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Photocatalytic degradation of Victoria Blue-B Dye using ZnS and ZnS/Fe_2O_3 composite nanoparticles under visible radiation

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ABSTRACT

ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 nanoparticles were prepared by Chemical and sol gel method under optimal conditions and characterized using XRD, TEM and UV-Visible spectroscopic techniques. As-synthesized nanomaterials were used as a photocatalysts for the degradation of Victoria Blue-B dye. Effects of photo-catalyst load and substrate initial concentration on degradation of the dye in aqueous solution have been investigated. Maximum degradation (97.2 %) of Victoria Blue-B was observed using catalyst load (Fe_2O_3) : 1.0g/250ml of 25 mgL^{-1}. Photocatalytic degradation of the dye follows pseudo first order kinetics. Using Victoria Blue-B initial concentration, 100mg/lit., the dye degradation rate constant under visible radiation and photocatalyst load, was 5.33 x 10^{-3} min^{-1}.

Keywords: degradation, Victoria Blue-B, nanoparticles, rate constant, XRD

INTRODUCTION

Organic dyes are one of the major groups of pollutants in wastewaters released from textile and other industrial processes [1-3].The textile industry extensively uses dyes has been condemned as being one of the world's worst offenders in terms of pollution because of chemicals. As many as 2,000 chemicals are used in textile industry, from dyes to transfer agents; the typical textile dye wastewater composition is quite complex. Over 15% of the textile dyes are lost in wastewater stream during dyeing operation. These waste streams contain dyeing process auxiliaries that may include xylenes, phenols, buffers, bleaches and scouring agents, water softeners, surfactants, enzymes, caustic compounds and acids. Which are generally toxic and resistant to biological degradation treatments. A necessary criterion for the use of these dyes is that they must be highly stable under light as well as during washing and resistant to microbial attack. Therefore, dyes in wastewater are neither readily degradable nor easily removed by conventional chemical treatment systems [4].

Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis is emerging as a cost-effective, efficient and environment friendly technique for the elimination of organic pollutants including dyes from aqueous and gaseous media [5, 6]. Several semiconductor photocatalysts being used for the treatment of waste water pollutants are: TiO_2, ZnO, WO_3, SnO_2, CdS and ZnS.

The photo-catalytic action of semiconductor nanomaterial involves the photo-excitation of their valence band electron(s) to its conduction band and creation of positively charged holes (h+) at the valence band. Such electron - hole separation, through a series of redox reactions, can result in the degradation of diverse organic pollutants, including the non-biodegradable dyes, in aqueous solutions. Unfortunately, generally used photo-catalysts, such as TiO_2 and ZnO, for this purpose, due to their high band gap energies (> 3.0 electron volts) require high energy photons in the ultra-violet region of electromagnetic radiation. This makes the photo-catalytic process costlier when

used for the large scale treatment of real polluted water. Since the sunlight reaching at the earth surface has merely 4-5% of its UV component, therefore, use of solar radiation in case of the above photo-catalysts provide low photo-catalytic efficiency in the degradation of pollutants.

In the recent years efforts have been made to improve the efficiency of photo-catalysts in the visible region by adopting various strategies such as doping of metals and non-metals [7-10] and compositing the photo-catalysts differing in their band gap energies [11,12]. A possible strategy to extend zinc sulfide photo-absorption to visible light may be achieved by creating a new band by Fe_2O_3 between its valance band and conduction band. This new created band lie between ZnS valance and conduction band thus electrons first exited to this newly created band and then exited to ZnS conduction band. This may induce visible photo-absorption thus enhancing photocatalytic activity of ZnS in ZnS/Fe_2O_3 composite in visible radiations.

Present work reports the effect of Fe_2O_3 in ZnS on the photocatalytic degradation of Victoria Blue-B dye in aqueous solution. Efforts have also been made to see the effects of operational parameters such as: photo-catalyst load and substrate (dye) initial concentration on the degradation of Victoria Blue-B.

MATERIALS AND METHODS

2.1. Chemicals

Zinc nitrate $Zn(No_3)_2.6H_2O$,M=297.47g/mol (MERCK), Sodium sulfide $Na_2S.xH_2O$, M=78.04g/mol (MERCK), Glucose $C_6H_{12}O_6$,M=180.16g/mol (SRL), Ferric chloride ($FeCl_3$, MW=162.21 g/mol, MERCK), Citric Acid Monohydrate ($C_6H_8O_7.H_2O$, MW=210.14 g/mol, SRL); Oxalic acid ($C_2O_4.2H_2O$, MW= 126, SRL), Victoria Blue-B ($C_{33}H_{32}ClN_3$), M=506.08 g/mol, SIGMA-ALDRICH Co.(USA) The structure of Victoria Blue-B is given in fig.1.

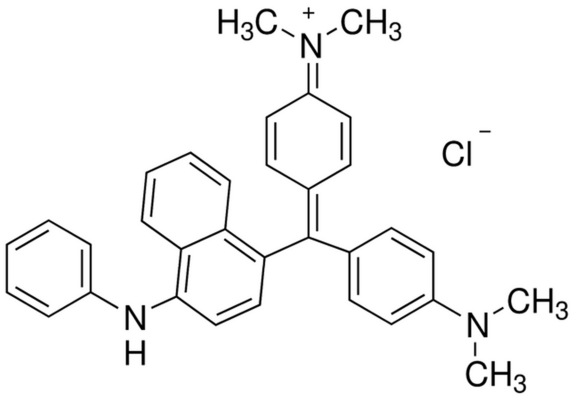


Fig 1 Structure of Victoria Blue-B dye (Source: SIGMA-ALDRICH)

2.2. Methods

2.2.1. Synthesis of ZnS Nanoparticles

1.0 M sodium sulfide was added, drop-wise, at 70^0C to equal volume of 1.0 M Zinc nitrate aqueous solution with simultaneous stirring using a magnetic stirrer for 15 hours. Now, 1.0 M glucose solution was added drop wise. The resultant mixture was heated and incubated at 70^0C for more than 6 hours. Precipitates thus obtained were centrifuged at 2,000 rpm for 15 minutes and the product was dried at 50^0C for 4 hours and then crushed to a fine powder [13]

2.2.2 Synthesis of Fe_2O_3 Nanoparticles

Using ferric chloride as precursor, nanosize Fe_2O_3 was prepared by modified sol-gel method [14]. Ferric chloride was dissolved in minimum quantity of distilled water. The solution was acidified with nitric acid followed by stirring at 65-70 ºC. A mixture of Citric acid and oxalic acid, in 1:1 ratio, was added to the reaction mixture with simultaneous stirring for one hour. The gel thus obtained was dried at 110 ^{0}C and then calcined at 500 ^{0}C for 4 hrs, cooled to room temperature and grinded to fine powder.

2.2.3 Synthesis of ZnS/Fe_2O_3 Nanocomposite

In a crucible, 10 gm each of as-synthesized ZnS and Fe_2O_3 was thoroughly mixed and then calcined at 400^0C for 2hrs and then cooled to room temperature.

2.3 Characterization of as synthesized material

2.3.1 XRD Analysis

X-ray diffraction patterns of as-synthesized photocatalysts were obtained using an X-ray differactometer (XRD) BRUKER D8 Advance XRD, AXS GMBH, Karisruhe, West Germany) equipped with a Cu target for generating a CuKα radiation (wavelength 0.15406 nm). The measurements were carried out using accelerating voltage 40 kV and applied current 30 mA. The instrument was operated under step scan type with step time and degree (2θ) of 1s and 0.020°, respectively, over 2θ = 4° to 64°.

2.3.2 TEM Analysis

Transmission electron microscopic (TEM) images of photo-catalyst samples were obtained at SAIF Punjab University, Chandigarh, using accelerating voltage 80 KV and magnification 200000x. As-synthesized photocatalyst powder was dispersed in acetone by stirring in a tank. A drop of the suspension thus obtained was mounted on a carbon-coated copper grid; the solvent was allowed to evaporate before TEM images were obtained.

2.3.4. UV-Visible absorption study

For the determination of photo absorption edge and band gap energy of as-synthesized photocatalysts, UV-visible diffuse absorption was recorded over 200-800 nm using a UV/Visible spectrophotometer (SANYO, SP65, GALANAKAMP, U.K).

2.4 Photocatalytic degradation study

Photo-catalytic degradation of Victoria Blue-B was carried out in a reactor consisting of a glass tube with an inlet tube for air purging through the dye solution and an outlet for the collection of samples from the reactor at different time intervals (Figure. A 1.0gm of as-synthesized photo-catalyst powder was added to 250 ml aqueous 100mg/L Victoria Blue-B solution taken in the reactor tube and the suspension was stirred in dark for 60 minutes to allow for chemisorptions to occur. Once this time had been elapsed sample of the solution was taken. During irradiation of the samples by UV or visible radiation, air was purged into the dye solution kept at room temperature. At 30 minutes interval, 10ml of the reaction mixture was withdrawn and the suspension was centrifuged at 3000rpm for 15 minutes. The supernant liquid was filtered through whatman no. 1filter paper. Absorption of the clear filtrate was measured at 400 nm using UV/visible spectrophotometer (Model ME 951C). The concentration of the dye in a solution was calculated by comparing the observed absorbance on the standard linear plot between the absorbance verses concentration of dye.

Percentage photo-catalytic degradation of dye was calculated using the relation –

$$\% \text{ Degradation} = [(A_0 - A_t)/A_0]x100 \quad (1)$$

Where A_0 is absorbance of dye at initial stage and A_t is absorbance at time "t".

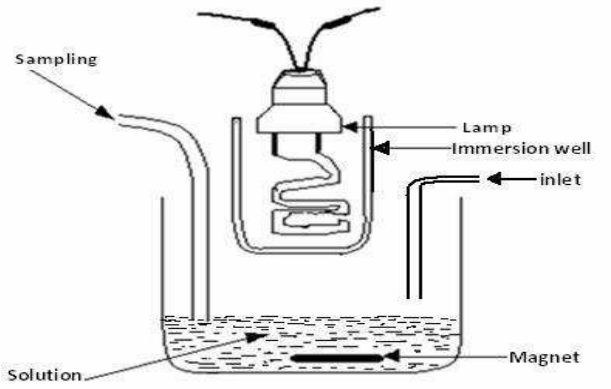


Fig 2 Photocatalytic Reactor

RESULTS AND DISCUSSION

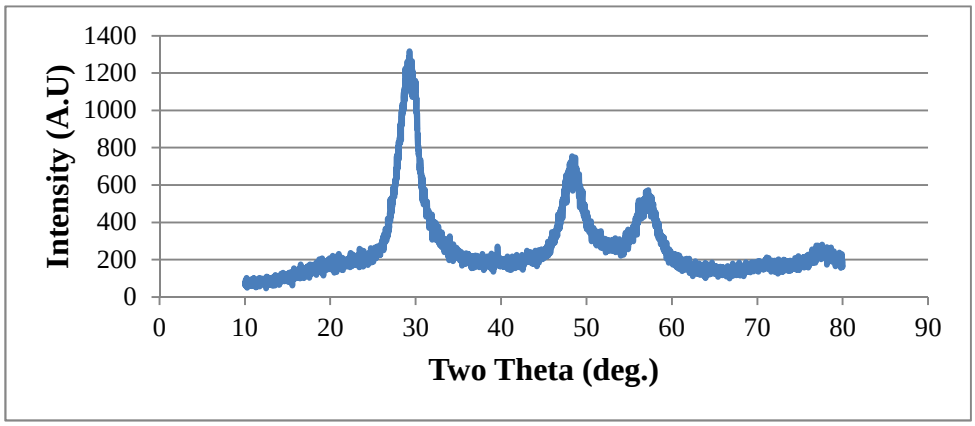
3.1. XRD Analysis

XRD patterns of ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite are exhibited in Figure 3. Diffraction peaks at 2θ= 29.2, 48.3 and 57.3^o correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of pure ZnS. Diffraction peaks at 2θ= 28.7, 47.5 and 56.6^o correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of N doped ZnS. Highest Intensity Diffraction peaks at 2θ= 33.140 ^{o} indexed with single phase rhombohedral α -Fe_2O_3 phase and for the ZnS-Fe_2O_3 composite highest intensity diffraction peak at 2θ was equal to 33.27 ^{o}.

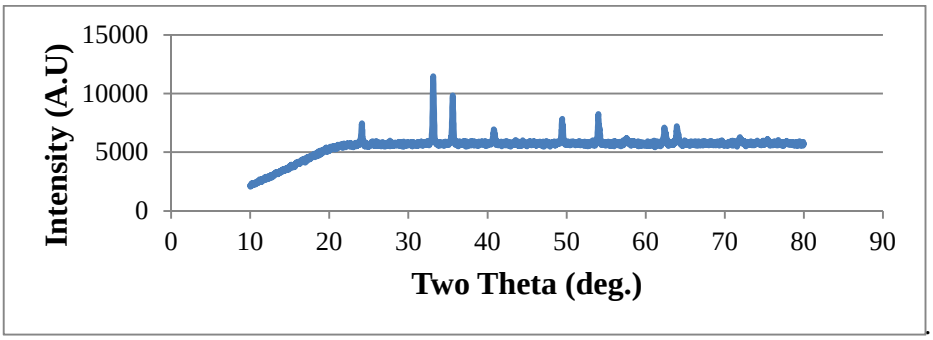
The average crystallite size of photo-catalysts were obtained using Debeye–Scherrer formula-

$$D = (K \lambda) / (\beta \cos \theta) \quad (3.1)$$

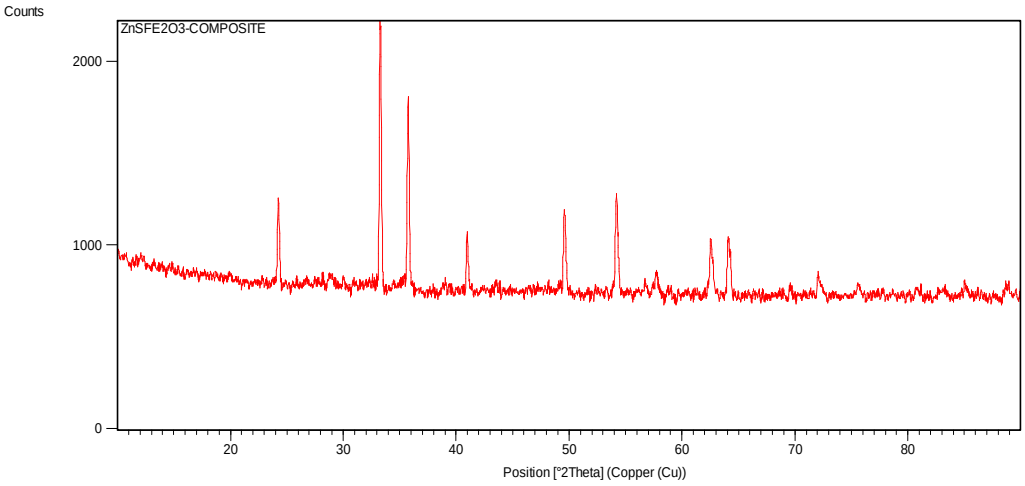
Where D is the average particle size, λ is wavelength (0.15406 nm) of X-ray; β is full width at half-maxima (FWHM) of diffraction peak appeared at $2\theta = 28.84^{o}$ and θ is the incident angle of X-ray; K is the geometric factor equal to 0.94. The average crystallite size of as-synthesized ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite obtained were 2.5 nm, 13.2nm and 45.20nm respectively.



(a)



(b)



(c)

Fig 3 XRD of as-synthesized photo-catalyst (a) ZnS, (b) Fe2O3 (c) ZnS/ Fe_2O_3 composite

3.2. TEM Analysis

TEM images of as-synthesized ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite particles are presented in figure 4. Their average particle sizes were found to be 2.4 nm, 13.0nm and 45.0nm respectively. These are in fair agreement with those obtained using XRD technique.

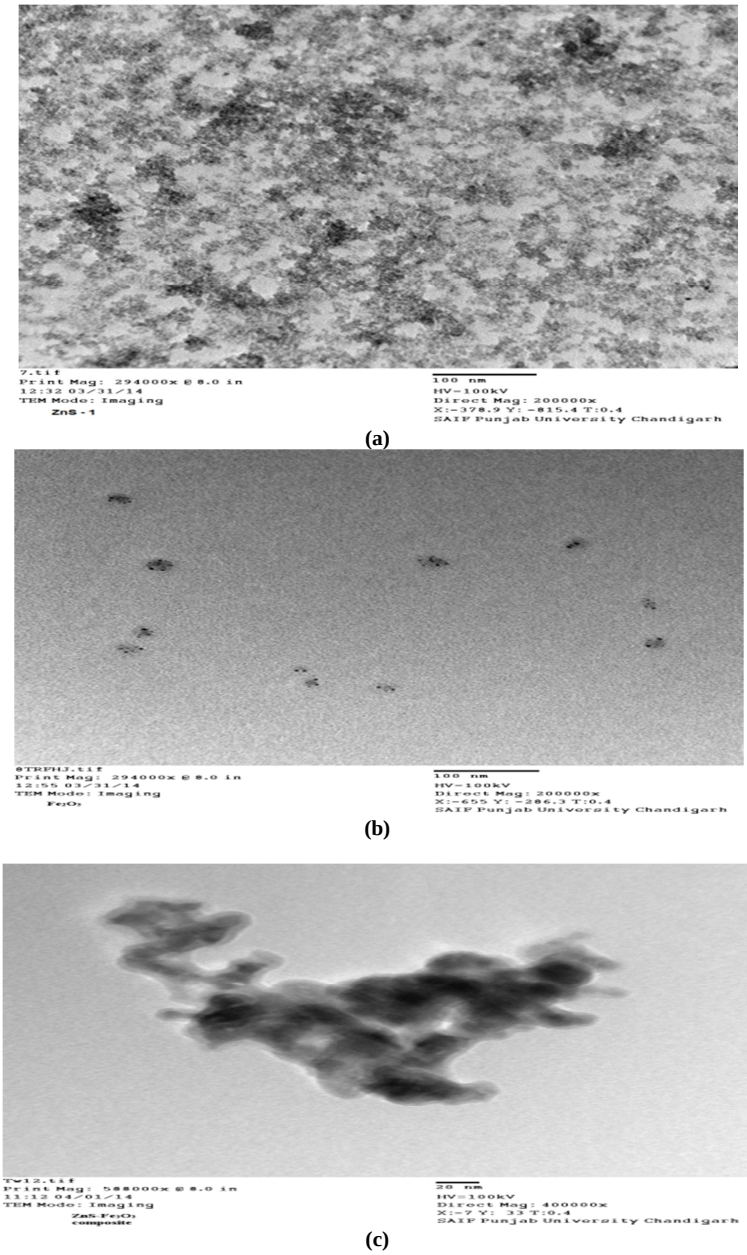
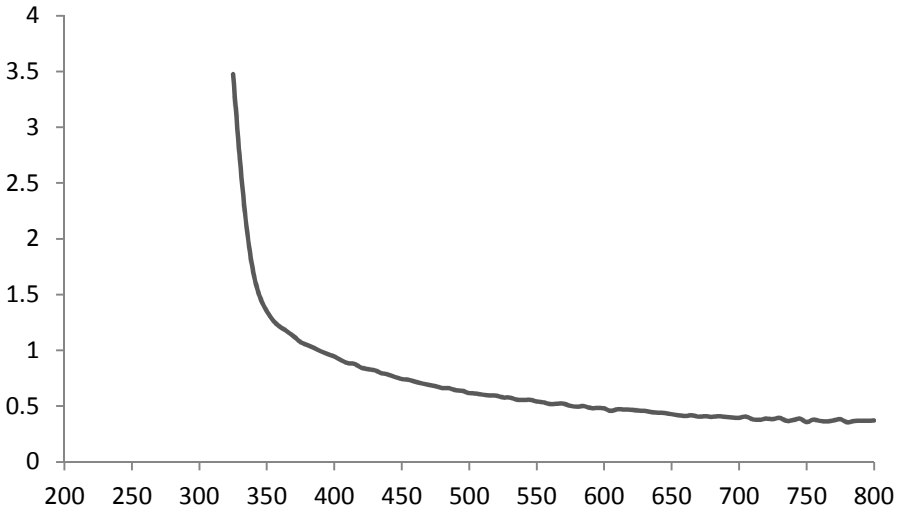


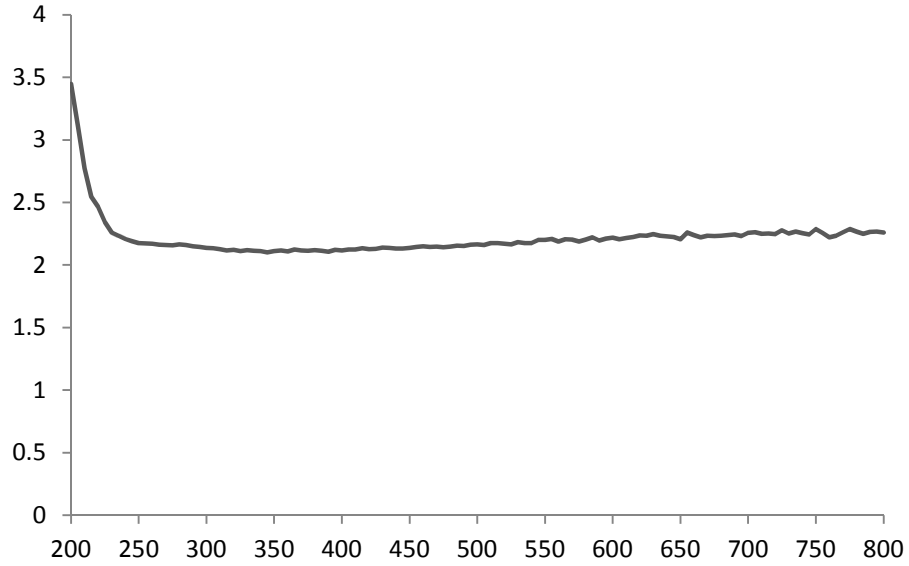
Fig 4 TEM image of as-synthesized (a) ZnS, (b) Fe_2O_3, and (c) ZnS/ Fe_2O_3 composite

3.3. UV/Visible Absorption study

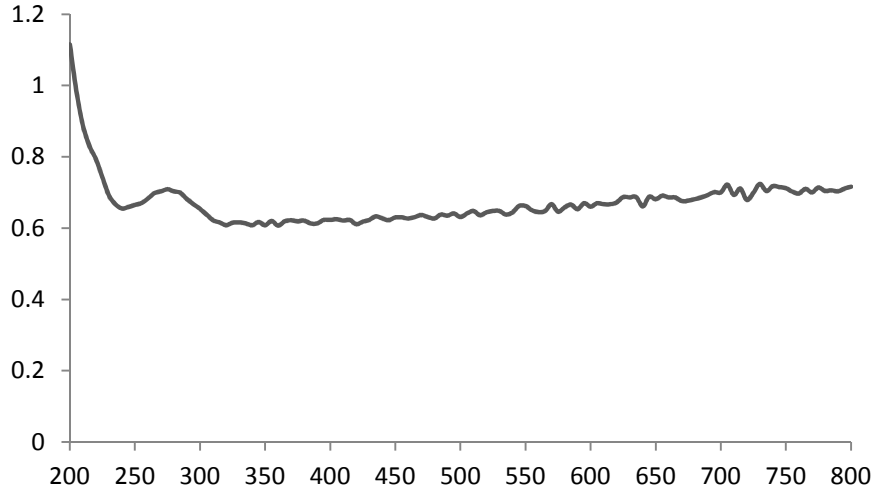
UV-visible absorption spectra of ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite scanned over 200-800 nm are shown in figure 5. The absorption edge of the above photo-catalysts, obtained from the tangential intercept on the wave length axis of respective absorption peak, were found to be 340 nm, 560 nm and 450 nm respectively. The observed red shift in the absorption edge in ZnS due to composite was due to creation of new electronic level by Fe_2O_3.



(a)



(b)



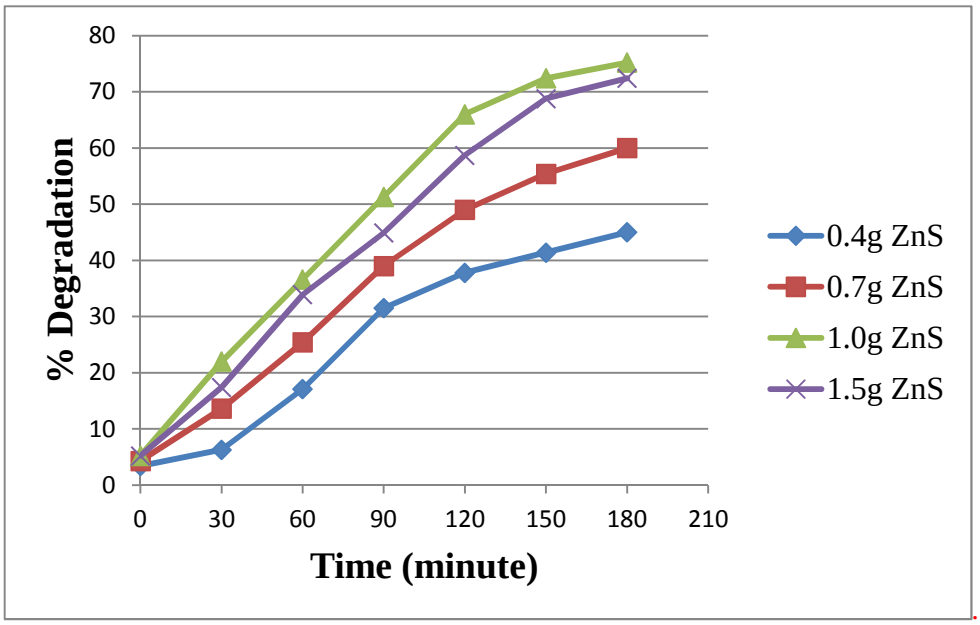
(C)

Fig 5 UV-Visible absorption spectra of as-synthesized synthesized (a) ZnS photocatalyst (absorption edge 340 nm), (b) Fe_2O_3 photocatalyst (absorption edge 560 nm), (c) ZnS/ Fe_2O_3 composite photocatalyst (absorption edge 450 nm)

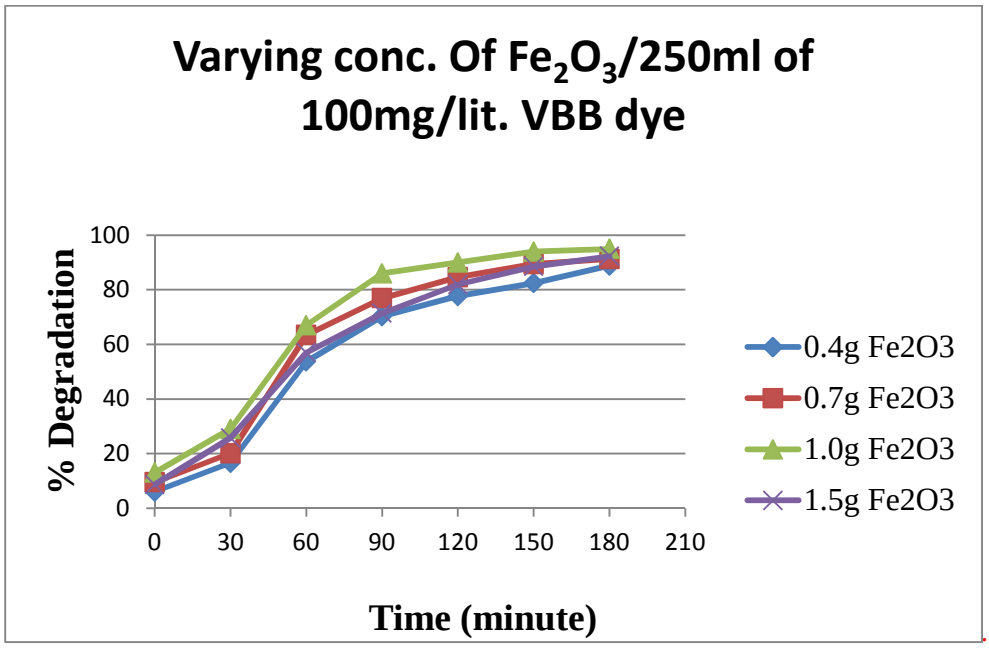
Band gap energy of as-synthesized photocatalysts was obtained using the relation [15].

$E_g = 1240 / \lambda$ (3.2)

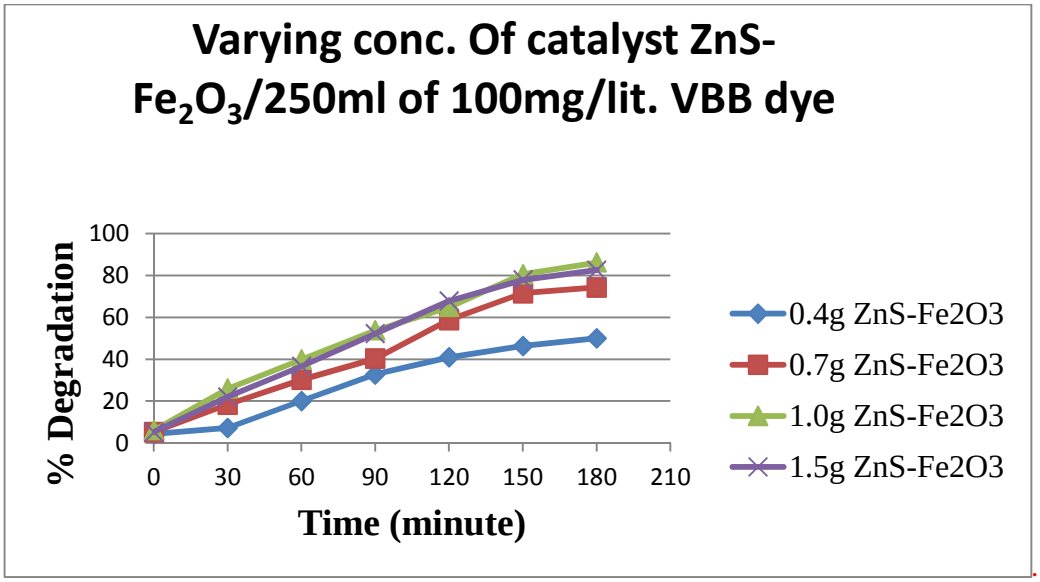
Where, E_g is band gap energy of photocatalyst in electron volts, and λ is absorption edge wavelength in nanometers. Band gap energy thus obtained for un-doped ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 nanoparticles are 3.64, 2.21and 2.75 eV, respectively. The lower band gap energy of composite ZnS/ Fe_2O_3 compared to undoped ZnS may be due to the incorporation of new energy states by in the former photo-catalyst.



(a)



(b)



(c)

Fig 6 Plots of the percent degradation of Victoria Blue-B (100mg/L) as a function of time under visible radiation at different catalyst load (mg/ 250ml) of (a) ZnS, (b) Fe_2O_3, and (c) ZnS/ Fe_2O_3 composite photocatalyst.

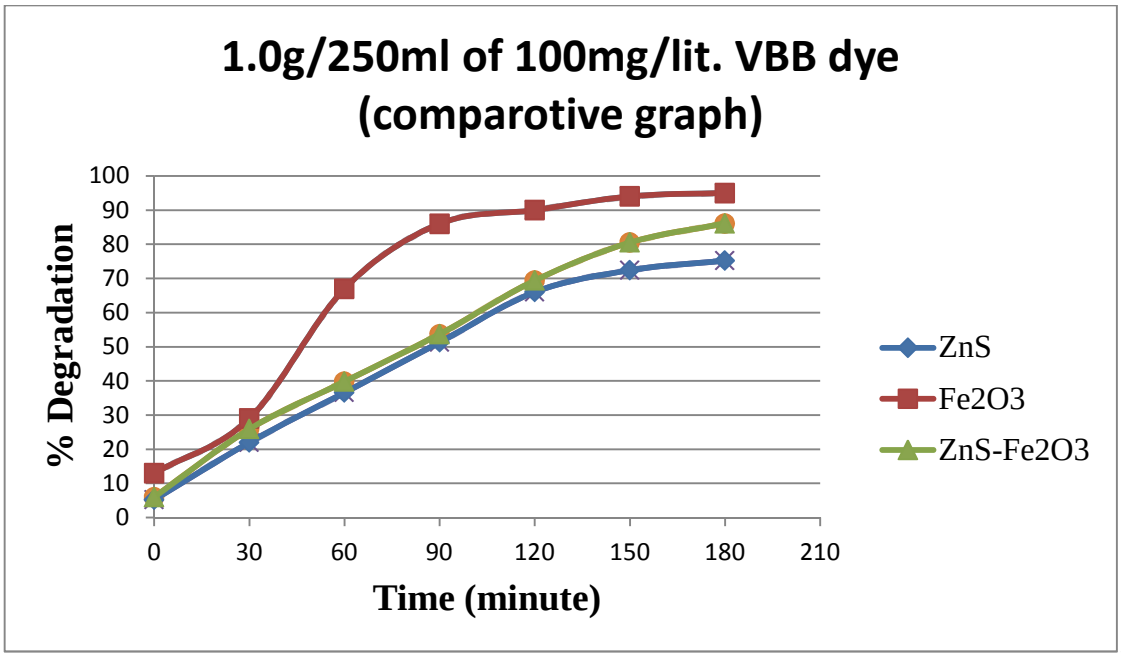


Fig 7 Plots of the percent degradation of Victoria Blue-B (100mg/L) as a function of time under visible radiation of 1.0g/250ml each of ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite photocatalyst.

3.4 Photocatalytic Degradation Study

3.4.1 Effect of Catalyst Load

Plots of percent adsorption under dark and percent photocatalytic degradation of VBB under visible radiation as a function of time at different load (mg/ 250ml) of ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite photocatalyst are presented in figures 6 and 7 respectively. Plot of percentage degradation of VBB under visible irradiation at 180 min as a function of amount (mg/ 250ml) of ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite is presented in figure-8. The percent adsorption of VBB under dark has been taken as reference for zero minute irradiations [7]. The optimum photo-catalyst load that led to maximum degradation (92.7%) of VBB under visible radiations was found to be 1000 mg/250ml of 100mg/L VBB.

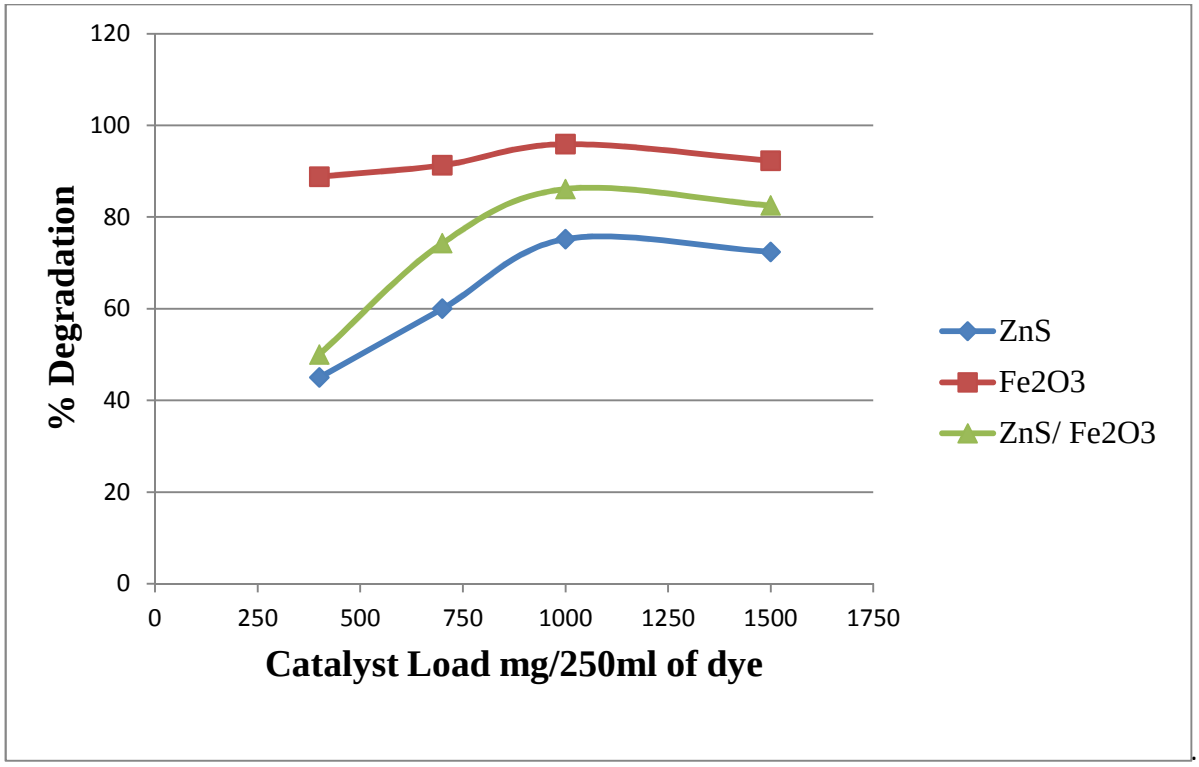


Fig 8 Plot of percentage degradation of Victoria Blue-B (100mg/L) under visible radiation at 180 min as a function of ZnS, Fe_2O_3 and ZnS/Fe_2O_3 composite load (mg/ 250ml)

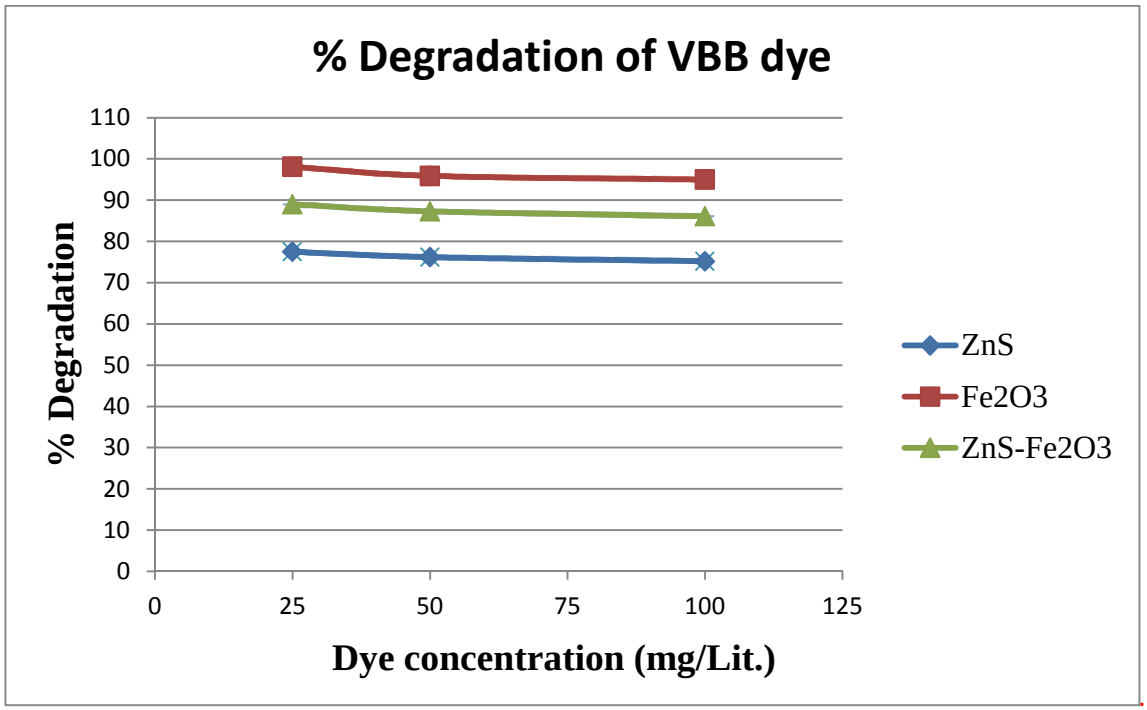


Fig 9 Plot of percentage photocatalytic degradation of VBB at 180 min under visible radiation as a function of dye initial concentration (Photocatalyst load: 1000mg/250ml)

Percent degradation of dye increases on raising the photo-catalyst load up to 1000 mg/250ml of 100mg/L of VBB dye but on further increasing the catalyst load, degradation of dye gradually falls. This can be explained in terms of the increased availability of photo-catalyst active sites per substrate (dye) molecule on raising catalyst load up to 1000 mg/250ml. On further increasing the photo-catalyst load above 1000 mg/250ml, degradation of the dye decreases. This may be due to (a) aggregation of photo-catalyst at its higher concentration that results in the

reduction of available active sites at photocatalyst surface and (b) diminished penetration of photons to the photo-catalyst surface, at higher catalyst load, due to the enhanced light scattering [16]. Similar effect of photo-catalyst (zinc sulfide) load on degradation of methylene blue under UV irradiation [17].

3.4.3 Effect of Dye Initial Concentration

Plot of percentage photo-catalytic degradation of VBB at 180 minutes under visible radiation as a function of dye initial concentration using photo-catalyst load: 1000 mg/250ml is presented in figure-9. The degradation of dye decreases with the increase of dye initial concentration over the studied dye concentration range: 2.5×10^{-6} to 1.0×10^{-5} M. The observed decrease of dye degradation at its higher concentration may be due to (a) the availability of fewer photo-catalyst active sites per dye molecule at a fixed catalyst load and (b) decrease in number of photons reaching the catalyst surface owing to light absorption/scattering [18].

CONCLUSION

Zinc sulfide, Fe_2O_3 and ZnS/ Fe_2O_3 composite photocatalysts nanoparticles have been synthesized by chemical method and sol-gel method. As synthesized photocatalysts were characterized using XRD, TEM and spectroscopic techniques. The synthesized ZnS, Fe_2O_3 and ZnS/ Fe_2O_3 composite photocatalysts have hexagonal wurtzite phase and rhombohedral α-Fe2O3 phase with average particle size 2.4 nm, 13nm and 45nm respectively. ZnS/ Fe_2O_3 composite results in the red shift of photo absorption in ZnS. Photocatalytic degradation of Victoria Blue-B dye at 180 minutes using optimum catalyst (Fe_2O_3) load 1000 mg/250ml was 97.2%. Effects of photo-catalyst load and dye initial concentration on the degradation of Victoria Blue-B have been investigated.

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