



## Photo-catalytic Degradation of Victoria Blue-B Dye using ZnS and Ag-N co-doped ZnS Nanoparticles under Visible Radiation

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### ABSTRACT

ZnS, Ag-doped, N-doped and Ag-N co-doped ZnS nanoparticles were prepared by Chemical method under optimal conditions and characterized using XRD, TEM and UV-Visible spectroscopic techniques. As-synthesized nanomaterial were used as a photo-catalysts 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 (94.8 %) of Victoria Blue-B was observed using catalyst load (ZnS-Ag-N): 1.0g 250mL of 25 mg L<sup>-1</sup>. Photocatalytic degradation of the dye follows pseudo first order kinetics. Using Victoria Blue-B initial concentration, 100mg L<sup>-1</sup>, the dye degradation rate constant under visible radiation and photocatalyst load, was 5.33 x 10<sup>-3</sup> min<sup>-1</sup>.

**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]. Over 15% of the textile dyes are lost in wastewater stream during dyeing operation. The textile industry produces large quantity of highly colored effluents, 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 and efficient 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<sub>2</sub>, ZnO, WO<sub>3</sub>, SnO<sub>2</sub>, CdS and ZnS.

The photo-catalytic action of semiconductor nonmaterial involves the photo-excitation of their valence band electron(s) to its conduction band and creation of positively charged holes (h<sup>+</sup>) 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  $\text{TiO}_2$  and  $\text{ZnO}$ , for this purpose, due to their high band gap energies ( $> 3.0$  electron volts) require high energy photons in the UV 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 modification of its valance band position by doping nonmetals such as nitrogen, fluorine, carbon, boron etc which may cause band-gap narrowing. By doping a non-metal, such as N, into a high band gap semiconductor, its photo-absorption edge may be shifted to visible region. It is because the energy states of substitutional and interstitial nitrogen doping configuration will lie in the valance and conductance band of zinc sulfide. This may induce visible photo-absorption thus enhancing photocatalytic activity of nitrogen doped zinc sulfide in visible radiations.

Present work reports the effect of N-doping, Ag-doping and Ag-N-co-doping in ZnS on the photo-catalytic 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

**Chemicals:** Zinc nitrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $M=297.47\text{g/mol}$  (MERCK), Sodium sulfide  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ,  $M=250.04\text{g/mol}$  (MERCK), Glucose  $\text{C}_6\text{H}_{12}\text{O}_6$ ,  $M=180.16\text{g/mol}$  (SRL), Silver nitrate  $\text{AgNO}_3$ ,  $M=169.87\text{g/mol}$  (MERCK), Urea  $\text{CH}_4\text{N}_2\text{O}$ ,  $M=60.06\text{g/mol}$  (MERCK), Victoria Blue-B ( $\text{C}_{33}\text{H}_{32}\text{ClN}_3$ ),  $M=506.08\text{g/mol}$ , SIGMA-ALDRICH Co.(USA) The structure of Victoria Blue-B is given in figure 1.

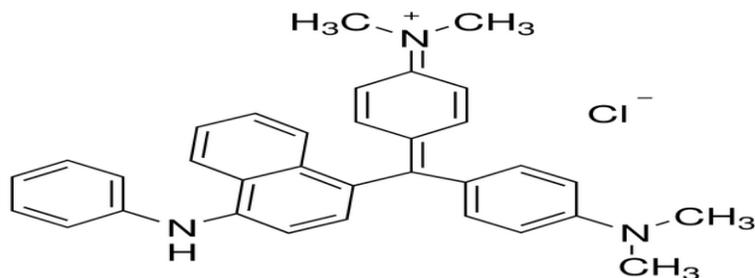


Figure 1. Structure of Victoria Blue-B dye (Source: SIGMA-ALDRICH)

### Methods

**Synthesis of ZnS Nanoparticles:** 1.0 M sodium sulfide was added, drop-wise, at  $70^\circ\text{C}$  to equal volume of 1.0 M Zinc nitrate aqueous solution with simultaneous stirring using a magnetic stirrer for 15 h. Now, 1.0 M glucose solution was added drop wise. The resultant mixture was heated and incubated at  $70^\circ\text{C}$  for more than 6 h. Precipitates thus obtained was centrifuged at 2,000 rpm for 15 min and the product was dried at  $50^\circ\text{C}$  for 4 h and then crushed to a fine powder.

**Doping of Nitrogen:** 10 g. of as-synthesized ZnS photo-catalyst and 30 g of urea was mixed well in an agate mortar. The mixture was transferred into a ceramic crucible and calcined at  $400^\circ\text{C}$  for four hrs and then cooled [13].

**Doping of Silver:** 10 g of as-synthesized ZnS photo-catalyst and 10 mL of 0.2 M  $\text{AgNO}_3$  aqueous solution was mixed in a ceramic crucible. The mixture was well agitated with glass rod and the solvent (water) was

evaporated in an oven at 110°C. The dried powder was calcined in a furnace at 400°C for four hours and then cooled to room temperature.

**Co-doping of Ag and N:** In a crucible, 10 g of as-synthesized N-doped ZnS was mixed with 10 ml of 0.2 M AgNO<sub>3</sub> aqueous solution. The liquid was evaporated at 110°C and the dried powder was calcined in a furnace at 400°C for 4 h and then cooled to room temperature.

#### Characterization of as synthesized material

**XRD Analysis:** X-ray diffraction patterns of as-synthesized photo-catalysts were obtained using an X-ray diffractometer (XRD) BRUKER D8 Advance XRD, AXS GMBH, Karlsruhe, West Germany) equipped with a Cu target for generating a CuK $\alpha$  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 (2 $\theta$ ) of 1s and 0.020°, respectively, over 2 $\theta$  = 4° to 64°.

**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 photo-catalyst 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.

**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).

**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 2). A 1.0g of as-synthesized photo-catalyst powder was added to 250 mL aqueous 100mg L<sup>-1</sup> Victoria Blue-B solution taken in the reactor tube and the suspension was stirred in dark for 60 min 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 min interval, 10mL of the reaction mixture was withdrawn and the suspension was centrifuged at 3000rpm for 15 min. The supernatant liquid was filtered through Whatman no. 1 filter 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 –

$$\% \text{ Degradation} = [(A_0 - A_t) / A_0] \times 100 \quad (1)$$

Where A<sub>0</sub> is absorbance of dye at initial stage and A<sub>t</sub> is absorbance at time “t”.

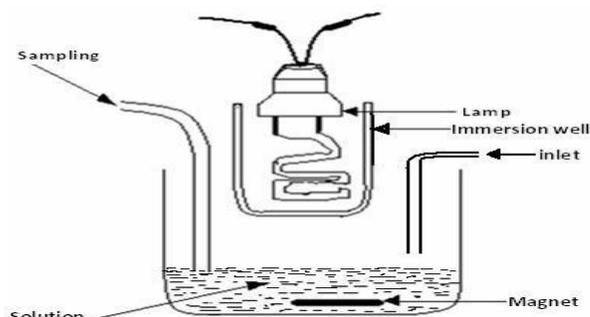


Figure 2. Photocatalytic Reactor

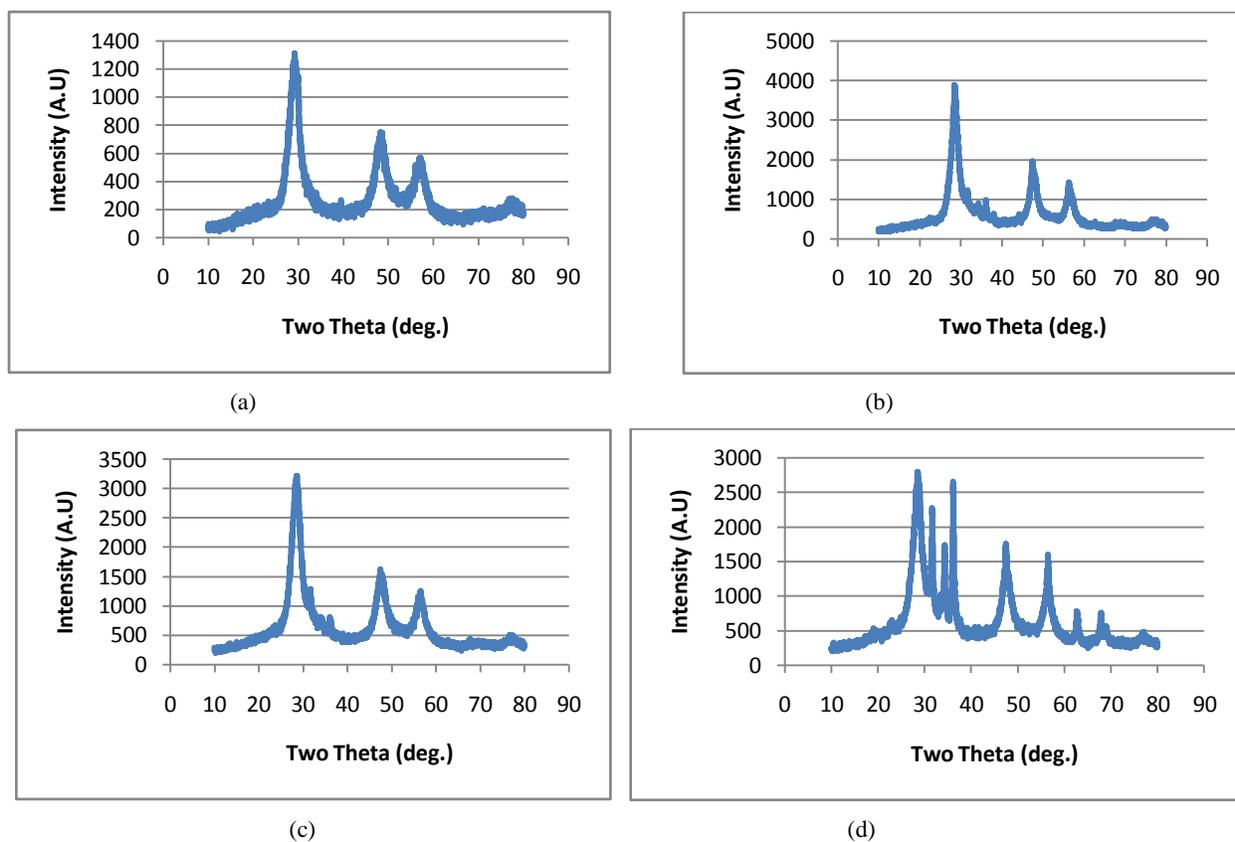
## RESULTS AND DISCUSSION

**XRD Analysis:** XRD patterns of ZnS, Ag doped ZnS, N-doped ZnS and Ag-N co-doped ZnS are exhibited in figure 3. Diffraction peaks at  $2\theta = 29.2, 48.3$  and  $57.3^\circ$  correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of pure ZnS. Diffraction peaks at  $2\theta = 28.7, 47.5$  and  $56.6^\circ$  correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of N doped ZnS. In the XRD pattern of N-doped ZnS two additional peaks appeared between  $30.0 - 40.0^\circ$ , indicates the creation of new crystal phases. However, it is difficult to assign the position of N in the doped ZnS. The same may either be occupying the interstitial sites or substituting the oxygen atoms at the lattice positions of ZnS crystal. Diffraction peaks at  $2\theta = 28.5, 47.5$  and  $56.4^\circ$  correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of Ag doped ZnS. In the XRD pattern of Ag-doped ZnS small additional peaks appeared between  $30.0 - 40.0^\circ$ , indicates the creation of new crystal phases. However, it is difficult to assign the position of Ag in the doped ZnS. Diffraction peaks at  $2\theta = 28.4, 47.4$  and  $62.2^\circ$  correspond to (101), (110) and (111) planes of hexagonal wurtzite phase of Ag-N co-doped ZnS. In the XRD pattern of Ag-N co-doped ZnS small additional peaks appeared at  $29.1, 31.6, 34.3$  and  $67.9^\circ$ , indicates the creation of new crystal phases.

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

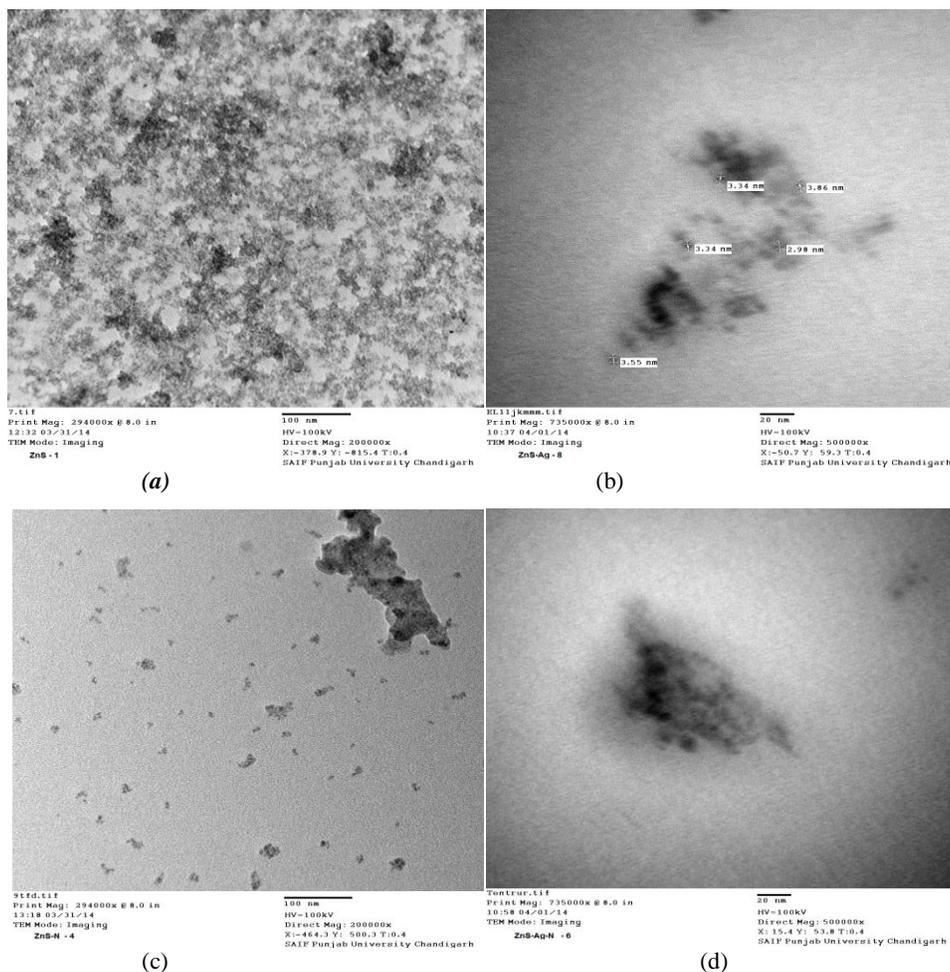
$$D = (K \lambda) / (\beta \cos \theta) \quad (3.1)$$

Where D is the average particle size,  $\lambda$  is wavelength (0.15406 nm) of X-ray;  $\beta$  is full width at half-maxima (FWHM) of diffraction peak appeared at  $2\theta = 29.2^\circ$  and  $\theta$  is the incident angle of X-ray; K is the geometric factor equal to 0.94. The average crystallite size of as-synthesized ZnS, Ag doped ZnS, N doped ZnS and Ag-N co-doped ZnS thus obtained were 2.5 nm, 3.6 nm, 2.7 nm and 2.7 nm, respectively.



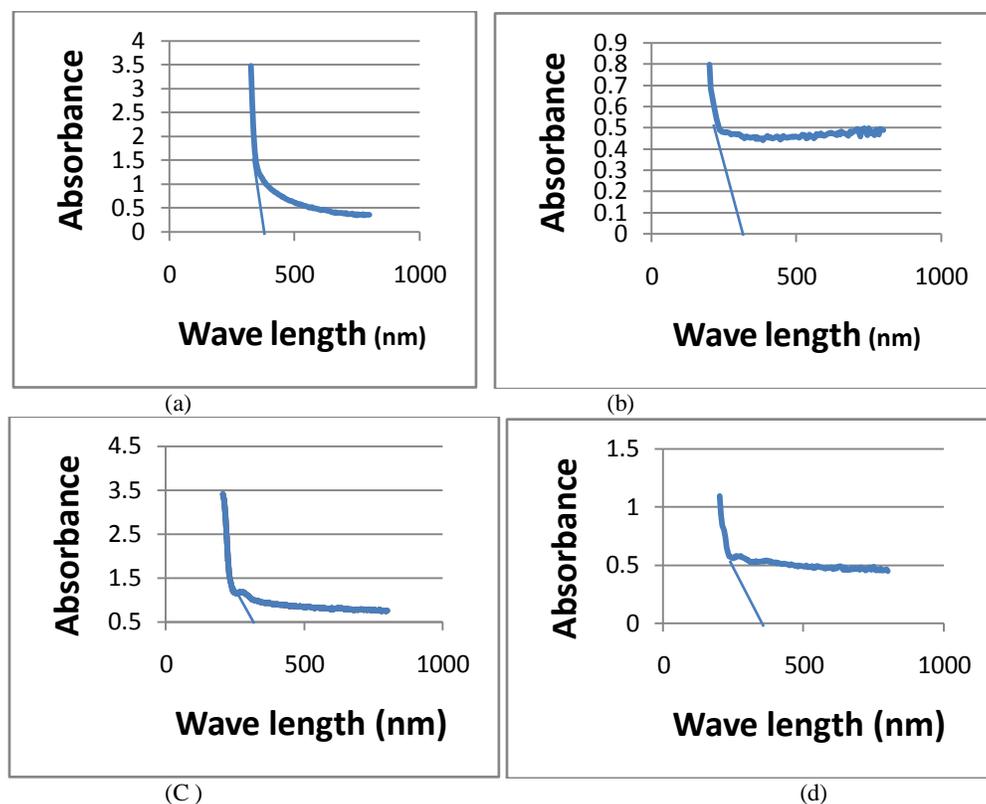
**Figure-3.** XRD of as-synthesized photo-catalyst (a) ZnS, (b) Ag-doped ZnS, (c) N-doped ZnS and (d)= Ag-N-co-doped ZnS

**TEM Analysis:** TEM images of as-synthesized ZnS, Ag-doped ZnS, N-doped ZnS and Ag-N-co-doped ZnS particles are presented in figure 4. Their average particle size were found to be 2.4 nm, 3.3 nm, 2.5 nm and 2.5 nm, respectively. These are in fair agreement with those obtained using XRD technique.



**Figure 4.** TEM image of as-synthesized (a) ZnS, (b) Ag-doped ZnS, (c) N-doped ZnS and (d) Ag-N co-doped ZnS photo-catalyst

**UV/Visible Absorption study:** UV-visible absorption spectra of ZnS, Ag-doped ZnS, N-doped ZnS and Ag-N co-doped ZnS 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, 375nm, 395nm and 450 nm, respectively. The observed red shift in the absorption edge on doping N into ZnS may be due to the modification of electronic levels of ZnS by doped N [14].



**Figure 5.** UV-Visible absorption spectra of as-synthesized synthesized (a) ZnS photo-catalyst (absorption edge 340 nm), (b) Ag- doped ZnS (absorption edge 375 nm), (c) N- doped ZnS (absorption edge 395 nm) and (d) Ag-N-co- doped ZnS (absorption edge 450 nm)

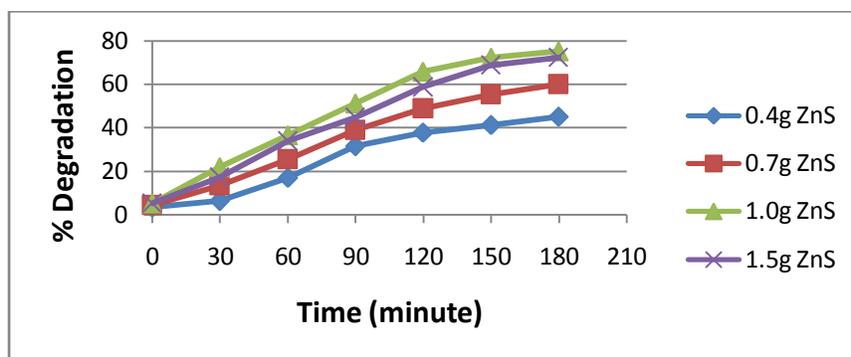
Band gap energy of as-synthesized photo-catalysts were obtained using the relation [15].

$$E_g = 1240 / \lambda \quad (3.2)$$

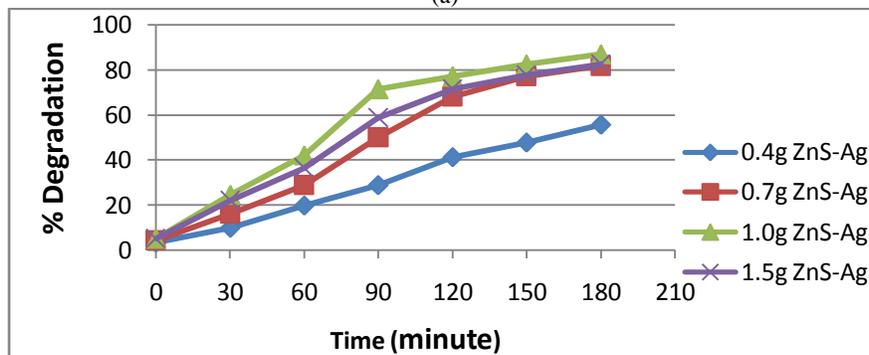
Where,  $E_g$  is band gap energy of photo-catalyst in electron volts, and  $\lambda$  is absorption edge wavelength in nanometers. Band gap energy thus obtained for un-doped ZnS, Ag-doped, N-doped and Ag-N co-doped ZnS nanoparticles are 3.64, 3.30, 3.13 and 2.75 eV, respectively. The lower band gap energy of Ag-doped, N-doped and Ag-N co-doped ZnS compared to un-doped ZnS may be due to the incorporation of new energy states by substitutionally and interstitially doped Silver and nitrogen in the former photo-catalyst.

### Photocatalytic Degradation Study

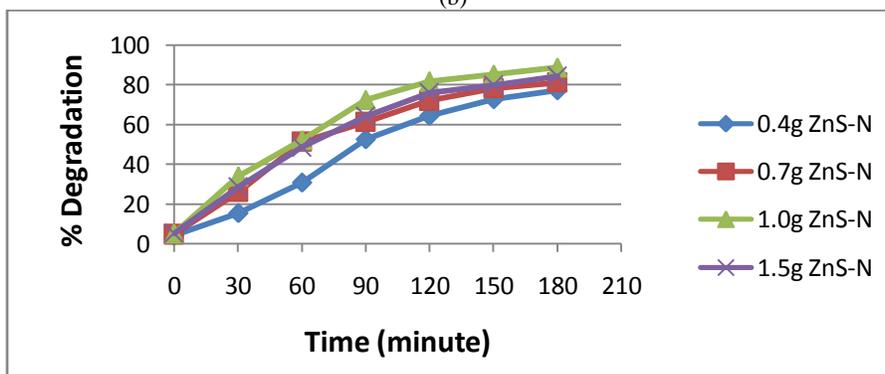
**Effect of Catalyst Load:** Plots of percent adsorption under dark and percent photo-catalytic degradation of VBB under visible radiation as a function of time at different load ( $\text{mg } 250\text{mL}^{-1}$ ) of ZnS, Ag doped ZnS, N-doped ZnS and Ag-N co-doped ZnS photocatalyst are presented in figures 6 and 7. Plot of percentage degradation of VBB under visible irradiation at 180 min as a function of amount ( $\text{mg}/ 250\text{ml}$ ) of ZnS, Ag doped ZnS, N doped ZnS and Ag-N co-doped ZnS is presented in figure 8. The percent adsorptions of VBB under dark has been taken as reference for zero minute irradiations [7]. The optimum photo-catalyst load that led to maximum degradation (94.80%) of VBB under visible radiations was found to be  $1000 \text{ mg } 250\text{mL}^{-1}$  of  $100\text{mg L}^{-1}$  VBB.



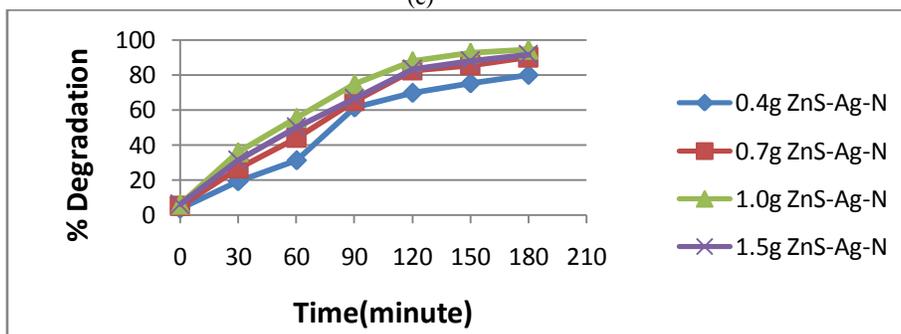
(a)



(b)

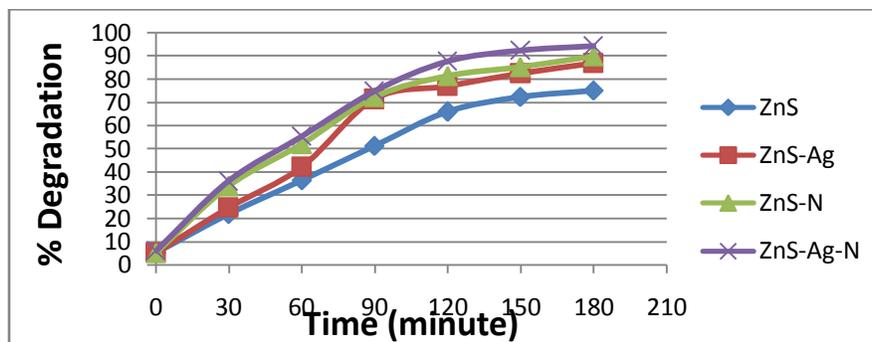


(c)

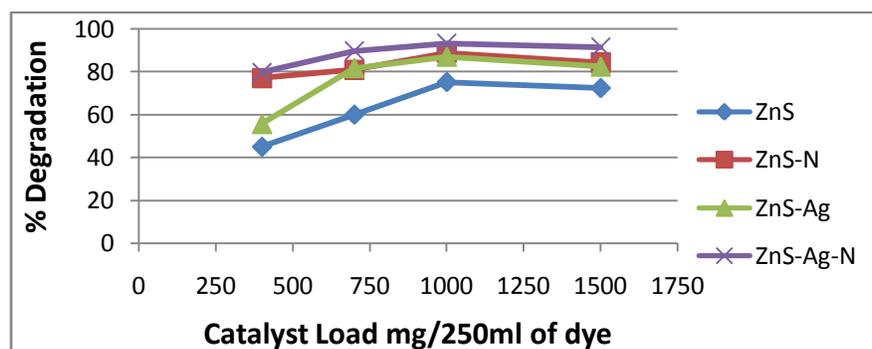


(d)

**Figure 6.** Plots of the percent degradation of Victoria Blue-B ( $100\text{mg L}^{-1}$ ) as a function of time under visible radiation at different load ( $\text{mg } 250\text{mL}^{-1}$ ) of (a) ZnS, (b) Ag-doped ZnS, (c) N-doped ZnS and (d) Ag-N-co-doped ZnS photocatalyt



**Figure 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, Ag doped ZnS, N doped ZnS and Ag-N co-doped ZnS photocatalyt.



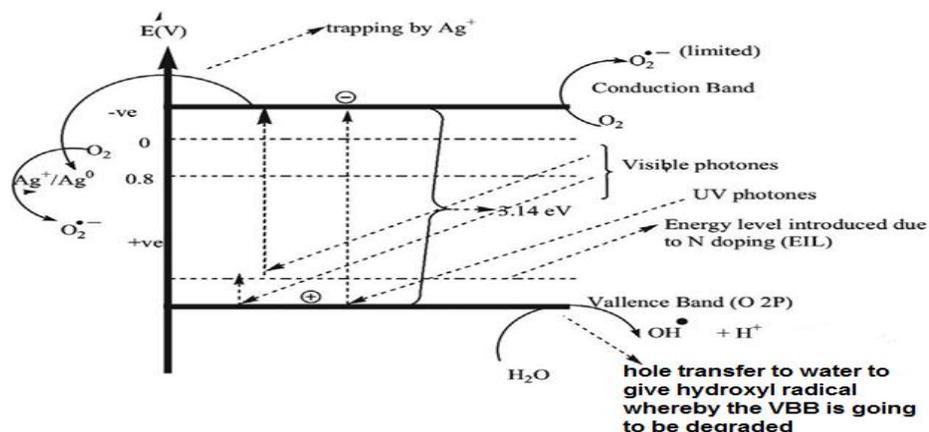
**Figure 8.** Plot of percentage degradation of Victoria Blue-B ( $100\text{mg L}^{-1}$ ) under visible radiation at 180 min as a function of ZnS, Ag-doped, N-doped, Ag-N co-doped ZnS load ( $\text{mg } 250\text{mL}^{-1}$ )

Percent degradation of dye increases on raising the photo-catalyst load up to  $1000\text{ mg}/250\text{ml}$  of  $100\text{mg}/\text{L}$  of VBB dye but on further increasing the catalyst load, degradation of dye gradually falls (Figure 8). 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  $1000\text{ mg}/250\text{ml}$ . On further increasing the photo-catalyst load above  $1000\text{ mg}/250\text{ml}$ , 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 photo-catalyst 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].

Photocatalytic activity of Ag-N co-doped ZnS is higher than the remaining as-synthesized photo-catalysts under visible radiation. Under visible radiation the percentage degradation of VBB is higher using N-doped ZnS as photo-catalyst than under Ag-doped ZnS. It is because doped N into ZnS modifies its electronic structure leading to the band gap narrowing [18] and thus enabling it to harvest more photons in the visible light [19-21].

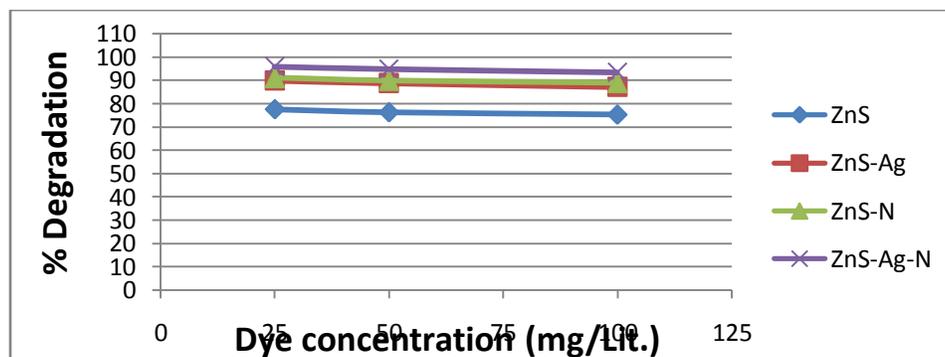
**Mechanism of synergetic effect of Ag-N co-doping on photo-catalysis:** The proposed mechanism of synergetic effect of Ag-N co-doping in ZnS on the photocatalytic degradation of VBB has been described in figure 9. In Photocatalysis process, excitation of electrons from the valence band (VB) to the conduction band (CB) of ZnS. The excited electron are tapped by  $\text{Ag}^+$  ion to form  $\text{Ag}^0$ , since the CB is at a lower reduction potential ( $-0.32\text{eV}$ ) compared to  $\text{Ag}^+$  ion reduction potential ( $0.8\text{eV}$ ). Neutral  $\text{Ag}^0$  atoms thus formed are then oxidized to their original state ( $\text{Ag}^+$ ) with simultaneous conversion of adsorbed  $\text{O}_2$  to superoxide ( $\text{O}_2^-$ ) radicals. In this way, the recombination of photo-generated electrons and holes is minimized. In the subsequent steps, superoxide radicals formed, generate hydroxyl (OH) radicals by combining with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  ions. OH radicals which are highly oxidizing agents, degrade the substrate

(Victoria Blue-B in the present case) molecules to non-toxic products. During photocatalysis under visible radiation, using N-doped ZnS excitation of electrons from VB of the photocatalyst to a newly generated energy level (created by doped nitrogen) takes place. It is followed by the absorption of new photons of visible radiation for the further transfer of electrons to the conduction band of ZnS. 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:  $1000 \text{ mg } 250\text{mL}^{-1}$  is presented in figure-10. The degradation of dye decreases with the increase of dye initial concentration over the studied dye concentration range:  $2.5 \times 10^{-6}$  to  $1.0 \times 10^{-5}$  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 [16].



**Figure 9.** Proposed mechanism of synergetic effect of Ag-N co-doping onto ZnS on the photocatalytic degradation of Victoria Blue-B dye

**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:  $1000 \text{ mg } 250\text{mL}^{-1}$  is presented in figure10. The degradation of dye decreases with the increase of dye initial concentration over the studied dye concentration range:  $2.5 \times 10^{-6}$  to  $1.0 \times 10^{-5}$  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 [21].



**Figure 10.** Plot of percentage photo-catalytic degradation of VBB at 180 min under visible radiation as a function of dye initial concentration (Photo-catalyst load:  $1000\text{mg } 250\text{mL}^{-1}$ )

## APPLICATIONS

The sample, ZnS and Ag-N co-doped ZnS, prepared showed excellent photo catalytic activity for the degradation of Victoria Blue B dye under visible light irradiation. Victoria blue B dye, also called Basic Blue 26, is a cationic dye and is used to dye anionic fabrics such as wool, silk, nylon and acrylics. When present in water even at very low concentration, it is a highly toxic substance for living bodies. This dye being hazardous in nature is needed to be removed from polluted water.

## CONCLUSIONS

Zinc sulfide and N-doped, Ag-doped and Ag-N co-doped ZnS photocatalysts nanoparticles have been synthesized by chemical method and characterized using XRD, TEM and spectroscopic techniques. The synthesized ZnS, Ag-doped, N-doped and Ag-N co-doped ZnS photo-catalysts have hexagonal wurtzite phase with average particle size 2.4 nm, 3.3 nm, 2.5 nm and 2.5 nm, respectively. Doping of Ag and N into ZnS results in the red shift of photo absorption. Photo-catalytic degradation of Victoria Blue-B dye at 180 minutes using optimum catalyst (Ag-N-co-doped ZnS) load 1000 mg 250mL<sup>-1</sup> was 94.8%. Effects of photo-catalyst load and dye initial concentration on the degradation of Victoria Blue-B have been investigated.

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