

RESEARCH PAPER

Antimicrobial Activity and Photocatalytic Degradation Properties of Zinc Sulfide Nanoparticles Synthesized by Using Plant Extracts

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ABSTRACT

Biological synthesis of zinc sulfide (ZnS) nanoparticles (NPs) was prepared by a simple co-precipitation method using methanol plant extracts of *Tridax procumbens*, *Phyllanthusniruri*, and *Syzygium aromaticum*. The as-prepared ZnS NPs was examined by several physicochemical techniques such as X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Visible spectroscopy, Fourier Transform infrared spectroscopy analysis (FTIR). The disk diffusion method was used to screen the antimicrobial activity of Pure and Plant extracts doped ZnS NPs against different gram positive, gram-negative bacteria and fungus culture. From this investigation synthesized ZnS NPs have a potential antimicrobial agent where showed a hot zone of inhibition (ZOI) at different concentration against all tested microorganisms. Biosynthesized ZnS NPs Photocatalytic degradation also evaluated for Methylene Blue Dye (MBD) and Methyl Orange Dye (MOD) degradation in aqueous solution under UV Light irradiation. Due to the smaller particles size, narrowing optical band gap and antimicrobial properties of synthesised ZnS NPs were improve the photocatalytic activity. Here we first time reported *Syzygium aromaticum* methanol extracts ZnS NPs exhibited excellent efficiency in Methylene Blue Dye (MBD) and Methyl Orange Dye (MOD) degradation with comparing other ZnS NPs.

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INTRODUCTION

The zinc sulfide (ZnS) is an essential semiconductor material in II-VI group with indirect and significant value of band gap energy (3.63–3.92 eV), with hexagonal wurtzite and cubic zinc blende crystal structure. The massive ionization transition and phase stable in normal atmosphere conditions is different properties of ZnS crystal [1-6]. There are various method has been utilized for the synthesis of ZnS NPs such as hydrothermal method, chemical vapor deposition, chemical bath deposition, chemical precipitation, chemical co-precipitation, γ irradiation route, sonochemical

method, microwave irradiation, sol-gel technique, microemulsion method, thermal decomposition, solid-state reaction and solvothermal method [7-22]. From last two decades, ZnS semiconductor NPs are extensively investigated in various fields in electronics because of its excellent properties including optical, electrical, luminescence and photochemistry. The ZnS NPs have versatile potential applications in optoelectronics, ultraviolet light-emitting diodes, solar cells, field emitters, injection lasers, spintronics, infrared windows, sensors, photocatalysis, flat-panel displays, thin film electroluminescent devices,

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and antimicrobial activity [23-28]. The ZnS NPs have excellent photocatalytic degradation property especially inorganic pollutants dye such as Methylene Blue Dye (MBD), Rhodamine Blue Dye (RBD) and Methyl Orange Dye (MOD). The rapid generation of electron-hole pairs by photo-excitation and the highly negative reduction potentials of excited electrons and metal-doped ZnS have been generated high electron-hole pair when treated under UV visible light, and it increases dye degradation property due to the influence of surface area and particle size of ZnS [29-40].

Recently, the green synthesis of ZnS NPs and the antibacterial ability was directly and strongly related to the concentration of ZnS NPs and different plant extract ZnS NPs using *Corymbia citriodora*, *Fusarium oxysporum*, Mushrooms, *Elaeocarpus floribundas*, *Tridax procumbens*, *Phyllanthus Niruri*, *Syzygium Aromaticum* extracts and plant family and medical usages also reported [41-48]. In this present work first time, we report biological synthesis of ZnS NPs using three different plants extracts of (*Tridax procumbens*, *Phyllanthus Niruri*, *Syzygium Aromaticum*), antimicrobial activity, Photocatalytic degradation of Methylene Blue Dye (MBD) and Methyl Orange Dye (MOD) degradation has been investigated.

MATERIALS AND METHODS

Preparation of plant extracts

The excellent growth, Matured *Tridax procumbens* and *Phyllanthus niruri* plants are collected from Nehru herbal garden Coimbatore, and *Syzygium aromaticum* crude was purchased from Agriculture University at Coimbatore. All collected material washed with running tap water and Distilled water for remove dust, soils and treated shadow dry at 24 hours in room temperature then the dried materials were crushed to coarsely powdered by mixer and 250 g of coarse powder was subjected to successive extraction in 250 ml methanol solvent at 40° - 60° C by using soxhlet Apparatus [49-50] and collected three extracts were stored, used as capping agents and stabilizer for ZnS Fabrications.

Synthesis of ZnS nanoparticles

ZnS NPs were synthesized by using zinc sulfate ($\text{ZnSo}_4 \cdot 7\text{H}_2\text{O}$), Thiourea (NH_2CSNH_2), Ammonia solution (NH_3) all materials good analytical grade (99% Purity) were purchased from Sigma-Aldrich,

India. Typical synthesis process of Pure ZnS solution was obtained by mixing, 0.1 M of ZnSo_4 , 0.1 M of Thiourea and 1% Ammonia solution 0.1 M of ZnSo_4 were dissolved in deionized water and the mixture was stirred for 30 min, then 1% ammonia solution was added drop by drop on this ZnSo_4 solution and the mixture was stirred continuously for 60 min while continuous stirring 0.1 M of Thiourea solution (which was kept continuous stirred for 30 min with deionized water and Thiourea) is added drop by drop on ZnSo_4 solution and mixture were kept 60 min stirring at room temperature. The resultant nanocolloid formation solution, it was centrifugation at 2000 rpm for 20 Min then the solution was further treated air heated furnace at 60°C for 5 hours then collected final crushed fine powder. For comparative evaluation of the three plant extract ZnS nanopowders was prepared the same experimental synthesis procedure presented above, but 20 ml of methanol extract was used as capping agent instead of ammonia complexing agent and the plant extract ZnS NPs was abbreviated as following namely *Tridax procumbens* plant extract synthesized ZnS - T:ZnS, *Phyllanthus niruri* plant extract synthesized ZnS - P:ZnS, *Syzygium aromaticum* crude extract synthesized ZnS - S:ZnS.

Characterization method

The pure and plant extracted ZnS NPs were successfully characterized by the following techniques, powder X-ray diffraction techniques used to determine the crystal structure of the NPs by (X'per PRO model) using CuK α radiation ($\lambda = 1.54056 \text{ \AA}$), at 40 keV in the 2 θ range of 10°–80° with the step size of 0.1°, The Hitachi S-4500 scanning electron microscope (SEM) help to found surface morphology and formation of nanoparticles with 5 kV acceleration voltage. The optical absorbance, electron absorbance spectra of the ZnS NPs is recorded by a Perkin Elmer UV/VIS/ NIR ($\lambda=19$) spectrophotometer with a wavelength range of 300–900 nm at room temperature. JASCO FT/1 IR-6600 instrument was used to measure different bimolecular bonding function group with 400-4000 cm^{-1} spectral range, at spectral resolution record IR was 2 cm^{-1} .

Antimicrobial susceptibility test preparation

In vitro antimicrobial activity of pure and plant extract synthesized ZnS NPs were investigated by disc diffusion method against two gram

+ve and gram -ve bacterial cultures such as Staphylococcus aureus (S.aureus), Bacillus subtilis (B.subtilis) and Escherichia coli (E.coli), Pseudomonas aeruginosa (P.aeruginosa), also investigated against two fungus culture such as Candida albicans (C.albicans), and Aspergillus niger (A.niger) in a different concentration, all the culture are obtained from Microbial Type Culture Collection (MTCC) Institute of Microbial Technology, Chandigarh, India. One of the best antimicrobial susceptibility tests is disc diffusion method using Muller Hinton Agar (MHA) plates. MHA is obtained from Hi-Media Mumbai used to screening In vitro antimicrobial activity all the stock culture (staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, Candida albicans, Aspergillus niger) was maintained 4^o C on slopes of nutrient agar, the loopful of cells process to treat transfer stock culture into test tube of Muller Hinton broth for bacteria that were incubated without agitation for 24 hrs at 37^oC and 25^oC respectively. The cultures were diluted with fresh Muller-Hinton broth to achieve optical densities corresponding to 2.0×10⁶ colony forming units (CFU/ml) for bacteria, and fungus strains were inoculated separately in Sabourad's dextrose broth for 6 hours, and suspensions were approximately 10⁵ CFU/ml. Before transfer the cultures the MHA plates are treated different process for purification, 15 ml pouring of molten media in to sterile plates, use to prepare MHA plates and allow 5 min for solidify then the minimum amount 0.1% of stock cultures inoculums were swapped in MHA plate surface and allowed 5 min to dry, The 60 mg/disc concentration disc is placed MHA plate surface each disc has 6mm width. The prepared pure and biosynthesized ZnS solution (for comparison evaluation) were loaded all disc surface with different concentration and allow 5 min to diffuse extracts, then the diffused MHA plates are kept Incubation at 37^oC for 24 hrs during the incubator zone of inhibition (ZOI) was formed around the disc, transparent millimeter ruler use to determine ZOI [51, 52].

Photocatalytic experiment setup

The photocatalytic activity of ZnS, T:ZnS, P:ZnS, S:ZnS were evaluated by the Methylene Blue Dye (MBD) and Methyl Orange Dye (MOD) degradation under the 120 Whigh-pressure mercury lamp irradiation, the lamp was

kept 10 cm distance between the liquid surface. Than 1.0 mg of photocatalyst was added in 100 ml (1 x 10⁻⁵ M) of MB and MO dye aqueous solution for comparative and mixture was stirred in dark for 30min to attain equilibrium condition on the catalyst solution and it was kept continuous stirring (180 min) throughout process of experiment, at regular time intervals (30 min), 3 ml of aqueous suspensions (MBD and MOD) was taken from the mixture and analyze concentration of degradation by using a Perkin Elmer UV/VIS/ NIR (λ=19) spectrophotometer at wavelength of 623 nm for MBD and 461nm for MOD respectively [53]. The photocatalytic degradation efficiency was calculated the following expression: Degradation efficiency (%) = (C₀ - C) / C₀ x 100 % Here C is the concentration of suspensions MBD and MOD at each irradiated time interval, and C₀ is the initial concentration of MBD and MOD when equilibrium is achieved. For comparison evaluation, pure and synthesized ZnS NPs are used as a photocatalyst in the above-mentioned degradation process.

RESULT AND DISCUSSION

Crystalline Structure

Fig. 1 shows the X-ray diffraction pattern of ZnS, T:ZnS, P:ZnS and S:ZnS analyzed samples and all the diffraction peaks exhibits to corresponding synthesized ZnS NPs consistent of cubic phase structures with lattice constant of a = b = 5.345 (Å) (JCPDS card no 80-0020), any other extra impurities diffraction peaks not detected from that so it is indicated well formation of ZnS NPs are obtained. Fig. 1(a) shows the diffraction peak pattern of pure ZnS in which 2θ at 28.9^o, 48.1^o, 57.7^o and 77.8^o corresponding planes to the (111), (200), (311) and (331) reflection. The XRD spectrum of T:ZnS NPs shows the same major diffraction peaks of ZnS (hkl = 111) but the additional peaks of 2θ at 33.5^o and 69.8^o to the corresponding plan (200) and (400) reflection, it was the evidence tridaxprocumbens plant extract were influenced crystalline growth of ZnS NPs as shown in Fig. 1(b). In addition Fig. 1 (c-d) shows the six significant diffraction peak pattern of P:ZnS and S:ZnS in which 2θ at 28.9^o, 33.5^o, 48.1^o, 57.7^o, 69.8^o and 77.8^o corresponding plane to the (111), (200), (220), (311), (400) and (331) reflection, in the presence XRD spectrum 2θ at 69.8^o of Syzygium aromatic extract was increase the peak broadening because of plant extract bonding with crystal content of sulfur during annealing process,

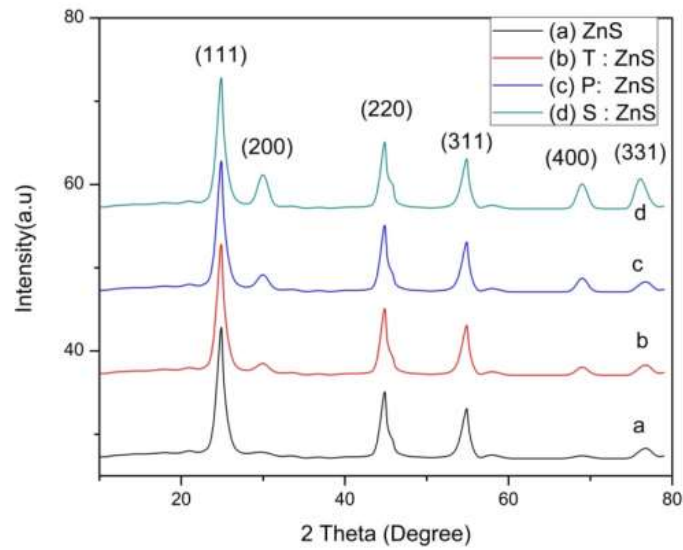


Fig. 1. XRD patterns of (a) ZnS, (b) T: ZnS, (c) P : ZnS, (d) S : ZnS

from this the plant extract are good bonding with ZnS NPs and influence to increase the crystallite size, the overall XRD spectrum intensity is increased with use of different plant extract . The average crystallite size (D) is estimated by Debye-Scherers formula based on the diffraction peak corresponding to the plane, In Table 1. The 2θ , full-width half maximum (FWHM), D spacing, Crystalline size and band gap energy of synthesized ZnS NPs is given.

$$D = 0.9\lambda / \beta \cos \theta$$

Where D is crystallite size, 0,9 is the constant shape factor, $\lambda=1.5405\text{\AA}$ represents the wavelength of incident beam CuKa1, β is a full-width half maximum of the peak, θ is diffraction angle in radian.

Morphological studies

The structural and morphological formation of pure and biosynthesized ZnS NPs are investigated by SEM image, and result are presented the NPs are spherical morphology with narrow particle size distribution, and the NPs formation was varied

depends on the gapping (ZnS, P:ZnS, T:ZnS, S:ZnS) and complexing agent (NH_3) as shown in Fig. 2(a-d).

The S : ZnS nanoparticles are much smaller than ZnS, T: ZnS, and P: ZnS NPs, this indicated the plant extract might affect size of the ZnS NPs and size of NPs can be controlled by the plant extract, The diameter of the ZnS, T: ZnS, P : ZnS, and S : ZnS NPs are 143.5, 165.9, 203.1 and 218.4 nm respectively. From the SEM image bio molecules of the plant extract were strong interaction with NPs surface, and quantities of the plant extract were leading the size reducing of spherical NPs [41-46].

Optical properties

The optical diffuse reflection absorbance spectroscopy of ZnS, T: ZnS, P : ZnS, and S: ZnS NPs are exhibited the maximum peak values, is shown in Fig. 3 from the result all the ZnS NPs have broad absorption peak at 323 nm for ZnS, 319 nm for P: ZnS, 313 nm for T: ZnS, 302 nm for S: ZnS respectively. The absorption peak of all plant extracts ZnS NPs maximum peak was blue shifted to compare pure ZnS. The band gap energy of Pure

Table 1. show the 2θ , (hkl), FWHM, D spacing, crystallite size and Band gap energy of pure and synthesized ZnS NPs

Sample	2θ (hkl)	FWHM (Radian)	D Spacing	Average Crystalline size (nm)	Band gap energy(eV)
ZnS	28.9 (111)	0.4795	3.13	17.87	3.85
T:ZnS	28.9 (111)	0.4799	3.15	17.84	3.90
P:ZnS	28.9 (111)	0.5056	3.28	16.94	3.97
S:ZnS	28.9 (111)	0.5102	3.45	16.71	4.12

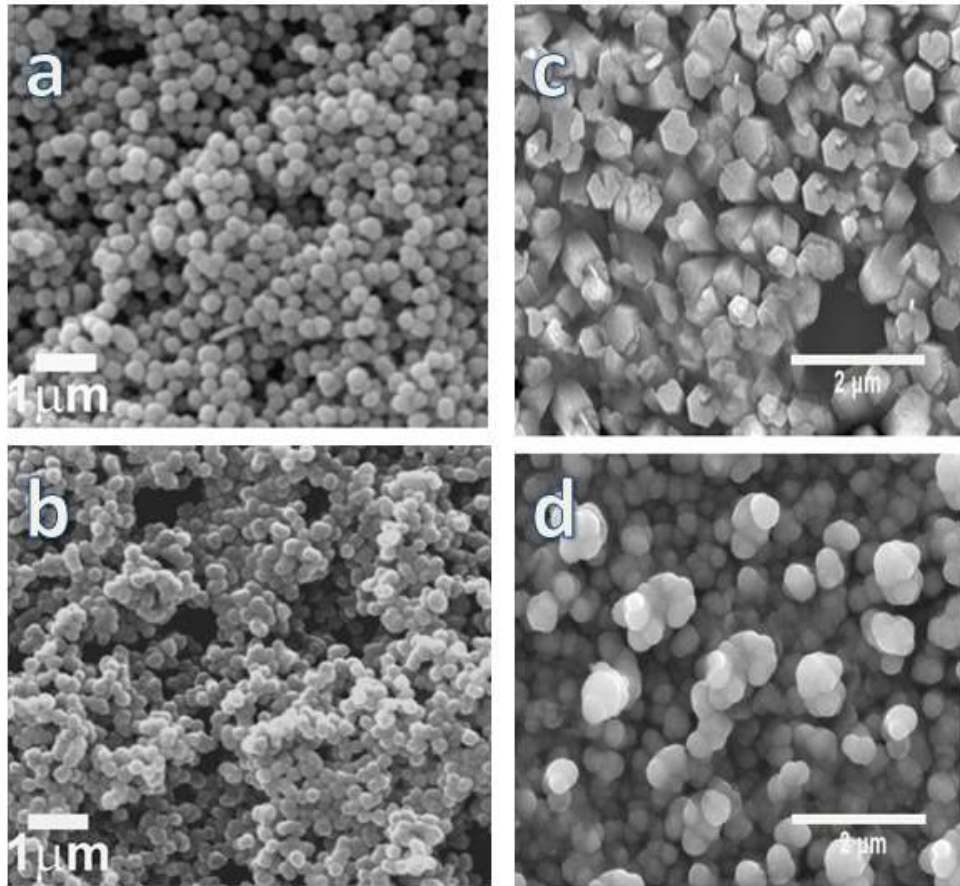


Fig. 2. SEM Image of (a) ZnS, (b) T: ZnS, (c) P : ZnS, (d) S : ZnS

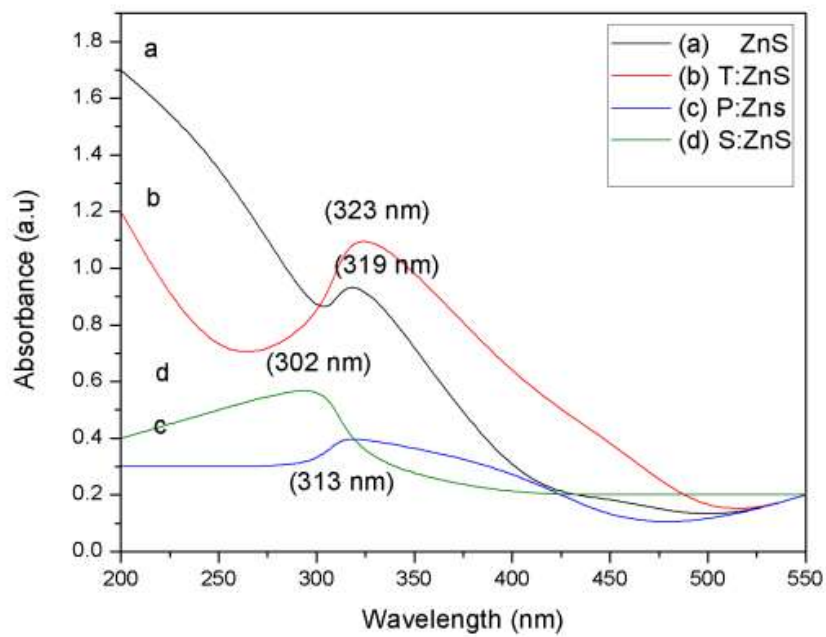


Fig. 3. Optical Absorbance of (a) ZnS, (b) T: ZnS, (c) P : ZnS, and (d) S : ZnS

and synthesized ZnS NPs was calculated using The Tauc's plots [54] for the samples and its relation between the absorption coefficient(α) and photon energy($h\nu$).

$$\alpha h\nu = (h\nu - E_g)^n$$

Where, h is Planck's constant, optical absorption coefficient is α , $h\nu$ is photon energy, E_g is optical band gap, and $n=1/2$ is parameter associated with the electron transition for directly allotted, $n=2$ is indirectly allotted. The estimated values of the optical band gap of ZnS, T: ZnS, P: ZnS, and S: ZnS NPs is 3.85(eV), 3.90(eV), 3.97(eV), and 4.12(eV) respectively. From the result value, band gap was increased 3.85 (eV) to 4.12(eV), it was much higher than the bulk ZnS (3.7 eV) value is shown in Fig. 4 and table 1. The band gap was obtained from maximum absorption according to the quantum coefficient theory it was related to the electrons in the conductance band holes in the valence band are controlled by the potential barrier of the NPs surface due to presence of electrons and holes. The lowest optical transition from the valence band and conductance band is increase the band gap energy efficiently, from this result the plant extract was act as gapping agent and influence to increase the band gap energy and the particles

size was reduced to compare pure ZnS.

Functional Group Analysis

The FTIR analysis for identifies the bimolecular absorption and different functional groups involved in the biosynthesis procedure, Fig. 5(a-d) shows the FTIR spectra for synthesized ZnS, T: ZnS, P: ZnS, and S: ZnS NPs. In Pure ZnS The broad absorbance peak 3110 cm^{-1} corresponds to hydroxyl, phenol(O-H) stretching, 1551 cm^{-1} corresponds to (C=O) stretching due to carboxylic, 1206 cm^{-1} absorbed (C-O) stretching correspond to epoxy, Amino acids, and 691 cm^{-1} is due to the presence of Zn-S water molecular stretching [55]. The plant extract ZnS FTIR was shown in Fig. 5(b-d) and all samples have the same absorption at (O-H, N-H), (C=O), (C-O) and Zn-S stretching peaks like pure ZnS. The T:ZnS have an additional peak at 2188 cm^{-1} due to (O=C=O) stretching, and broad peak 3110 cm^{-1} corresponds to (N-H) stretching in all plant extract ZnS. In P:ZnS have small peak at 2115 cm^{-1} and 2683 cm^{-1} due to alkenyl (C-H) stretching, The S:ZnS have very low peak at 1033 cm^{-1} and minimum absorption at 2194 cm^{-1} corresponding to the stretching of (C-C) due to alkenes and aromatics (C=C) from the various shifting of the peaks indicate different function group bioactive

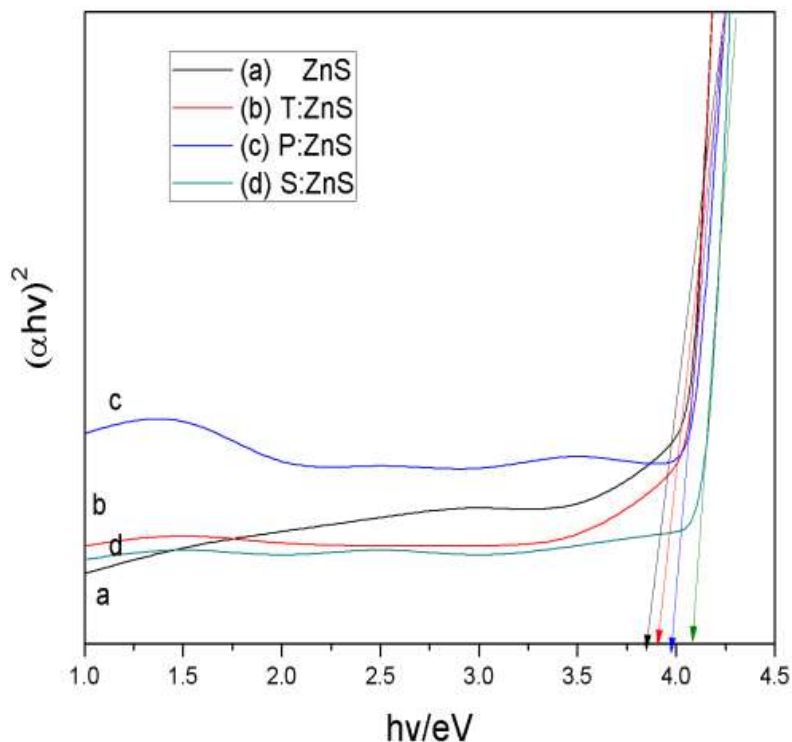


Fig. 4. Tauc's plot of (a) ZnS, (b) T: ZnS, (c) P : ZnS, and (d) S : ZnS

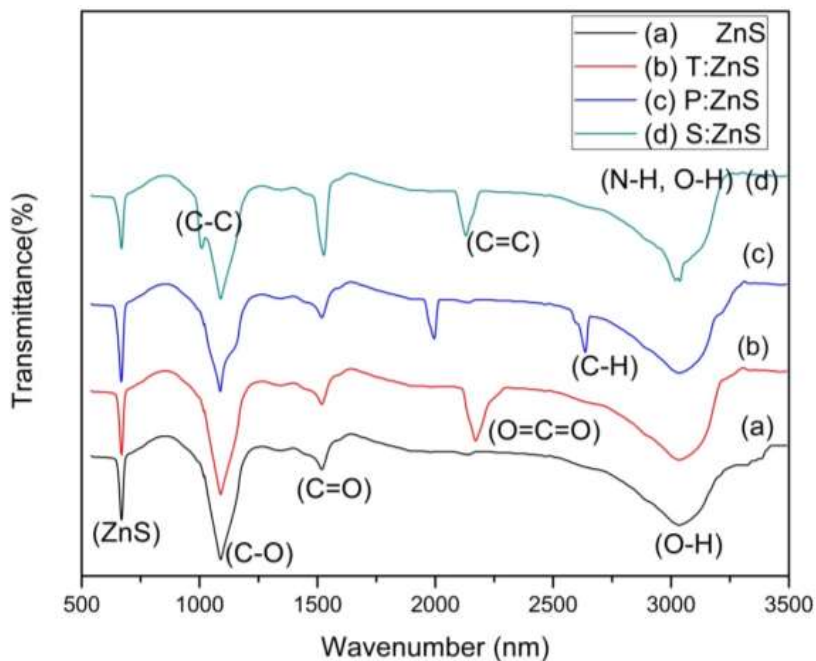


Fig. 5. FTIR spectra of (a) ZnS, (b) T: ZnS, (c) P : ZnS, and (d) S : ZnS

components (proteins, carbohydrate. Phenolic compounds, Amino acids) are commonly reduce and stabilize the ZnS NPs [46-48].

Antimicrobial Activity Analysis

The Antimicrobial activity of pure and biosynthesized ZnS NPs was evaluated by measuring zone of inhibition with various concentrations (40,50 and 60 (µg/mL)) against all tested microorganisms. The Antimicrobial activity of ZnS, T:ZnS, P:ZnS, and S:ZnSNPs were compared with two gram +ve and gram –ve bacterial cultures such as Staphylococcus aureus (S.aureus), Bacillus subtilis (B.subtilis) and Escherichia coli (E.coli), Pseudomonas aeruginosa (P.aeruginosa), also investigated against two fungus culture such as Candida albicans (C.albicans), and Aspergillus niger (A.niger) in a different concentration it was clearly shown in Table 2 and Fig. 6.

The pure ZnSNPs has highest inhibition zone was observed against E.coli (17± 0.1 mm) and C.albicans (17± 0.3 mm) followed by P.aeruginosa (16± 0.1 mm), S.aureus (14± 0.2 mm), A. niger (14± 0.1 mm) and B.subtilis (13± 0.3 mm) at concentration of 60(µg/mL) from this result concentration of ZnS NPs when extended the inhibition zone also increased. In T:ZnS NPs highest inhibition zone was formed against P.aeruginosa (22± 0.1 mm)

followed by E.coli (20± 0.1 mm), C.albicans (20± 0.2 mm), S.aureus (14± 0.2 mm), B.subtilis (18± 0.1 mm) and A. niger (15± 0.1 mm) at concentration of 60(µg/mL), from the starting concentration P.aeruginosa has lead highest inhibition zone to compare other microorganisms. The P:ZnS NPs highest inhibition zone was observed against C.albicans (29± 0.1 mm) followed by E.coli (25± 0.1 mm), S.Aureus (23± 1.2 mm), B.subtilis (22± 0.3 mm), P.aeruginosa (22± 0.2 mm) and A. niger (20± 0.3 mm) at a concentration of 60(µg/mL), from this result C.albicans inhibition zone was well formed from the beginning concentration. The S:ZnS NPs exhibits excellent antimicrobial activity against all tested microorganisms to compare other ZnS NPs, at concentration of 60(µg/mL) highest inhibition zone was observed against C.albicans (29± 0.3 mm) followed by E.coli (24± 0.1 mm), S.aureus (23± 1.2 mm), P.aeruginosa (23± 0.1 mm) B.subtilis (22± 0.2 mm) and A. niger (21± 0.2 mm). From this results plant extract, ZnS NPs was high inhibition zone against gram +ve, gram –ve bacteria and fungus culture in various concentrations to compare pure ZnS NPs. From the comparison result maximum antimicrobial activity was observed by gram-negative bacterial than the gram-positive bacterial due to their cell structure. The cell structure of both bacteria is different,

Table 2. show the Antimicrobial screening data of pure and synthesized ZnS NPs ZoI value* in (mm) concentration at (µg/mL)

Samples / Concentrations (µg/mL)	Gram (+ve) Inhibition zone (mm)						Gram (+ve) Inhibition zone (mm)						Fungi Inhibition zone (mm)					
	S.aureus			B.subtilis			E.coli			P.aeruginosa			C.albicans			A. niger		
	40	50	60	40	50	60	40	50	60	40	50	60	40	50	60	40	50	60
ZnS	9	11	14	7	10	13	13	14	17	9	15	16	11	13	17	8	11	14
T:ZnS	15	18	20	10	13	18	16	17	20	16	19	22	14	18	20	11	13	15
P:ZnS	16	19	23	14	19	22	18	23	25	14	18	22	24	27	29	16	18	20
S:ZnS	14	20	23	16	20	22	15	19	24	16	19	23	18	25	29	18	20	21

* Average inhibition zone was varied from ± 0.1 to ±0.3 mm at all concentration

gram-positive bacteria have a single thick cell wall made up of peptidoglycan layer, and toxicity is very less due to the presence of thick layer. The gram-negative bacteria have double thin layered cell wall made up of lipopolysaccharide layer followed by peptidoglycan layer, this peptidoglycan layer is very thin to compare gram-positive layer and also it consist repeated unit of amino acids and carbohydrate, Thickness of the gram +ve bacteria cell layer is 20-80 nm and gram -ve bacteria cell layer 5-10 nm respectively. Here the ZnS, T: ZnS, P: ZnS, and S: ZnS NPs was discharged irons and react with amide phosphate, carboxyl in the protein of cell membrane and continuously disrupting the cell process and finally broke the cell wall and stop cell growth and formed inhibition zone around cell wall. The inhibition zone of C.albicans and A. niger fungus culture also investigated from the result C.albicans has formed maximum inhibition zone to compare A.niger because all ZnS NPs easily affect and penetrate the fungus cell membrane [46, 56]. The plant extracts ZnS NPs has a high antimicrobial activity to compare pure ZnS because plant extracts functional group biomolecules was controlled or killed the cell membrane of microorganisms. The small particle size and large surface area NPs exhibit high antimicrobial activity in which S:ZnS NPs have an excellent antimicrobial activity to compare other ZnS NPs.

Photocatalytic Activities

The photocatalytic activities of ZnS, T: ZnS, P: ZnS, and S: ZnS NPs sample were evaluated by degradation of Methylene Blue Dye (MBD)

and Methyl Orange Dye (MOD) under visible light irradiation. Before adding the photocatalyst the MBD and MOD was treated photocatalytic degradation process to check the concentration efficiency under visible light irradiation from the result both dye only degrade 2% after 180 min of visible light irradiation, on the other side above the same process repeated MBD and MOD with 1.0 mg of ZnS, T: ZnS, P: ZnS, and S: ZnS NPs as a photocatalyst. During the irradiation electrons from the conduction band (CB) will excite to the valence band (vb) to increase electron-hole pair, a good photocatalyst act the adequate separation of electron and holes pair during the photogeneration, the holes of the valence band react with surface of the MBD and MOD bounded, react with water (H₂O) or Hydroxyl groups (OH⁻) and generate hydroxyl radical (OH[·]) finally the conduction band(OH[·]) electrons reduce the MBD and MOD molecular oxygen to superoxide molecule to exert the degradation [42, 53]. The degradation of MBD and MOD concentration was higher in plant extract ZnS to compare pure ZnS.

Fig. 7 shows the degradation percentage of MBD at each 30 min Time interval using ZnS, T: ZnS, P: ZnS, and S: ZnS NPs, after 180 minute of irradiation, the photocatalytic degradation efficiency of MBD with ZnS, T: ZnS, P: ZnS, and S: ZnS NPs as photocatalyst (1.0 mg) is 55%, 68%, 73% and 81% respectively, the result plant extract using ZnS NPs have high photocatalytic efficiency to compare pure ZnS NPs, because the band gap energy of T: ZnS, P: ZnS, and S: ZnS NPs were increased, so it influence to increase photogeneration rate of electron/hole

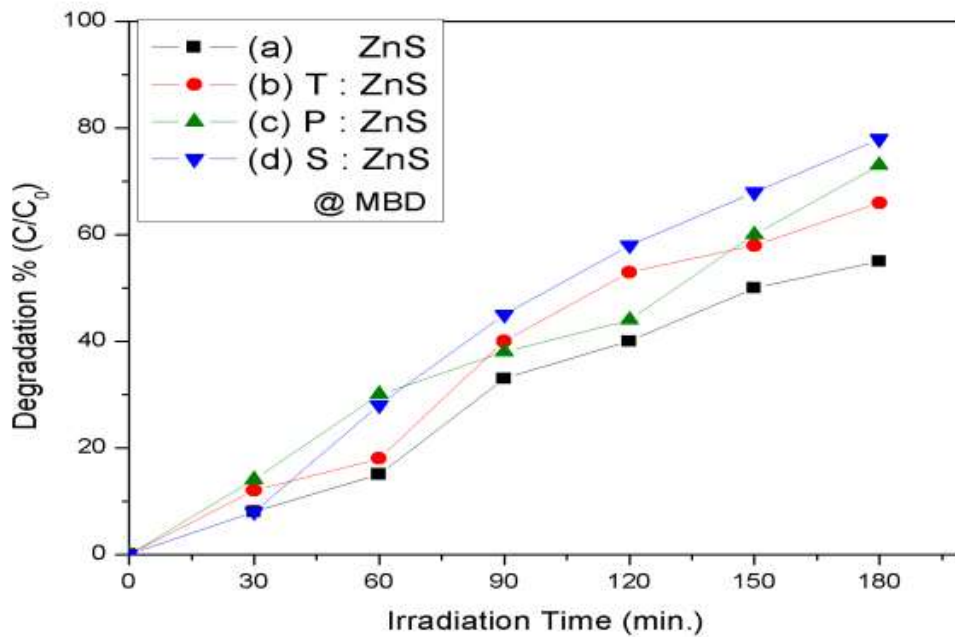


Fig. 7. Photocatalytic degradation efficiency of Methylene blue dye (MBD) using (a) ZnS, (b) T: ZnS, (c) P: ZnS, and (d) S: ZnS

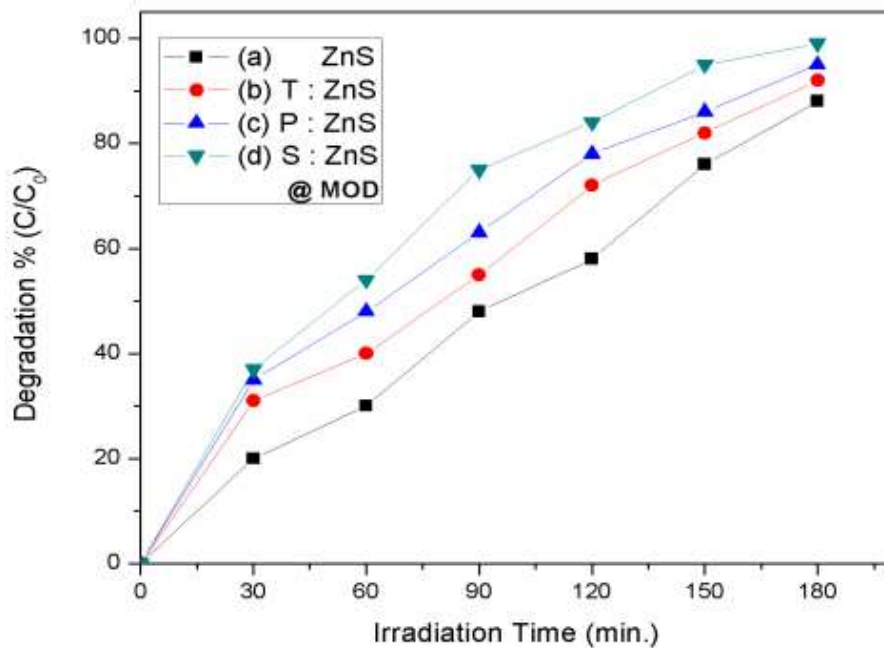


Fig. 8. Photocatalytic degradation efficiency of Methyl orange dye (MOD) using a) ZnS, (b) T: ZnS, (c) P: ZnS, and (d) S: ZnS

pair during light irradiation. Similarly, After 180 minute of irradiation the degradation efficiency of MOD using ZnS, T: ZnS, P: ZnS, and S: ZnS NPs

as photocatalyst (1.0 mg) was investigated, from the Fig. 8 MOD degradation efficiency was found 90%, 92%, 95% and 99% respectively it was

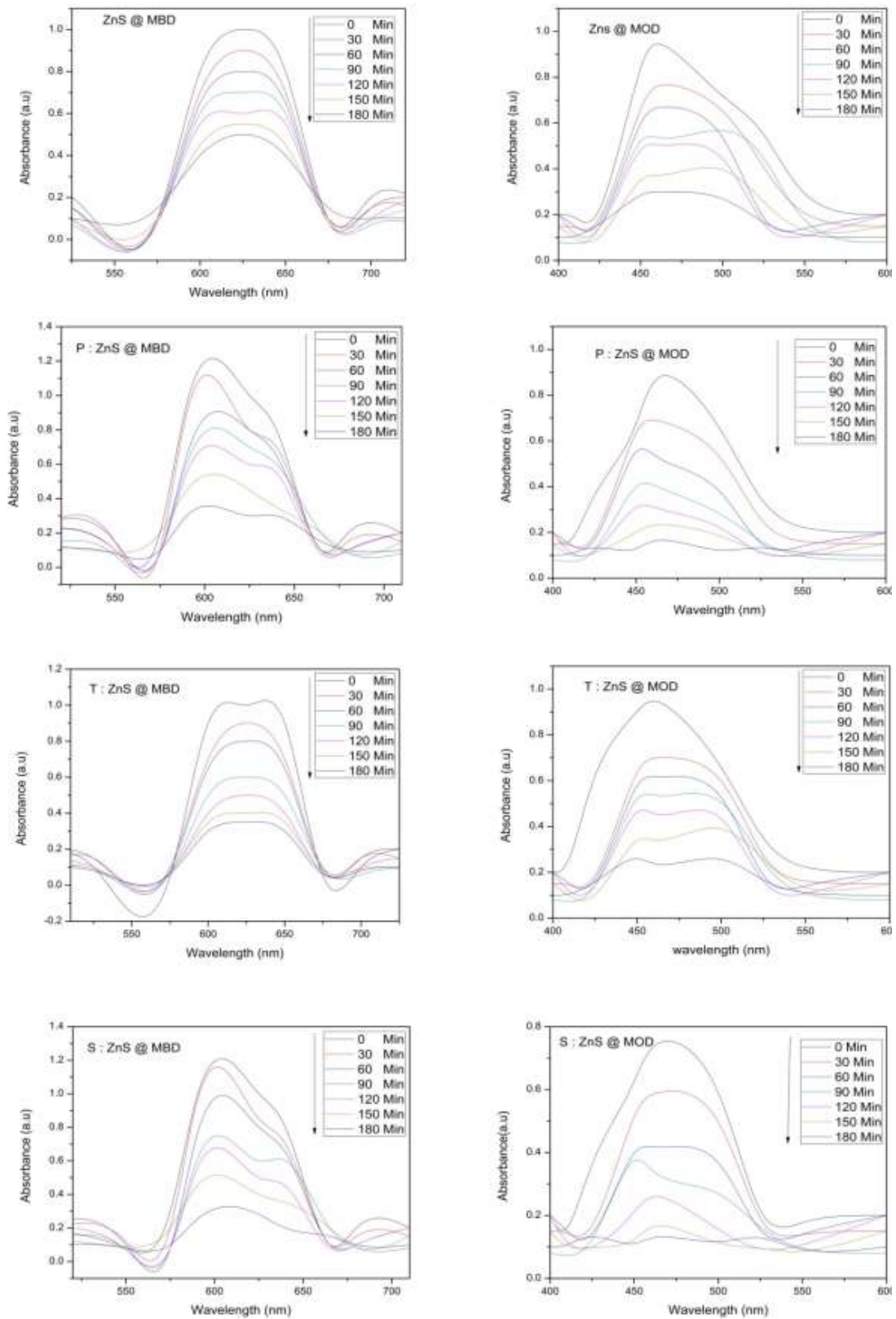


Fig. 9. UV Visible spectra of Photocatalytic degradation of Methylene blue dye (MBD) and Methyl orange dye (MOD) using ZnS, T: ZnS, P: ZnS, and S: ZnS NPs

evidence ZnS, T: ZnS, P: ZnS, and S: ZnS NPs is an excellent photocatalyst with MOD when compared with MBD. Hence the percentage of photocatalyst was increased then the degradation efficiency also increases. The degradation spectra of MBD and MOD under the visible light irradiation was shown in Fig. 9 at constant time interval with using ZnS, T: ZnS, P: ZnS, and S: ZnS NPs separately. From the result degradation properties of the MBD and MOD was increased depends on the irradiation time and quantity of the photocatalyst.

CONCLUSION

In summary, the ZnS NPs were successfully synthesized by simple chemical co-precipitation method using plant extracts of *Tridax procumbens*, *Phyllanthus niruri* and *Syzygium aromaticum*. All the ZnS NPs were confirmed the cubic crystalline structure, and the average particle size was 17 nm, to compare pure ZnS NPs the plant extract crystallite size was decreased and morphology of the ZnS NPs revealed the spherical shape of the particles and different diameters respectively. The optical band gap energy of pure and plant extract ZnS NPs was calculated from UV visible absorption spectra it is efficiently tuned from 3.83 eV to 4.10 eV efficiently. Tauc plots show this. The presence of different biomolecules bonding was confirmed by using FTIR spectra, which are involved in the synthesis and stabilization of the ZnS NPs formation by using plant extracts. The antimicrobial activity of pure and plant extract ZnS NPs was investigated against gram positive, gram negative bacterial and fungus cultures, the excellent inhibition zone was formed against gram-negative bacterial and fungus, plant extract ZnS NPs has been reported high inhibition zone to compare pure ZnS NPs due to particle size and biomolecules present, the concentration of ZnS NPs was increased inhibition zone also increased. The synthesized ZnS NPs were found an efficient photocatalyst for the degradation of Methylene blue dye (MBD) and Methyl orange dye (MOD). From the result *Syzygium aromaticum* extract ZnS NPs (1.0 mg) exhibited excellent photocatalytic degradation of Methylene blue dye (MBD-81 %) and Methyl orange dye (MOD-99 %) under the visible light irradiation, organic pollutants dye degradation was increased depends on the photocatalyst percentage and irradiation time.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript

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