

Photocatalytic Activity of N-doped ZnS Nanoparticles for Degradation of Organic Pollutant (Methylene Blue)

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Abstract: Nanoparticles of undoped ZnS and N-doped-ZnS were prepared by using chemical co-precipitation method. The precursors used to synthesize the photocatalyst nanoparticles were: $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Na_2S \cdot 9H_2O$. The characterization of nanoparticles was done using X-ray powder diffraction (XRD) and UV-VIS Spectrophotometric technique. The average crystalline size of as-synthesized photocatalysts calculated using the Debye-Scherrer formula was 7.80 and 7.48 nm for Zc and NZ respectively. The percentage degradation of methylene blue under UV irradiation at 180 minutes were: 10.12, 24.85 and 38.09 for uncalcined zinc sulfide (Zc), calcined zinc sulfide (Zc) and N-doped zinc sulfide (NZ) respectively. Under solar irradiation the Percentage photodegradation of MB were: 13.53, 30.17 and 57.30 for Zc, Zc and NZ respectively. The pseudo first order rate constant (k) of MB photodegradation for Zc, Zc and NZ were 5.72×10^{-4} , 1.64×10^{-3} and $2.54 \times 10^{-3} \text{ min}^{-1}$ and 0.8×10^{-3} , 2.15×10^{-3} and $4.16 \times 10^{-3} \text{ min}^{-1}$ under UV irradiation and under solar irradiation, respectively.

Keywords: Chemical co-precipitation, Degradation, Photocatalysis, Rate constant, XRD

1. Introduction

Organic dyes are one of the major groups of pollutants in waste waters released from textile and other industrial processes (Hun *et al.*, 1999; Kiwi *et al.*, 1993 and Li *et al.*, 2004). Over 15% of the textile dyes are lost in wastewater stream during dyeing operation. The textile industry produces large quantity of high colour effluents, which are generally toxic and resistant to degradation by biological treatment methods. A necessary criterion for the use of these dyes is that they must be highly stable towards light and during washing. They must also be resistant to microbial attack. Therefore, dyes in waste water are not readily degradable and are not easily removed from water by conventional chemical treatment systems (Tang *et al.*, 1995). Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a cost-effective alternative for water remediation (Hoffman *et al.*, 1995).

Recently, use of nanosize semiconductors photocatalytic oxidation to toxic pollutants is being increasingly valued. A lot of organic matter can be decomposed into inorganic and less toxic simpler compound. Because, this kind of reaction needs only light, catalyst and air, the processing cost is lower, thus becoming a new promising method for waste water treatment (Legrini *et al.*, 1993; Hu *et al.*, 1995).

Several semiconductor photocatalysts being used for the treatment of waste water pollutants are: TiO_2 , ZnO, WO_3 , SnO_2 , CdS and ZnS (Herrmann, 1999). In particular TiO_2 has drawn much attention in research and industrial fields in recent years because of its characteristic powerful oxidation capability, non-toxicity, chemical stability, and cost-effectiveness.

In other words, semiconductor materials are materials whose valence band and conduction band are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-

gap, electrons in the valence band can be excited and jump up into the conduction band, and thus charge carriers are generated. In order to have a photocatalyzed reaction, the e^- - h^+ recombination, subsequent to the initial charge separation, must be prevented as much as possible (Gerven *et al.*, 2007).

The wide band gap energy (3.7 eV) of ZnS limits light absorption in the UV region. A possible strategy to extend zinc sulfide photo-absorption to visible light may be modification of its valence band position by doping nonmetals such as nitrogen, fluorine, carbon, boron in semiconductor which can cause band-gap narrowing. By nitrogen doping photo-absorption edge of zinc sulfide may be shifted to visible region because energy states of substitutional and interstitial nitrogen doping configuration will lie in the valence and conductance band of zinc sulfide. This may induce visible photo-absorption thus enhancing photocatalytic activity of nitrogen doped zinc sulfide in solar radiations.

The main objective of this paper was preparing Zinc Sulfide (ZnS) Nanoparticle and Nitrogen doped Zinc Sulphide (N-doped ZnS) Nanoparticle for photocatalytic degradation of organic pollutant (methylene blue).

2. Principles of Photocatalytic Oxidation

In the photocatalyst oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalyst an energetic light source and an oxidizing agent such as oxygen or air. Only photons with energies greater than the band-gap energy can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants. The absorption of photons with energy lower than the band-gap energy or longer wavelengths usually causes energy dissipation in the form of heat. The illumination of the photocatalyst with sufficient energy leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The

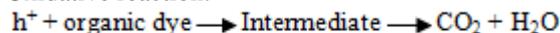
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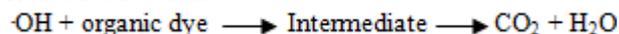
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positive hole oxidizes either the pollutant directly or water to produce hydroxyl radical $\cdot\text{OH}$, whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst (Ahmed *et al.*, 2010).

Oxidative reaction:



Reductive reaction:



Hydroxyl radical generation by the photocatalytic oxidation process is shown in the above steps. In the degradation of organic pollutants, the hydroxyl radical generated from the oxidation of adsorbed water is the primary oxidant, and the oxygen present reacts with electron at the conduction band to form peroxide radicals followed by a number of steps forming H_2O_2 or $\cdot\text{OH}$ radical thus can prevent the recombination of an electron-hole pair. The $\cdot\text{OH}$ attacks organic compounds resulting in various reaction intermediates depending on the nature of the compounds (Hoffmann *et al.*, 1995; Herrmann, 1999). The resulting intermediates further react with $\cdot\text{OH}$ to produce final degradation products such as CO_2 and H_2O . In the photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, there is an electron accumulation in the CB, thereby causing an increase in the rate of recombination of e^- and h^+ (Cui *et al.*, 2001 and Lei, 2001)

3. Experimental

3.1. Preparation of Zinc Sulfide Nanoparticles

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), 1M of 100 ml and 100 ml of 1M solution of sodium sulphide were mixed at 80 °C using magnetic stirrer and 100 ml of ethanol was added with stirring. Then 30 ml of deionized water containing 2g of EDTA was added drop by drop and the process was continued for two hours. After 2 hours, the solution was cooled at room temperature (Murugadoss *et al.*, 2009). The precipitate was washed at several times using distilled water and alcohol to remove the impurities, if any. Finally the wet precipitate was dried in hot air oven and labeled as uncalcined zinc sulfide (Znc). Some portion of the product (Znc) was calcined at 350°C for 2hrs, cooled to room temperature, ground in agate mortar and labeled as calcined zinc sulfide (Zc).

3.2. Preparation of Nitrogen-doped Zinc Sulfide

5g of Zinc sulfide was added to 15 g of urea, ground in an agate mortar and mixed well. The mixture was calcined in a ceramic crucible at 350°C for 2 hrs, cooled to room temperature and was ground in an agate mortar (Zheng and Wu, 2009). The product was labeled as nitrogen-doped zinc sulfide (NZ).

3.3. Photocatalytic degradation studies

Photocatalytic degradation of methylene blue (MB) was carried out using a reactor consisting of a glass tube with an inlet tube for provision of air purging during photocatalysis and outlet for the collection of samples from the reactor at different time intervals. A 0.15g of the as-synthesized photocatalyst powder and 500 ml aqueous solution of methylene blue of known concentration was taken in the reactor tube and the suspension was stirred in dark for 40 minutes to obtain adsorption/desorption equilibrium before irradiating the dye. 10 ml of the sample was withdrawn at 20 minutes regular time interval. The suspension was centrifuged at 2500 rpm for 5 minutes and filtered to remove the catalyst particles before measuring absorbance. The absorbance of the clear solution was measured at $\lambda_{\text{max}} = 665$ nm using UV/Vis spectrophotometer (SP65) for quantitative analysis. The degradation efficiency of MB has been calculated as (Pouretedal *et al.*, 2009).

$$\% \text{ Degradation} = [(C_0 - C)/C_0] \times 100 \% \dots \dots \dots (1)$$

Where C_0 is the initial concentration of MB and C is the concentration of MB after irradiation at a given time.

4. Result And Discussion

4.1 XRD analysis

In the XRD pattern of Zinc sulfide (Fig.1) there were three diffraction peaks at $2\theta = 28.66^\circ$, 47.56° and 56° which correspond to (111), (220) and (311) planes of the cubic crystalline ZnS (Pedro *et al.*, 2006). Due to size effect, the XRD peaks were broadened and their widths become larger as the particles become smaller. The obtained XRD results were very well matched with the standard cubic ZnS. The XRD peaks of the cubic crystallite Zinc sulfide nanoparticles proved to be broad due to small particle size (Pedro *et al.*, 2006). The broadness of peaks indicates the formation of nanoparticles and sharp peaks indicates the crystalline nature of the materials.

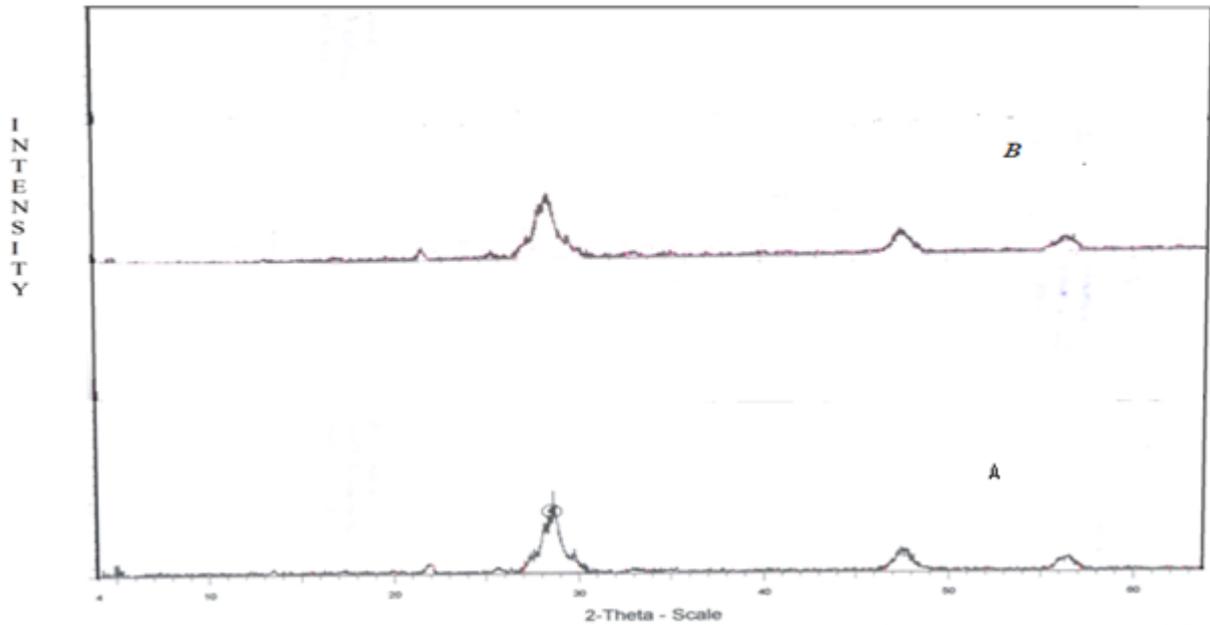


Figure 1: XRD spectra (A) Calcined ZnS, (B) N-doped ZnS

On doping N-in zinc sulfide there is no additional peak at $2\theta = 31.2^\circ$ is observed suggesting that there is no distortion of ZnS cubic structure. Based on the observed full width at half maximum (FWHM) value of the (111) peak and using Debye-Scherrer formula the average particle size were calculated from equation (2) and recorded in (Table 1).

$$D = 0.9\lambda/\beta \cos\theta \text{ (Wu, 2004)} \dots\dots\dots(2)$$

Where D is the average crystallite size, λ is the wavelength of the X-ray = 0.15406 nm for Cu target $K\alpha$ radiation, β is the full width at half maximum of an XRD peak and θ is the Bragg's angle. The average crystallite size (D) of the photocatalysts is given in table 1.

Sample	2θ (Degree)	β (Radian)	D (nm)
Zc	28.66	0.0183	7.80
NZ	28.87	0.0191	7.48

4.2 UV/Vis diffuse absorption measurements

The optical absorption spectra of photocatalysts i.e. Zinc Sulfide and Nitrogen doped Zinc sulfide measured in the UV-Vis region are shown below in Figures 2 and 3. Absorption edge for ZnS and N-ZnS are: 336, 385 nm, respectively.

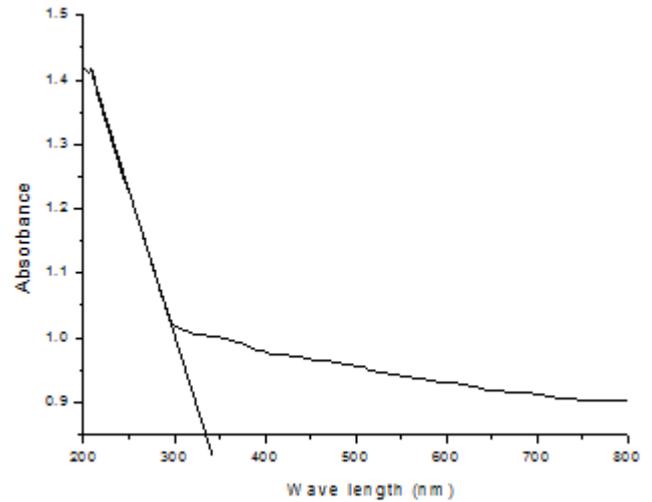


Figure 2: UV-Visible absorption spectra of calcined zinc sulfide (absorption edge 336 nm)

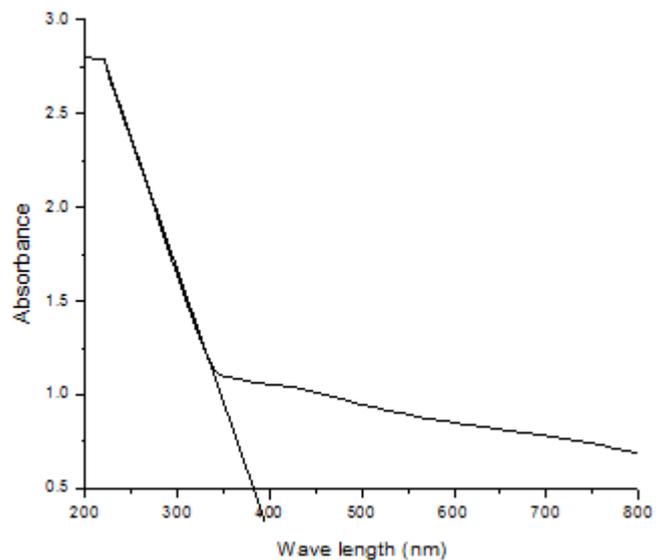


Figure 3: UV-Visible absorption spectra of N- doped zinc sulfide (absorption edge 385 nm)

Band gap energy of the as-synthesized photocatalysts was obtained using the relation (El-Kemary *et al.*, 2009).

$$E_g \text{ (eV)} = hc/\lambda = [1240\text{eV nm} / \lambda] \dots \dots \dots (3)$$

The band gap energies of photocatalysts Zc, NZ, were found as 3.69 and 3.22 eV respectively.

4.3. Photocatalytic Degradation Study

The plots of percentage adsorption/degradation of methylene blue as a function of time under no irradiation, UV irradiation and solar irradiation are shown from Fig.4-6. The

rate of decolorization was recorded with respect to the change in intensity of absorbance at 665 nm.

The percentage adsorption of MB without irradiation using the adsorbents: Znc, Zc and NZ at 180 minutes were: 0.55, 1.50 and 2.21 respectively (Fig. 4). The percent adsorption of MB in dark are used as reference as zero minute irradiations (Patil *et al.*, 2010). The percentage photodegradation of MB for Znc, Zc and NZ under UV irradiation are: 10.12, 24.85 and 38.09 respectively at 180 minutes (Fig.5) and such values under solar irradiation are: 13.53, 30.17 and 57.30 respectively (Fig.6).

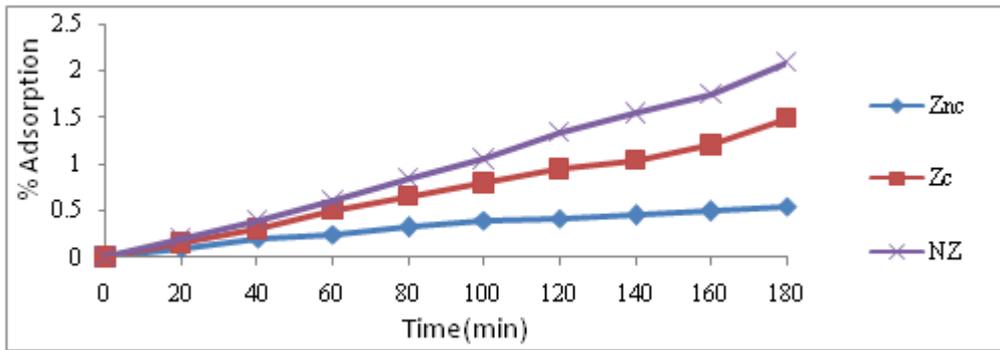


Figure 4: Plots of percentage adsorption of MB as a function of time (without irradiation)

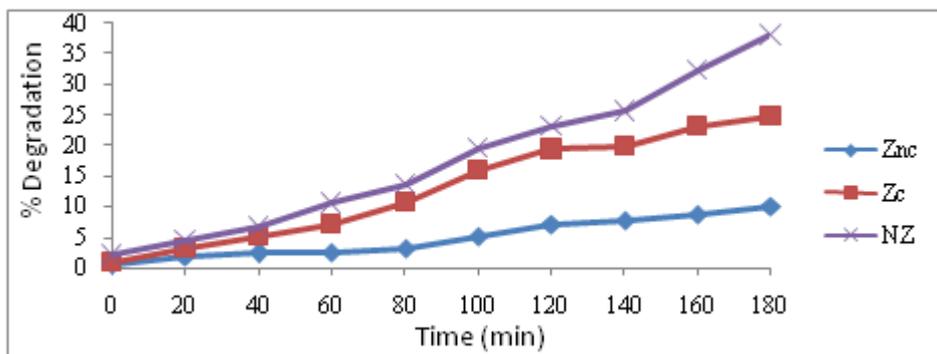


Figure 5: Plots of percentage degradation of MB as function of time (under UV irradiation)

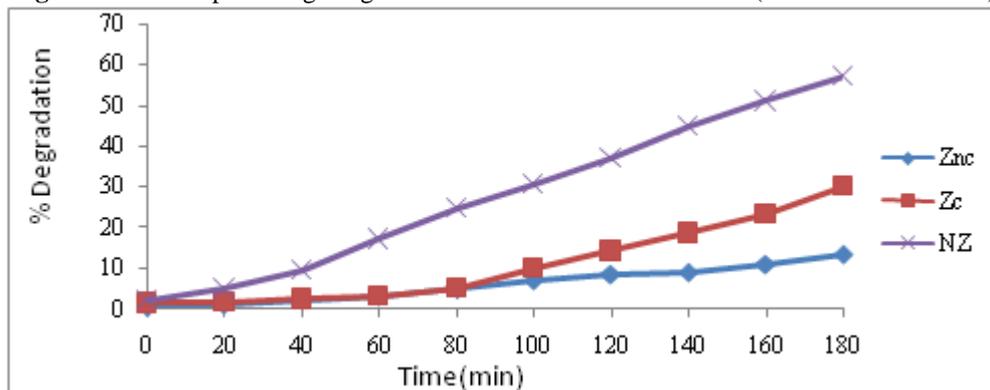


Figure 6: Plots of percentage degradation of MB as function of time (under solar irradiation)

Note: Znc: uncalcined zinc sulfide, Zc: calcined zinc sulfide, MZ: Mn-doped zinc sulfide, NZ :N-doped zinc sulfide and MNZ: Mn-N co-doped zinc sulfide

4.2.4. Kinetic Studies of Photocatalytic Degradation of MB

The kinetics behavior of photocatalytic reaction can be described by a modified Langmuir-Hinshelwood model (Zhang *et al.*, 1998 and Fu *et al.*, 2005). The kinetics

adsorption/photodegradation of MB for an initial concentration of 25 mg/l shows that the photocatalytic decolorization of dye can be described by the first order kinetics (eq.4).

$$\ln(C_0/C) = kt \dots \dots \dots (4)$$

Where C_0 is the initial concentration of MB and C is its concentration at any time, t

The rate constant for adsorption of MB without irradiation using the adsorbents: Znc, Zc and NZ are: 0.95×10^{-4} , 1.17×10^{-4} and $1.39 \times 10^{-4} \text{ min}^{-1}$ respectively (Fig.7). The rate constants (k) for the degradation of MB, using Znc, Zc and NZ under UV irradiations: 5.72×10^{-4} , 1.64×10^{-3} and $2.54 \times$

10^{-3} min^{-1} respectively (Fig.8). Under solar irradiation the rate constants of dye degradation were: 0.8×10^{-3} , 2.15×10^{-3} and $4.16 \times 10^{-3} \text{ min}^{-1}$ (Fig.9).

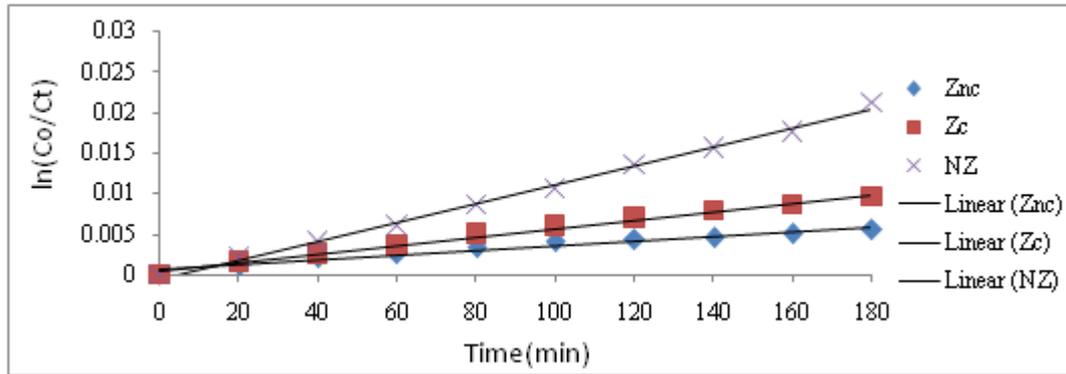


Figure 7: Plot of $\ln(C_0/C_t)$ vs. time curves for photocatalytic degradation of MB using zinc sulfide and modified zinc sulfide photocatalysts (without irradiation)

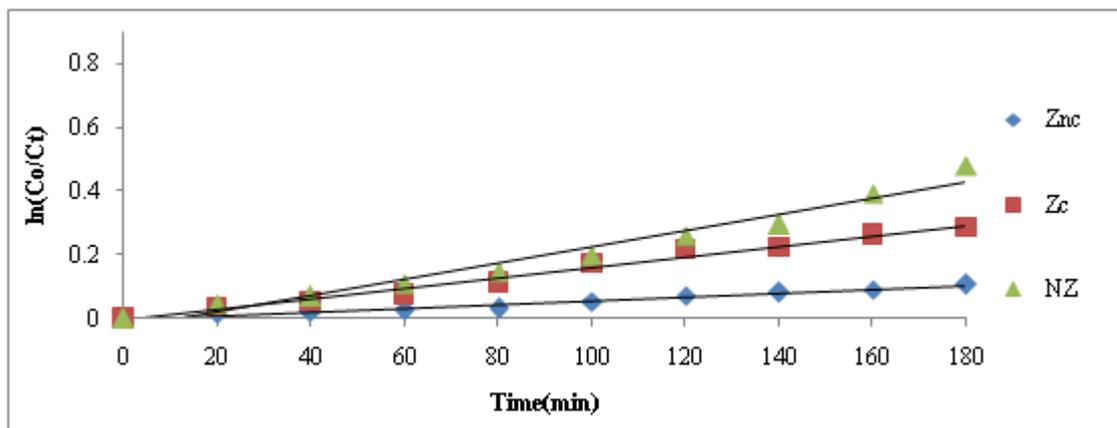


Figure 8: Plot of $\ln(C_0/C_t)$ vs. time curves for photocatalytic degradation of MB using zinc sulfide and modified zinc sulfide photocatalysts (under UV irradiation)

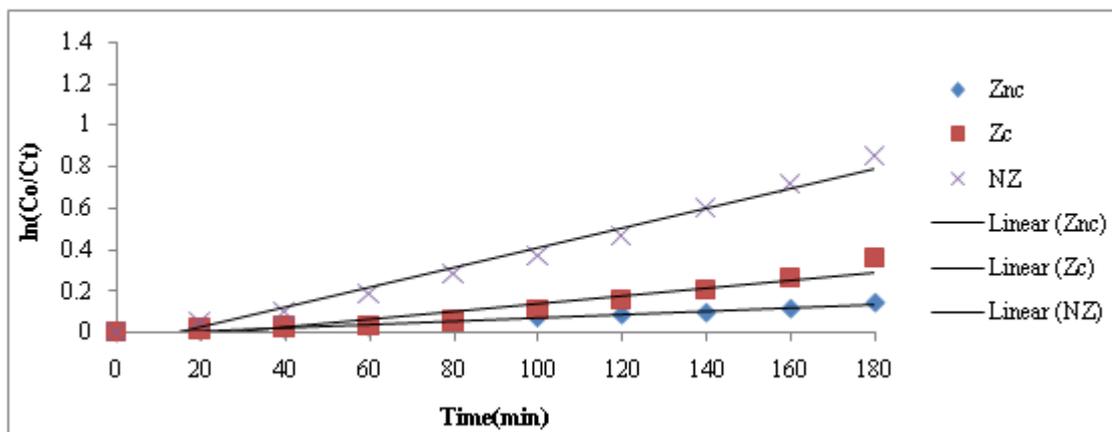


Figure 9: Plot of $\ln(C_0/C_t)$ vs. time for photocatalytic degradation of MB using zinc sulfide and modified zinc sulfide photocatalysts (under solar irradiation)

5. Summary and Conclusion

Zinc sulfide and N-doped zinc sulfide photocatalyst nanoparticle have been synthesized. The characterization of nanoparticles was done using X-ray powder diffraction (XRD) and UV-VIS Spectroscopy. XRD results reveal that N-doped in ZnS replace some of S atom in the crystal lattice

and Nitrogen doped in ZnS extends the photo-absorption in the visible range.

The photocatalytic activity of N-doped ZnS is highest among the studied photocatalysts under both solar as well as UV irradiations. It may be due to the extend zinc sulfide photo-absorption to visible light may be modification of its valance band position by doping nitrogen which can cause

band-gap narrowing. The results also indicate that decolorization of methylene blue using N-doped ZnS occurs at a fasterrate with solar light in comparison to UV radiation.

The photocatalytic degradation of methylene blue using as synthesized photocatalysts follows pseudo-first order kinetics. Since correlation coefficient $R^2 > 0.96$ it was found that all reactions were found to follow a pseudo-first-order kinetics. The order of photocatalytic efficiency of as-synthesized nanomaterials under solar irradiation is: NZ >Zc>Znc and at the same time under UV irradiation NZ >Zc>Znc.

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