

# Study of Dye Interaction with Mn Doped ZnS Using Photoluminescence Characteristics in Degradation of Malachite Green

Jyoti Tolia, Mousumi Chakraborty, and Z.V. P Murthy

**Abstract**—Mechanochemical method was used to synthesize Mn doped ZnS and undoped ZnS. The particles were characterized using XRD measurements and TEM analysis. The particle size for different doping concentration was found to be 4.19nm, 3.8nm, 2.68nm. Also the particle size of pure ZnS was found to be 4.79nm. The FTIR results showed that Mn<sup>2+</sup> ions were incorporated in host ZnS. The dye adsorption was maximum at pH=4. The photoluminescence study revealed that PL intensity increased with increase in doping concentration. The as prepared nanoparticles were further used for degradation of malachite green dye where the dye adsorption/ interaction on photocatalyst were studied using PL spectra. The PL spectra of dye absorbed photocatalyst showed that PL intensity increased manifolds due to dye adsorption. The maximum dye degradation (97%) was found for Zn<sub>1-x</sub>Mn<sub>x</sub>S (x=0.01) concentration with maximum rate constant (0.026 min<sup>-1</sup>).

**Index Terms**—Malachite green, mechanochemical method, photocatalytic degradation, Mn doped ZnS,

## I. INTRODUCTION

The ZnS nanoparticles belong to group II-VI semiconductor with wide bandgap of 3.6eV. The important property of a semiconductor material is that, it can be doped with impurities that can alter its electronic properties for wide applications as optoelectronic devices such as electroluminescent, photoluminescent, photocatalyst, photoconductor, photovoltaic cells, DNA markers, bio sensors, light emitting diodes and lasers [1]-[3]. To understand the physics and applications of ZnS as nanophosphors through doping as quantum dots in size range of 3-5nm huge amount of research efforts are being done in recent years. The original result of doped quantum-dot material or doped nanocrystals with high luminescent efficiency and ultrafast decay time was reported by Bhargava et al. [4] Thus, ZnS quantum dots are particularly suitable for the use as luminescent host materials for a very large variety of dopants like Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup> and rare- earth elements. The doping ions act as recombination centers for the excited electron-hole pairs and results in strong and characteristic luminescence [5]-[7]. The size of

typical QDs ranges between 2–20 nm, but according to some literature their diameter should be strictly below 10 nm [8]. Various synthesis methods like, chemical precipitation, micro-emulsion, precipitation in a solid polymer matrix, solgel, laser ablation, electrochemical fabrication and solvothermal are reported in literature for controlling size, shape and crystallinity of these materials [9]-[11]. As ZnS can be doped with Mn very easily, where few Mn atoms substitute for Zn atoms; here in present work, synthesis of ZnS and Mn doped ZnS was carried out using mechanochemical method. The as- prepared particles were characterized using XRD, TEM, FTIR and were further used to study the effect of Mn concentration on luminosity. The particles were used as photocatalyst for degradation of malachite green (MG) dye and were studied to observe the change in PL of dye absorbed photocatalyst.

## II. EXPERIMENTAL

### A. Material and Method

Metal acetate (AR grade, sd fine chemicals) and sodium sulfide (LR grade, Loba chemicals) in 1:1 molar ratio were used as starting material for synthesis of ZnS and Mn doped ZnS were sealed under air atmosphere inside tungsten-carbide vial along with 1:10 powder mixture to ball ratio. The mixture was milled for 6h in Planetary ball mill (Fritsch Pulverisette 6) at 350 rpm. Similar synthesis method was used for the preparation of ZnS<sub>1-x</sub>Mn<sub>x</sub>S, where x=0.01, 0.05 and 0.1. The as prepared nanoparticles were used for photocatalytic degradation of malachite green dye in a cylindrical quartz glass batch reactor of 250ml with UV irradiation (125W lamp). The dye molecules were allowed to get adsorbed over nanoparticles at different pH ranging from 2-5. The effect of dye adsorption at different pH was studied (30 minute) in dark with constant stirring to prevent degradation before irradiation of UV light. The pH of dye solution was adjusted using appropriate amount of NaOH and/or HCl. The dye solution (25mg/L) along with catalyst (1g/L) was placed inside the cylindrical quartz glass such that the reaction mixture was between the reactor walls. The samples were removed after 60 minutes to measure % adsorption at different pH. The pH was optimized from this experiments and remaining experiments were conducted pH=4 to study the photoluminescence effect. The dye sample (50mg/L) with catalyst (2g/L) was taken in reactor and UV light irradiation was started. The initial sample was taken at start time, when UV irradiation was started. The samples were collected at every 15minutes time interval till 90minutes. The samples collected were analyzed for

Manuscript received February 8, 2012; revised March 15, 2012.  
J. Tolia is with the Department of Chemical Engineering, V.V.P. Engineering College, Rajkot, and Gujarat, India.  
J. Tolia, M. Chakraborty, and Z.V. P Murthy are with the Department of Chemical Engineering, SVNIT, Surat 395007, Gujarat, India

concentration change in dye using spectrophotometer.

### B. Testing Equipments

The mechanochemically synthesized samples of ZnS and Mn-ZnS nanoparticles were characterized before using them as photo-catalysts. XRD measurement was carried out using a diffractometer (Philips, X' Pert-MPD) and XRD were compared with the data obtained from TEM (Technai-20, 200KV, Phillips, Holland). IR spectra (Thermonicolet, model no 6700, USA) was used to confirm Mn doping in ZnS. The absorption spectra were analyzed at different time interval using a UV-Vis spectrophotometer (HACH, Germany). For photoluminescence spectral studies, the samples were excited by 200-400nm ultraviolet light from (Horiba Jobin Yvon, Fluoromax-4, Japan) spectrofluorometer. The luminescence intensity was measured over the wavelength range 250-800 nm.

## III. RESULTS AND DISCUSSION

### A. Characterization

The as prepared ZnS particles were characterized using TEM analysis (Fig. 1) and XRD analysis (Fig. 2a). Mn-doped ZnS photocatalyst was prepared by mechanochemical method and also characterized using XRD. XRD analysis in Fig. 2(a) revealed hexagonal wurzite  $\alpha$ -ZnS (JCPDS 72-0163) along with cubic spherulite  $\beta$ -ZnS (JCPDS 5-0566). The presence of cubic and hexagonal phase was also revealed in TEM analysis. The coexistence of both the phases had also been reported in literature [12]-[13]. This could be due to phase transformation as the consequence of the motion of dislocations in activated solid state.

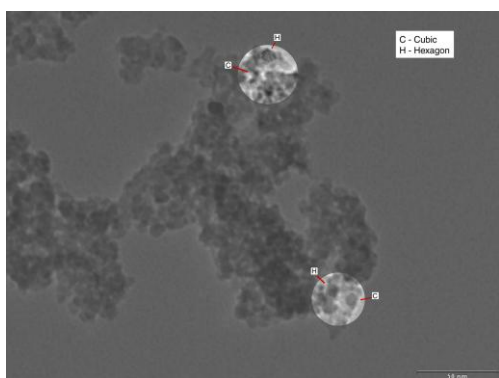


Fig. 1. TEM image of ZnS

The spectra was matched for various diffraction peaks at  $2\theta$  values of  $29.03^\circ$ ,  $48.49^\circ$  and  $56.87^\circ$  corresponding to the diffraction planes (103), (1011) and (203) respectively for wurzite ZnS, while the peaks were also found to match at  $28.792^\circ$ ,  $48.121^\circ$  and  $56.874^\circ$  corresponding to the diffraction planes (111), (220) and (311) respectively for cubic ZnS. The particle size of 4.79nm was calculated using Scherrer formula [14]. The XRD patterns in Fig. 2 (b, c and d) corresponding to zinc blend as per JCPDS No: 05-0566, showed very broad diffraction peaks with increasing concentration of manganese which was the characteristics of nanosized material. The diffraction peaks from manganese impurities were detected at  $2\theta$  position value  $35.734^\circ$ ,  $36.375^\circ$  and  $35.953^\circ$  for  $Zn_{1-x}Mn_xS$  where  $x=0.01$ , 0.05 and 0.1 respectively. The crystalline size were calculated to

be 4.19nm, 3.86nm and 2.68nm for  $Zn_{1-x}Mn_xS$  where  $x=0.01$ , 0.05 and 0.1 respectively. The particle size was found to decrease with increase doping concentration. In IR spectra in Fig. 3(a,b,c,d), the bands around  $3000-3600\text{cm}^{-1}$  (corresponds to occluded water) were due to the hydrogen stretching frequency (O-H stretching). The weak bands at  $2373.7\text{cm}^{-1}$  in Fig. 3a represented C=O stretching vibrations. This absorption peak had completely disappeared on adding Mn for doping to ZnS. The bands around  $1625.9\text{cm}^{-1}$ ,  $1625.4\text{cm}^{-1}$ ,  $1629.4\text{cm}^{-1}$ ,  $1637.1\text{cm}^{-1}$  and  $1618.3\text{cm}^{-1}$  corresponded to O-H bending. The bands around  $1200$  and  $1100\text{cm}^{-1}$  were for ZnS-Mn $^{2+}$  ions due to symmetric stretching and the characteristic frequency of these inorganic ions. The bands at  $1090.6\text{cm}^{-1}$ ,  $1008.9\text{cm}^{-1}$ ,  $1009.5\text{cm}^{-1}$ ,  $1015.4\text{cm}^{-1}$ ,  $1012.6\text{cm}^{-1}$ ,  $1012.8\text{cm}^{-1}$  were weak shoulders with asymmetric stretching.

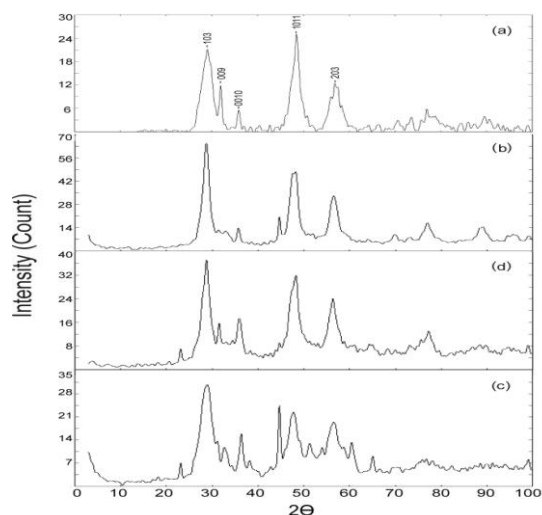


Fig. 2. XRD of ZnS and  $Zn_{1-x}Mn_xS$ , where  $x=0.01$ (b), 0.05(c) and 0.1(d)

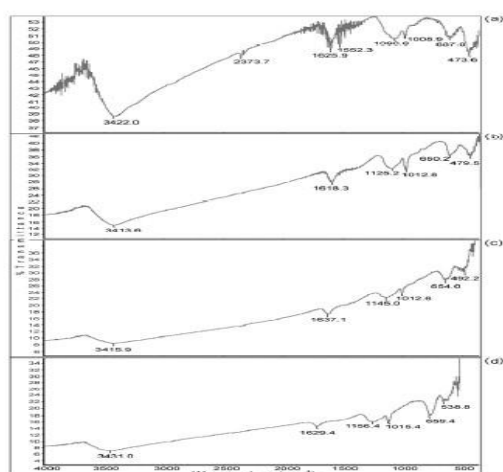


Fig. 3. IR spectra of ZnS and  $Zn_{1-x}Mn_xS$ , where  $x=0.01$ (b), 0.05(c) and 0.1(d)

The peaks at  $637\text{cm}^{-1}$ ,  $621\text{cm}^{-1}$ ,  $669\text{cm}^{-1}$ ,  $664\text{cm}^{-1}$  and  $650\text{cm}^{-1}$  were assigned to the ZnS band and symmetric bending, which was due to Zn-S and Mn-S vibrations.

### B. Effect of Dye Adsorption and PH

From the results in Fig. 4, it was noticed that the

adsorption/desorption equilibrium of malachite green at different pH values under 25 mg/l initial concentration was reached at about 30 min of equilibrium time and could not be degraded in the given experimental conditions without light irradiation. The maximum absorption of 50% was seen at pH=4. The % adsorption was found to increase from 33.3% to 50% for increase in pH from 2 to 4 but it was found to decrease at pH=5. The pH of the system had profound influence on the adsorptive uptake of adsorbate molecules presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule [15]. At low pH value (2.0 to 3.0), there was an increase in H<sup>+</sup> ion concentration in the system and the surface of the photocatalyst would have acquired positive charge by absorbing H<sup>+</sup> ions. On the other hand, increase of the pH value at 5 led to increase the number of negatively charged sites. As the catalyst surface was negatively charged at high pH=5, there occurred negatively charged catalyst surface leading to minimum adsorption of dye from solution. The similar trend was reported by Mittal [16] and Gandhi et. al [17] in degradation of malachite green.

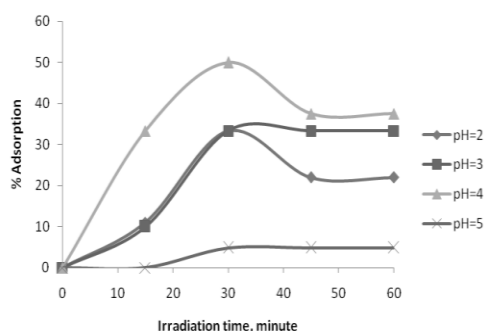


Fig. 4. Dye adsorption at different pH

### C. Dye Adsorption on Photo catalyst and Its Effect on Photoluminescence

The optical property of Mn doped ZnS nanocrystal was studied. The transfer of electron and hole from electronic level of Mn ions led to emission in ZnS. The PL spectra of doped samples excited at 320nm and 350nm were shown in Fig. 5, 6, and 7 at different concentration of dopant (dye unabsorbed and dye absorbed). It was observed from the figures, that the spectra were having two emission bands ranged from 460nm to 540nm while the other emission band was centered at 600nm showing orange-red shift. With increase in concentration of manganese, the intensity of orange emission increased which could have been due to incorporation of Mn<sup>2+</sup> into ZnS lattice. It was possible to introduce Mn<sup>2+</sup> into the lattice of host ZnS by lattice distortion taking place due to ion size difference between Zn<sup>2+</sup> and Mn<sup>2+</sup> influencing the energy levels of defect state in host ZnS. This could be attributed to radiative recombination [5],[18]. According to Bhargava et.al [4], when Mn<sup>2+</sup> ions were incorporated into the ZnS lattice and substituted for host cation site, the mixing between the s-p electrons of the host ZnS and the d electrons of Mn<sup>2+</sup> occurred and allowed partially the forbidden transition of 4T<sub>1</sub> - 6A<sub>1</sub>. This resulted in the characteristic emission from Mn<sup>2+</sup>. For 350nm excitation wavelength, shown in Fig. 5, 6 and 7, the PL spectra showed relatively same variation and

the maximum emission was centered at nearly 600nm in each sample. However, comparing excitation wavelength in PL spectra for all the samples, the maximum intensity was obtained in Mn<sup>2+</sup> (x=0.05) with mere red shift. The PL intensity was found to decrease at x=0.1, which could be due to quenching effect. Quenching effect at higher concentrations had also been observed in literature [11]. The Mn doped nanoparticles were further used for malachite green dye degradation. The malachite green dye molecules exhibited maximum absorption at 618nm [19]. It was observed that addition of ZnS nanoparticles to MG dye led to increase in absorption intensity at 631nm. This indicated interaction between nanoparticles and MG dye. To support these results, photoluminescence spectra were also measured at excitation wavelength 320nm and 350nm for dye absorbed Mn-ZnS

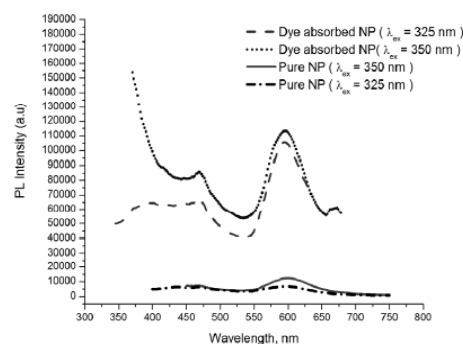


Fig. 5. PL spectra of Mn doped ZnS for x=0.01at excited wavelength 320nm and 350nm

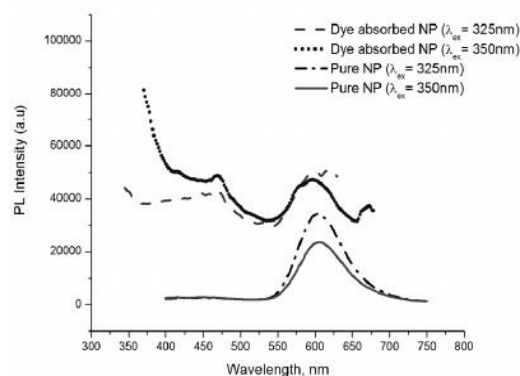


Fig. 6. PL spectra of Mn doped ZnS for x=0.05at excited wavelength 320nm and 350nm

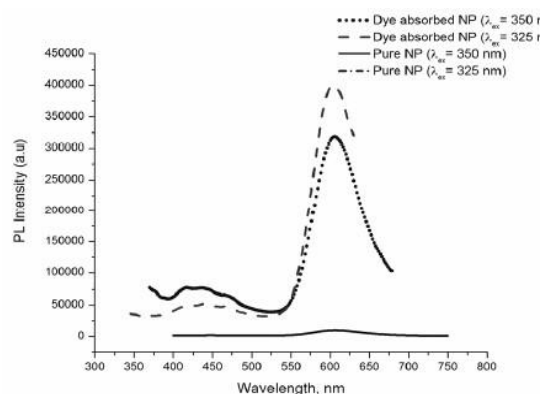


Fig. 7 PL spectra of Mn doped ZnS for x=0.1at excited wavelength 320nm and 350nm

TABLE I: COMPARISON OF PHOTO LUMINOSITY

| Photo luminosity data                      | Mn doped ZnS(x=0.01) |       |              |        | Mn doped ZnS (x=0.05) |       |              |       | Mn doped ZnS (x=0.1) |       |              |        |
|--|----------------------|-------|--------------|--------|-----------------------|-------|--------------|-------|----------------------|-------|--------------|--------|
|  | Pure                 |       | Dye absorbed |        | Pure                  |       | Dye absorbed |       | Pure                 |       | Dye absorbed |        |
| Excitation wavelength h, nm                | 325                  | 350   | 325          | 350    | 325                   | 350   | 325          | 350   | 325                  | 350   | 325          | 350    |
| Maximum wavelength h, $\lambda_{max}$ , nm | 596                  | 596   | 597          | 598    | 603                   | 607   | 598          | 596   | 603                  | 602   | 604          | 606    |
| Intensity, count(a.u)                      | 7280                 | 13100 | 107210       | 116310 | 35970                 | 24170 | 52840        | 48050 | 10930                | 16200 | 18620        | 323880 |

nanoparticle. From Fig. 5, 6 and 7, it could be seen that the intensity of photoluminescence increased due to dye absorption. Thus, comparing dye absorbed Mn doped and unabsorbed Mn doped nanoparticles, the photoluminescence was found to increase in photoinduced dye absorbed doped ZnS nanoparticles. From PL spectra (Fig. 5, 6 and 7) and table: 1, the increase in photoluminescence was found to increase in range of 1.5 to 14 times for 320nm excitation wavelength, whereas for 350nm excitation wavelength increase in intensity was found in range of 2 to 20 times. This could be because the excited states were subjected to electronic changes upon binding to the nanoparticles and due to changes of the molecular orbital symmetries of the dye in the presence of doped ZnS nanoparticles.

#### D. Photo catalytic degradation of Mn doped ZnS

ZnS was doped with different manganese concentration to  $Zn_{1-x}Mn_xS$  ( $x = 0.01, 0.05$  and  $0.1$ ). In order to study the effect of dopant on degradation efficiency, photodegradation experiments were carried out in presence of doped/undoped catalysts for 90minutes UV irradiation. The degradation efficiency for doping concentration  $x=0.01, 0.05$  and  $0.1$  was found to be 97%, 96% and 96% respectively with maximum efficiency at  $x = 0.01$ . Doping ions offered a way to trap electrons and/or holes on the surface or during interface charge transfer because of the different positions of the dopant in the host lattice. During the degradation reaction manganese ion were reduced and acted as strong oxidative agents for dyes as per following equations:

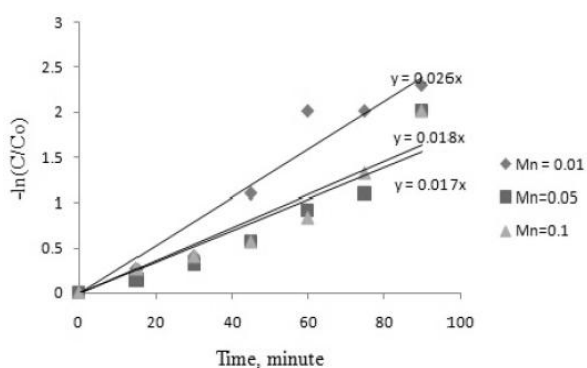
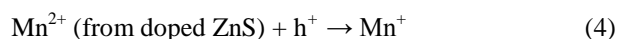
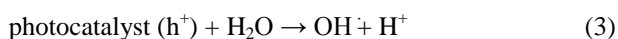
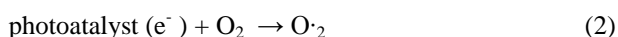
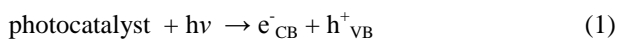


Fig. 8. Kinetics of UV/ Mn doped ZnS

The MG degradation was observed as a function of irradiation time and data were fitted to a first-order rate model (Fig. 8)  $\ln(C/C_0) = -k t$ , where  $C_0$  and  $C$  were the concentrations of dye at irradiation times  $t=0$  and  $t=t$  respectively,  $k$  was the first-order rate constant ( $\text{min}^{-1}$ ) and  $t$  was the irradiation time (min). Fig. 8 showed that rate of reaction ( $0.026 \text{ min}^{-1}$ ) was faster at doping concentration ( $x=0.01$ ).

#### IV. CONCLUSION

The particle size was found to decrease with increasing doping concentration. Also, the PL spectra showed that maximum intensity that could be obtained for doping concentration at  $x=0.05$ . The coupling of dye molecules with doped ZnS nanoparticles led to increase in PL intensity in all by 1.5 to 20 times. The maximum degradation efficiency (97%) was obtained at concentration  $x=0.01$ . These results showed many interesting optical and electronic properties which might be relevant for a variety of applications such as biological sensing, light emitting diodes, etc. Compared to use of conventional dye as bio-marker, dye coupled with nanoparticle could be used for long emission life.

#### REFERENCES

- [1] B. Remadevi, R. Raveendran, and A. Vaidyan, "Synthesis and characterization of Mn<sup>2+</sup> doped ZnS nanoparticles," *Parmana J. Phys.*, vol. 68, no. 4, pp. 679-687, April 2007.
- [2] A. Cadis, E. Popovici, E. Bica, I. Perhait, L. Barbu-Tudoran, and E. Indrea, "On the preparation of manganese-doped zinc sulphide nanocrystalline powders using the wet-chemical synthesis route," *Chalcogenide Lett.*, vol. 7, no. 11, pp. 631-640, November. 2010.
- [3] K. Manzoor, S. Vadera, N. Kumar, and T. Kutty, "Synthesis and photoluminescent properties of ZnS nanocrystals doped with copper and halogen," *Mater. Chem. and Phys.*, vol. 82, no. 3, pp. 718-725, June 2003.
- [4] R. Bhargava, D. Gallagher, X. Hong, and A. Nurmikko, "Optical properties of manganese-doped nanocrystals of ZnS," *Phys. Rev. Lett.*, vol. 72, no. 3, pp. 416-419, January 1994.
- [5] W. Peng, S. Qu, G. Cong, and Z. Wang, "Concentration effect of Mn<sup>2+</sup> on the photoluminescence of ZnS:Mn nanocrystals," *J. Crystal Growth*, vol. 279, no. 3-4, pp. 454-460, April 2005.
- [6] J. Bang, R. Helmich, and S. Kenneth, "Nanostructured ZnS: Ni<sup>2+</sup> photocatalysts prepared by ultrasonic spray pyrolysis," *Adv. Mater.*, vol. 20, no. 13, pp. 2599-2603, May 2008.
- [7] W. Peng, G. Cong, S. Qu, and Z. Wang, "Synthesis and photoluminescence of ZnS:Cu nanoparticles," *Optical Materials*, vol. 29, no. 2-3, pp. 313-317, November 2006.
- [8] J. Drbohlavova, V. Adam, R. Kizek, and J. Hubalek, "Quantum Dots — Characterization, Preparation and Usage in Biological Systems," *Int. J. Mol. Sci.*, vol. 10, no. 2, pp. 656-673, February 2009.
- [9] S. Wei Lu, B. Lee, Z. Lin Wang, W. Tong, B. Wagner, W. Park, and C. Summers, "Synthesis and photoluminescence enhancement of Mn<sup>2+</sup>-doped ZnS nanocrystals," *J. Luminescence*, vol. 92, no. 1-2, pp. 73-78, 2001.
- [10] D. Denzler, M. Olschewski, and K. Sattler, "Luminescence studies of localized gap states in colloidal ZnS nanocrystals," *J. Appl. Phys.*, vol. 84, no. 51, pp. 2841-2845, September 1998.
- [11] E. Mohaghehpour, M. Rabiee, F. Moztafzadeh, M. Tahriri, M. Jafarbeglou, D. Bizari, and H. Eslami, "Controllable synthesis, characterization and optical properties of ZnS:Mn nanoparticles as a novel biosensor," *Mater. Sci. Eng. C*.
- [12] B. Geng, X. Liu, and X. Wei, a vol. 29, no. 6, pp. 1842-1848, August 2009. nd L. Zhang, "Structure and optical properties of periodically twinned ZnS nanowires," *Appl. Phys. Lett.* vol. 88, no. 16, pp. 163104-1-163104-3, April 2006.
- [13] S. Sambasivam, S. Joseph, D. Reddy, B. Reddy, and C. Jayasankar, "Synthesis and characterization of thiophenol passivated Fe doped ZnS nanoparticles," *Mater. Sci. Eng. B*, vol. 150, no. 2, pp. 125-129, May 2008.

- [14] S. Nazerdeylami, E. Saievar-Iranizad, Z. Dehghani, and M. Moalei, "Synthesis and photoluminescent and nonlinear optical properties of manganese doped ZnS nanoparticles," *Physica B*, vol. 406, no. 1, pp. 108-111, January 2011.
- [15] T. Santhi, S. Manonmani, and T. Smitha, "Kinetic and isotherm studies on cationic dyes adsorption onto Annona Squamosa seed activated carbon," *Int. J. Engg. Sci. and Tech.*, vol. 2, no. 3, pp. 287-295, March 2010.
- [16] A. Mittal, "Adsorption kinetics of removal of toxic dye, malachite green, from wastewater by using hen feather," *J. Hazard. Mater.* Vol. B, no. 133, pp. 196-202, May 2006.
- [17] J. Gandhi, R. Dangi, J. C. Sharma, N. Verma, and S. Bhardwaj, "Photocatalytic bleaching of malachite green and brilliant green dyes using ZnS-CdS as semiconductor: A comparative study," *Der Chemica Sinica*, vol. 1, no. 3, pp. 77-83, 2010.
- [18] J. Cao, J. Yang, Y. Zhang, L. Yang, Y. Wang, M. Wei, Y. Liu, M. Gao, X. Liuc, and Z. Xied, "Optimized doping concentration of manganese in zinc sulfide nanoparticles for yellow-orange light emission," *J. Alloys Compd.*, vol. 486, no. 1-2, pp. 890-894, November 2009.
- [19] G. Parshetti, S. Kalme, G. Saratale, and S. Govindwar, "Biodegradation of malachite green by *Kocuria rosea* MTCC 1532" *Acta Chim. Slov.* vol. 53, no.1-2, pp. 492-498, August 2006.