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Photo Catalytic Activity of Mn-N Co-Doped ZnsNanoparticles for Degradation of Organic Pollutant (METHYLENE BLUE)

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Abstract

Nanoparticles of undoped ZnS, Mn-doped-ZnS, N-doped-ZnS and Mn-N co-doped ZnS were prepared by using chemical co-precipitation method. The precursors used to synthesize the photo catalyst nanoparticles were: Zn $(CH_3COO)_{2.2H2O}$, Mn $(CH_3COO)_{2.4H2O}$ and $Na_2S.9H_2O$. The characterization of nanoparticles was done using X-ray powder diffraction (XRD) and UV–VIS Spectrophotometric technique. The average crystalline size of as-synthesized photo catalysts calculated using the Debye- Scherrer formula was 7.80, 7.48, 6.61 and 6.59 nm for 60 for uncalcined zinc sulfide (Znc), calcined zinc sulfide (Zc), Mn-doped zinc sulfide (MZ), N-doped zinc sulfide (NZ) and Mn-N co-doped zinc sulfide (MNZ) respectively. The percentage degradation of methylene blue under UV irradiation at 180 minutes was: 10.12, 24.85, 45.19, 38.09, and 55.60 for Znc, Zc, MZ, NZ and MNZ respectively. Under solar irradiation the Percentage photo degradation of MB were: 13.53, 30.17, 49.00, 57.30 and 70.75 for Znc, Zc, MZ, NZ, and MNZ respectively. The pseudo first order rate constant (k) of MB photo degradation for Znc, Zc, NZ, MZ, and MNZ were 5.72×10^{-4}, 1.64×10^{-3}, 2.54×10^{-3}, 3.23×10^{-3} and 4.48×10^{-3} min^{-1} and 0.8×10^{-3}, 2.15×10^{-3}, 4.16×10^{-3}, 5.3×10^{-3} and 8.66×10^{-3} min^{-1} under UV irradiation and under solar irradiation, respectively.

Key words: Chemical co-precipitation, Degradation, Photo catalysis, Rate constant, XRD

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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). The textile industry produces large quantity of high colour effluents, which are generally toxic and resistant to degradation by biological treatment methods. For treatment of waste waters, heterogeneous photo catalysis has been considered as a cost-effective alternative for water remediation (Hoffman et al., 1995).

Photo catalysis is the combination of using a photo catalyst and UV or visible light for the treatment of wastewaters and gaseous pollutants. By using Nano size semi-conductors a lot of organic matter can be decomposed into inorganic and less toxic

simpler compound. 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 (Hu et al., 1995). Radicals formed at the surface dissolve in solution and then react with pollutants (Chen et al., 2007).

ZnS photo-absorption to visible light may be modification of its valance band position by doping non-metals such as nitrogen in semiconductor which can cause band-gap narrowing. By nitrogen doping photo-absorption edge of ZnS may be shifted to visible region because energy states of substitution and interstitial nitrogen doping configuration will lie in the valance and conductance band of ZnS and this enhancing photo catalytic activity of N-doped ZnS in solar radiations. Co-doping of metal-non-metal may further improve photo catalytic activities of ZnS by reducing anodic photo-corrosion, improving its stability in acidic/basic solutions, further narrowing of the band gap energy of ZnS and minimizing electron-hole recombination.

Through various modification techniques are reported to improve the photo catalytic activity of ZnS for degradation of organic pollutants, little work has been done on metal-doping. To the best of the researcher's knowledge no work has been reported on the effect of Mn-N co-doping ZnS nanoparticles for the degradation of methylene blue dye. Therefore, the impetus behind this work was to study the effect of Mn-N co-doping ZnS nanoparticles on the photo catalytic degradation of methylene blue.

1.1 General Objective:

To study the effect of manganese-nitrogen co-doping in zinc sulfide on the photo catalytic degradation of methylene blue.

1.1.2 Specific Objectives:

To prepare nanoparticles of zinc sulfide, manganese-doped zinc sulfide, nitrogen-doped zinc sulfide and manganese-nitrogen co-doped zinc sulfide

To characterize the as-synthesized Nano-materials

To study the photo catalytic degradation of methylene blue using the as-synthesized nanomaterial's under UV and solar irradiations.

2. Materials and Methods

2.1. Experimental Site

The synthesis of nanoparticle zinc sulfide, manganese-doped zinc sulfide, nitrogen-doped zinc sulfide, and Manganouse-nitrogen co-doped zinc sulfide, photo catalytic degradation of methylene blue, and UV/Vis diffuse absorbance spectra were done at Haramaya University Research Laboratory, whereas XRD analysis was done at Addis Ababa Geolegical Survey.

2.2. Materials and Equipments

The Materials and equipments used were: XRD, UV/Visible spectrophotometer, analytical balance, Oven, hot plate, centrifuge, Deionizer, measuring cylinder, reactor tube, agate mortal, ceramic crucible, volumetric flask, pipettes, magnetic stirrer, desiccators and beakers.

2.3. Chemicals

Chemicals used were zinc acetate dehydrate (Zn $(CH_3COO)_{2.2H2O}$), sodium sulfide hydrate, ethanol, manganese acetate tetra hydrate (Mn $(CH_3COO)_{2.4H2O}$), urea ($(NH_2)_2CO$), ethylene diamine tetra acetic acid ($C_{10}H_{12}N_2O_8.NH_4$) and methylene blue ($C_{16}H_{18}N_3SCl$).

2.4. Methods

2.4.1. Preparation of Zinc Sulfide Nanoparticles

Zinc acetate dehydrates, 1M of 100 ml and 100 ml of 1M solution of sodium sulphide were mixed at 80 °C and 100 ml of ethanol was added with stirring. Then 30 ml of deionized water containing 2g of EDTA was added drop by drop for two hours. Then, the solution was cooled at room temperature (Murugadoss et al., 2009). Finally the wet precipitate was dried in hot air oven and labelled as uncalcined zinc sulfide. The dried powder was calcined at 350^0C for 2hrs, cooled to room temperature, ground in agate mortar and labelled as calcined zinc sulfide (Zc).

2.4.2. Preparation of Manganese-Doped Zinc Sulfide

Zinc acetate dehydrates 1M of 50 ml, 10 ml of 0.1M solution of manganese acetate and 50 ml of 1M solution of sodium sulphide were mixed at 80 °C stirring. Then 100 ml of ethanol was also added during stirring. Then 15 ml of deionized water containing 1g of EDTA was added drop by drop for two hours. After 2 hours, the solution was cooled at room temperature (Murugadoss et al., 2009). The dried powder was calcined at 350^0C for 2 hrs. ground in agate mortar and the obtained product was labelled as manganese-doped zinc sulfide (MZ).

2.4.3. 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 350^0C for 2 hrs. cooled to room temperature and was ground in an agate mortar. The product was labelled as nitrogen-doped zinc sulfide (NZ).

2.4.4. Preparation of Manganese-Nitrogen Co-Doped Zinc Sulfide

5 g of manganese-doped-zinc sulfide (MZ) was added to 15 g of urea, ground in an agate mortar and mixed well. The mixture was calcined at 350^0C for 2 hrs. cooled to room temperature and was ground in an agate mortar. The product was label as MNZ.

2.4.5. Photo catalytic Degradation Studies

Photo catalytic degradation of methylene blue (MB) was carried out using a reactor tube. A 0.15g of the as-synthesized photo catalyst 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. The absorbance was measured at λ_{max} = 665 nm using UV/Vis spectrophotometer and the degradation efficiency of MB has been calculated as (Pouretedal et al., 2009).

% Degradation = $[(C_O\text{-}C)/C_O] \times 100\%$……..…… (1)

Where Co is the initial concentration of MB and C is the concentration of MB after irradiation at a given time.3. RESULT AND DISCUSSION

3.1. Synthesis of Zns Photo catalyst

The following chemical reaction is involved during the synthesis of zinc sulfide nanoparticle $Zn(CH_3COO)_{2.2H2O} + Na_2S.9H_2O \rightarrow ZnS + 2Na^+ + 2CH_3COO^- + 11H_2O$

3.2. Characterization of the As-Synthesized Photo catalysts

3.2.1. XRD Analysis

In the XRD pattern of Zinc sulfide (Fig.2) there were three diffraction peaks at $2\theta = 28.66^o$, 47.56^o and 56^o which corresponded 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. Furthermore, all of the peaks are plane-indexed with Miller indices (hkl), which are (111), (220) and (311). The XRD peaks of the cubic crystallite Zinc sulfide nanoparticles proved to be broad due to small particle size (Pedro et al., 2006).

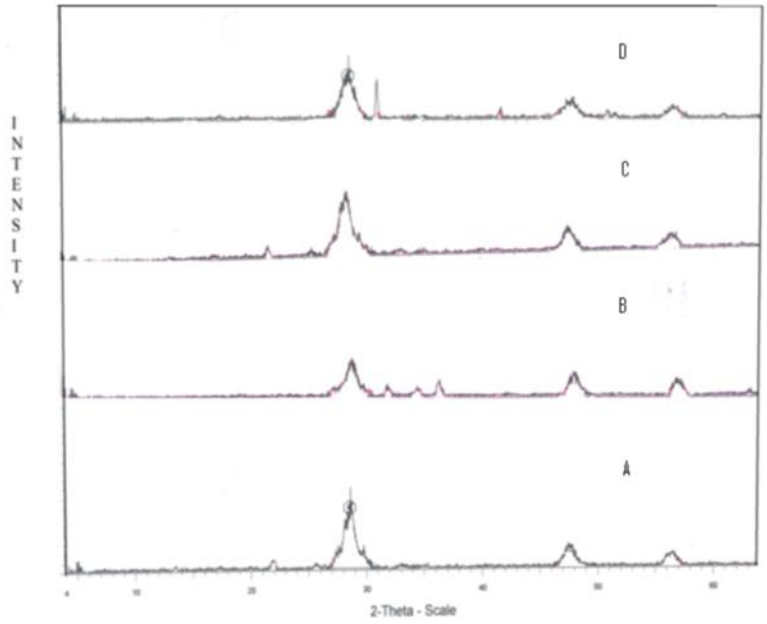

Figure 2. XRD spectra (A) Calcined ZnS, (B) Mn-doped ZnS , (C) N-doped ZnS , and (D) Mn-N codoped ZnS The XRD patterns of ZnS and N- doped ZnS have similar pattern in (Fig.2A and 2C) almost have no additional diffraction peaks due to the dopant species nitrogen are well dispersed into ZnS crystal lattice. On doping Mn-ZnS and Mn-N-co-doped ZnS an additional peak at $2\theta = 31.2^{o}$ (compare Fig.2B and 2D) was observed suggesting distortion of ZnS cubic structure to partial tetragonal structure. It was due to substitution of some of zinc atom by manganese atoms in ZnS crystal lattice, thus distorting its 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).

$D = 0.9\lambda/\beta \cos\theta$ (Wu, 2004)……..…… (2)

Where D is the average crystallite size, λ is the wavelength of the X-ray = 0.15406 nm for Cu target Kα radiation, β of an XRD peak and θ is the Bragg's angle.

Table 0.1. Average crystallite size (D) of as-synthesized photo catalysts

Sample	2θ (Degree)	β (Radian)	D (nm)
Zc	28.66	0.0183	7.80
NZ	28.87	0.0191	7.48
MZ	28.57	0.0216	6.61
MNZ	28.71	0.0211	6.59

3.2.2. UV/Vis Diffuse Absorption Measurements

The optical absorption spectra of photo catalysts i.e. ZnS, Mn-doped ZnS, N-doped ZnS, and Mn-N-co-doped ZnS measured in UV-Vis region the Absorption edges were 336, 334, 385 and 400 nm, respectively shown below in Figures 3-6. UV-Vis absorption spectra edge of N-ZnS and Mn-N-ZnS photo catalysts were well extended to visible region compared to ZnS and Mn-ZnS. This may be due to the modification of electronic levels of zinc sulfide by N-doping. For Mn-doped ZnS absorption edge shifted to a higher energy as compared to the pure ZnS sample due to quantum confinement effect (Yang et al., 2001). The blue shift in the absorption spectrum edge is a clear indication for the incorporation of dopant inside the ZnS lattice.

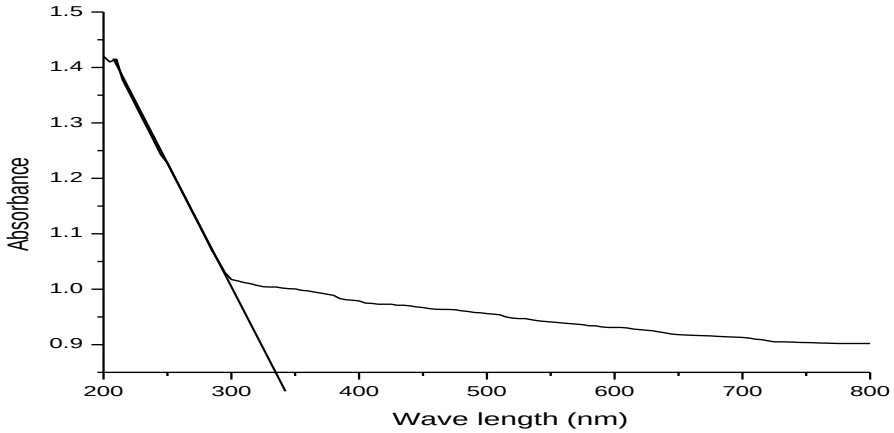

Figure 3. UV-Visible absorption spectra of calcined ZnS (absorption edge 336 nm)

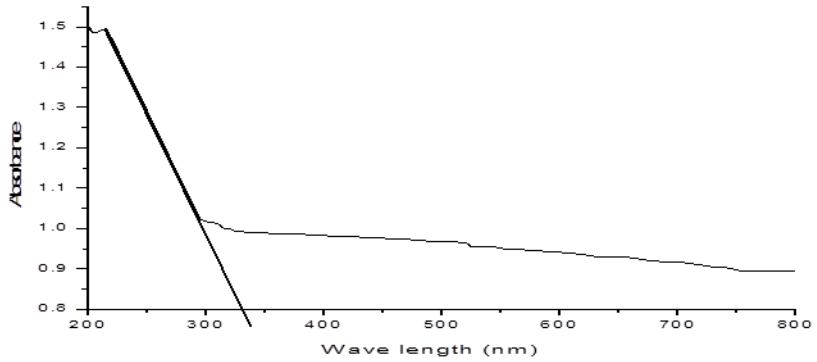

Figure 4. UV-Visible absorption spectra of Mn-ZnS (absorption edge 334 nm)

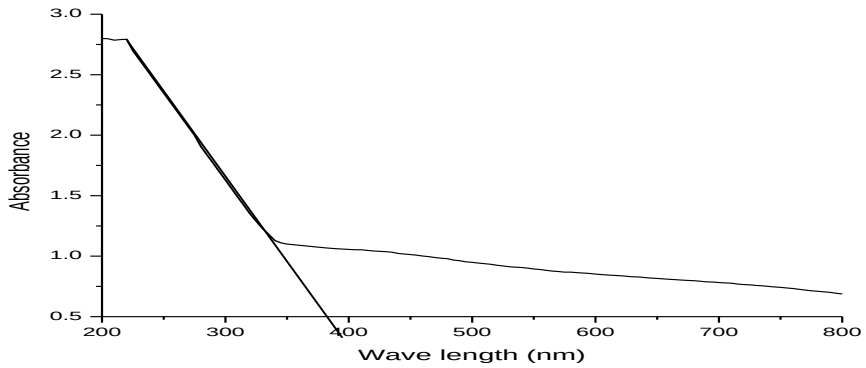

Figure 5. UV-Visible absorption spectra of N- doped ZnS (absorption edge 385 nm)

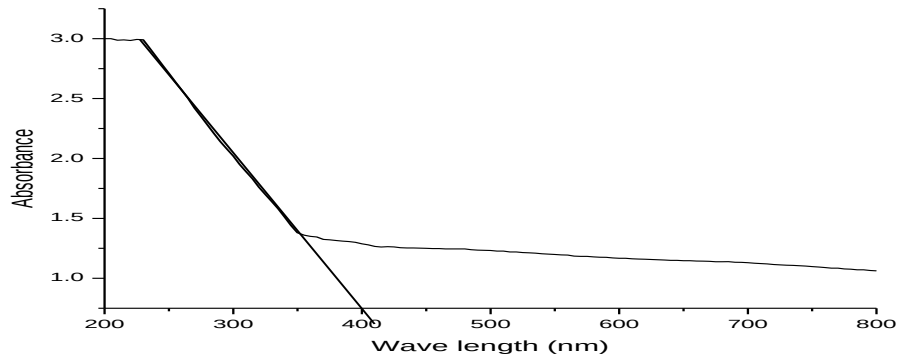

Fig 6. UV-Visible absorption spectra of Mn-N-co-doped ZnS (absorption edge 400 nm)

Band gap energy of the photo catalysts was obtained using the relation (Elkemary et al., 2009).

$$E_g\,(eV) = hc/\lambda = [1240eV\ nm\ /\lambda] \ldots\ldots\ldots\ldots\ldots\ldots\ldots . (3)$$

Where E_g is the band-gap energy, h is Planck's constant, c is the speed of light, and λ (nm) is the wavelength of the absorption edge in absorption spectrum. The band gap energies (E_g) of photo catalysts Zc, MZ, NZ, and MNZ were found as 3.69, 3.71, 3.22, 3.10 eV, respectively.

3.2.3. Photo catalytic 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. 7-9. The intensity of absorbance (at 665 nm) of MB dye and the percentage adsorption/ degradation have been calculated using equation (Pouretedal et al., 2009).

$$\% \text{ Degradation} = [(C_O - C)/C_O] \times 100 \ldots\ldots\ldots\ldots (4)$$

Where C_o is the initial conc'n of MB (25 mg/l) and C is the conc'n of MB at a given time

The percentage adsorption of MB without irradiation using the adsorbents: Znc, Zc, MZ, NZ, and MNZ at 180 minutes were: 0.55, 1.50, 2.40, 2.21 and 2.50 respectively (Fig. 7). The Percent adsorption of MB in dark are used as reference as zero minute irradiations. The percentage photo degradation of MB for Znc, Zc, MZ, NZ and MNZ under UV irradiation is: 10.12, 24.85, 45.19, 38.09, and 55.60 respectively at 180 minutes (Fig.8) and such values under solar irradiation are: 13.53, 30.17, 49.00, 57.30 and 70.75 respectively (Fig.9).

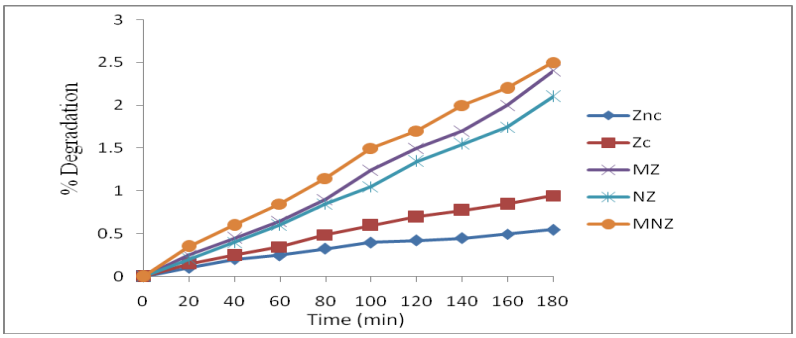

Figure 7. Plots of percentage adsorption of MB as a function of time (without irradiation)

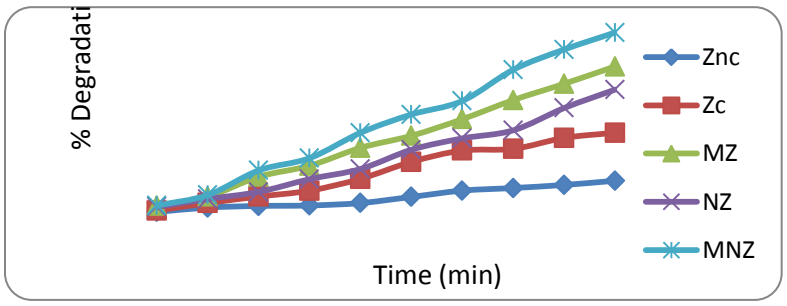

Figure 8. Plots of percentage degradation of MB as function of time (under UV irradiation)

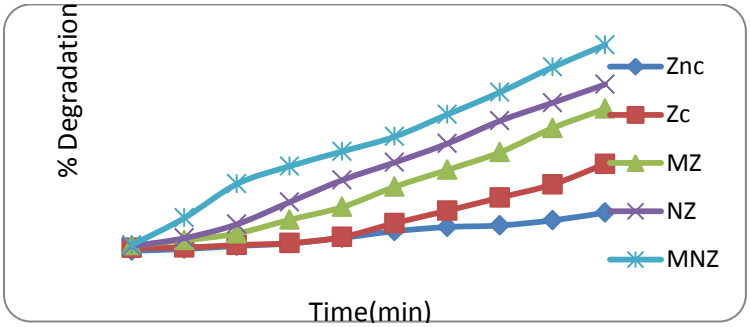

Figure 9. Plots of percentage degradation of MB as function of time (under solar irradiation)

Znc: uncalcined ZnS, Zc: calcined ZnS, MZ: Mn-doped ZnS, NZ :N-doped ZnS and MNZ: Mn-N co-doped ZnS

3.2.4. Kinetic Studies of Photo catalytic Degradation of MB

The kinetics of photo catalytic can be described by a modified Langmuir-Hinshelwood model (Fu et al., 2005). An initial concentration of 25 mg/l without, UV and solar irradiation shows that the decolorization of dye can be described by the first order kinetics (eq.5).

$$\ln(C_0/C) = kt \quad \ldots\ldots (5)$$

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

The pseudo first order rate constant (k) of MB photo degradation for Znc, Zc, NZ, MZ, and MNZ were 5.72×10^{-4}, 1.64×10^{-3}, 2.54×10^{-3}, 3.23×10^{-3} and 4.48×10^{-3} min^{-1} and 0.8×10^{-3}, 2.15×10^{-3}, 4.16×10^{-3}, 5.3×10^{-3} and 8.66×10^{-3} min^{-1} under UV irradiation and under solar irradiation, respectively.

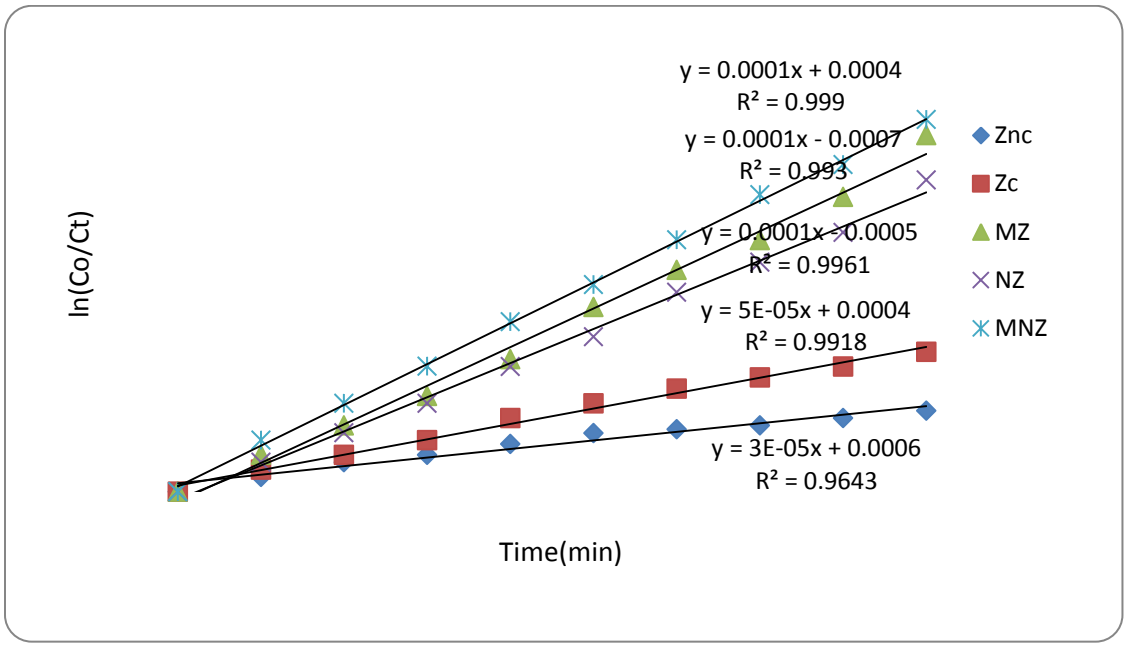

Fig 10. Plot of ln (C_0/C_t) vs. t for PCD of MB using ZnS and modified ZnS (without irrad'n)

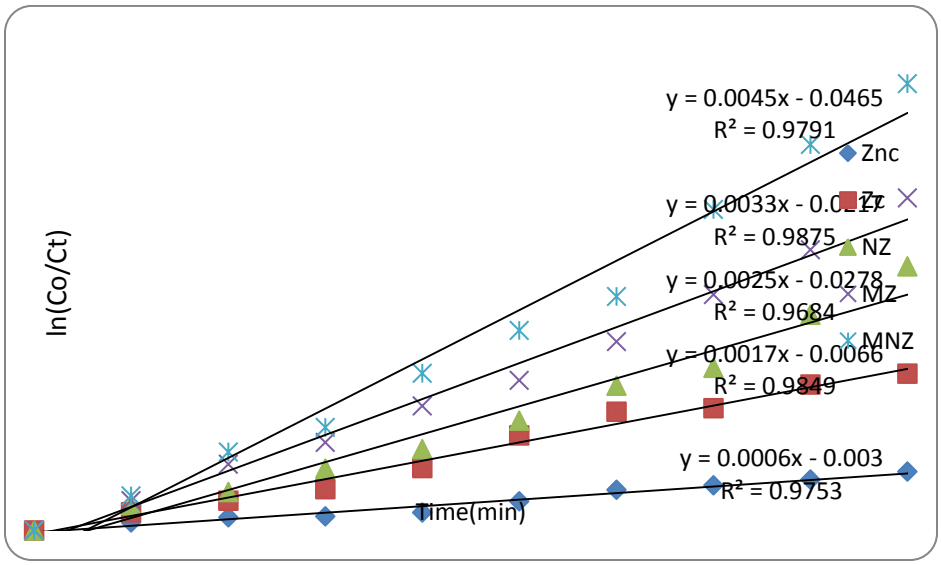

Fig 11. Plot of ln (C_0/C_t) vs. time for PCD of MB using ZnS and modified ZnS (under UV)

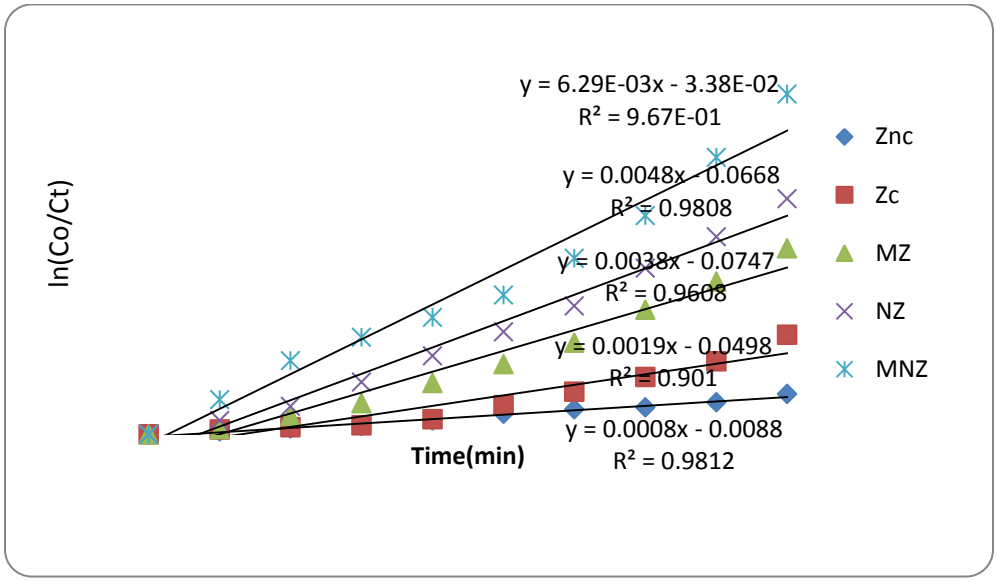

Fig 12. Plot Of Ln(C_0/C_t) Vs. Time for PCD Of MB Using Zns and Modified Zns (Under Solar)

4. Conclusion

Zinc sulfide, Mn-doped zinc sulfide, N-doped zinc sulfide and Mn-N co-doped zinc sulfide photo catalyst nanoparticle have been synthesized. The characterization of nanoparticles was done using X-ray powder diffraction (XRD) and UV–VIS Spectroscopy.

XRD results reveal that doped Mn merely adheres at the surface of ZnS, but N-doped in ZnS replace some of S atom in the crystal lattice and thus distorts the ZnS cubic structure. Manganese and Nitrogen co-doping into ZnS exhibited synergetic effect towards enhancing its photo catalytic activity. Whereas Mn doped ZnS entraps the photo-excited electron at the conduction band of ZnS thereby minimizing electron-hole recombination. Nitrogen doped in ZnS extends the photo-absorption in the visible range.

The photo catalytic activity of Mn-N co-doped ZnS is highest among the studied photo catalysts under both solar as well as UV irradiations. It may be due to the synergetic cumulative effect of manganese and nitrogen co-doping in enhancing the photo catalytic activity. The results also indicate that decolorization of methylene blue using N-doped ZnS occurs at a faster rate with solar light in comparison to UV radiation. Maximum decolorization 70.75% was observed at 180 min under solar light. Under UV irradiation

the decolorization was only 55.60 %. The photo catalytic degradation of methylene blue using as synthesized photo catalysts 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 photo catalytic efficiency of as-synthesized nanomaterials under solar irradiation is: MNZ > NZ > MZ > Zc> Znc and at the same time under UV irradiation MNZ > MZ > NZ > Zc> Znc.

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