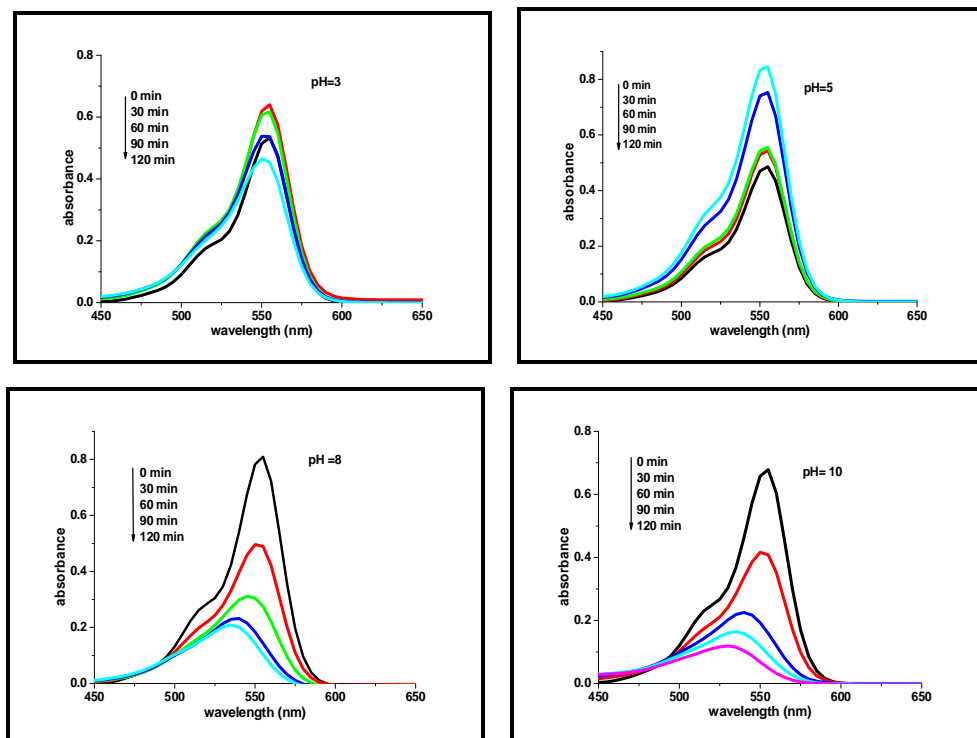


Figure 4. Photocatalytic degradation of Rh-B at pH = 3, 5, 8 and 10 with ZnWO₄ Photocatalyst.

Effect of amount of catalyst: Rate of photocatalytic degradation effected also by the amount of catalyst. As increasing amount of catalyst in the photocatalytic process rate of photodegradation also enhanced. This can be explained on the basis that as increase in amount of catalyst commonly enhance the number of active sites on the surface of the photocatalyst thus causing an increase in the formation of number of $\bullet\text{OH}$ radicals which can take part in actual discoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing [23]. Figure 5 depicts UV-visible absorption spectra of Rhodamine-B by changing the amount of ZnWO_4 i.e 50 mg, 100 mg, 200 mg and 300 mg. From the figure, rate of degradation of Rh-B is more for 100 mg photocatalyst than 50 mg, 200 mg and 300 mg.

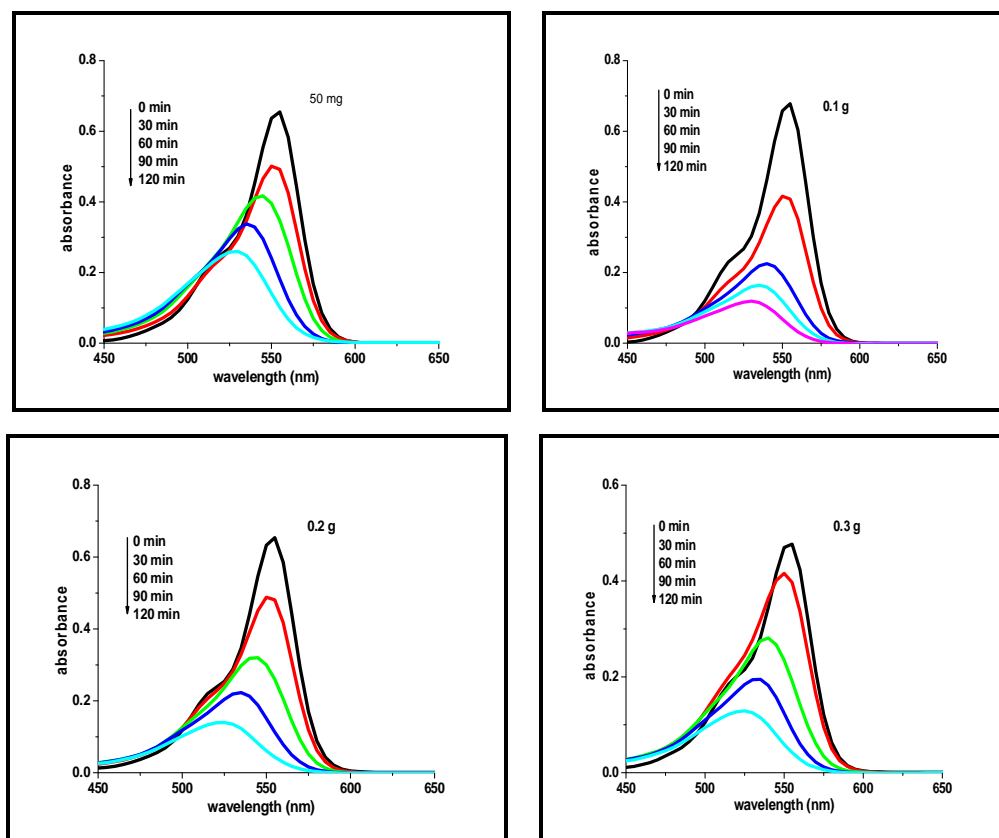


Figure 5. Photocatalytic degradation of Rh-B by changing the amount of ZnWO_4 Photocatalyst.

Effect of dye concentration: The initial concentration of dye in a given photocatalytic reaction is an important factor which needs to be taken into account. Generally speaking the percentage degradation decreases with increasing amount of dye concentration, while keeping a fixed amount of catalyst [24]. This can be rationalized on the basis that as dye concentration increases, more organic substances are adsorbed on the surface of Photocatalyst, whereas less number of photons are available to reach the catalyst surface and therefore less $\bullet\text{OH}$ are formed, thus resulting in less degradation percentage. Figure 6 depicts UV-visible absorption spectra of Rhodamine-B with change initial concentration of dye. The reaction is conducted in different concentrations such as 3 ppm, 5 ppm, 7 ppm and 10 ppm with suprapstoichiometric Ferric molybdate under visible light irradiation.

APPLICATION

This study useful for the removal of organic pollutants present in the industrial waste water effluents and also for the pharmaceutical pollutants obtained from pharma industries.

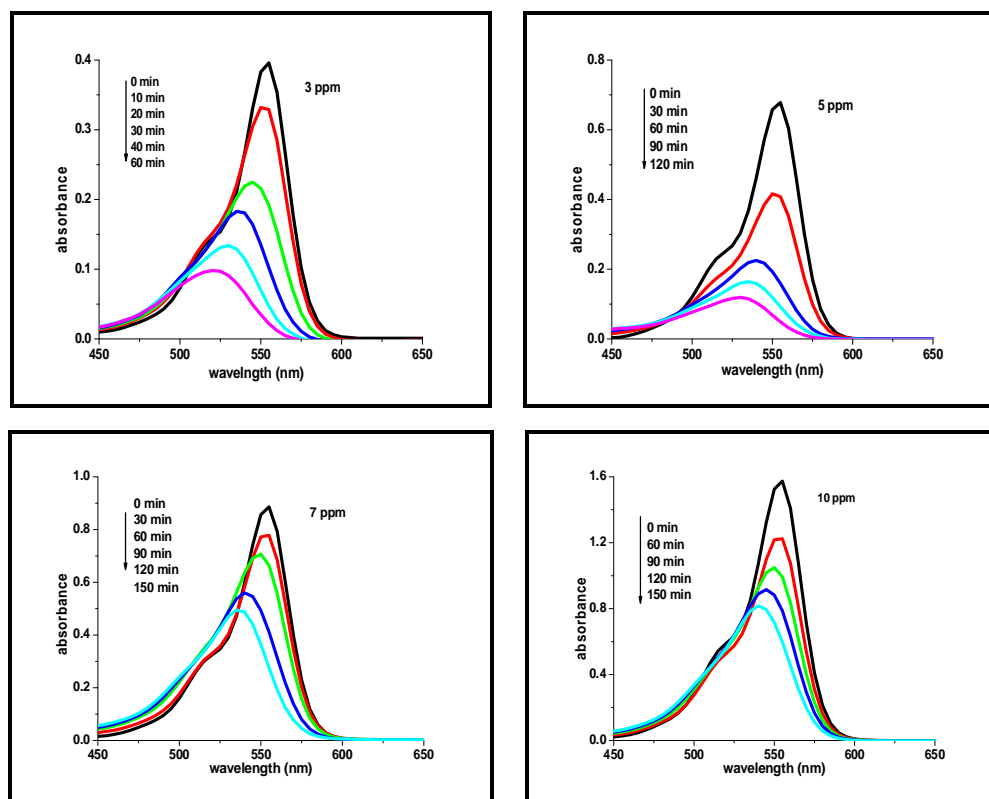


Figure 6. Degradation of Rh-B by changing the initial concentration with ZnWO₄ Photocatalyst.

CONCLUSIONS

ZnWO₄ photocatalyst has been synthesized by glycine combustion method at 400°C. The calcined powder showed good photocatalytic activity for the degradation of Rhodamine-B under visible light irradiation by changing the pH of the solution, amount of catalyst and concentration of the dye.

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