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NANO-STRUCTURED ZINC SULFIDE TO ENHANCE *Cucumis sativus* (CUCUMBER) PLANT GROWTH

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ABSTRACT

The development of green synthesis route for the synthesis of nanomaterials using plants extract have received attention in the recent times as it is environment eco-friendly and economical method. Zinc sulfide nanoparticles (ZnSNPs) have been synthesized using *Punica granatum* (Pomegranate) peel aqueous extract at ambient temperature and in one single step. The synthesized zinc sulfide nanoparticles were investigated by X-ray diffraction (XRD), Energy dispersive analysis of X-rays (EDS), Scanning electron microscopy (SEM), UV-vis optical absorption and Fourier transform infrared spectroscopy (FTIR). UV-vis absorption studies revealed surface plasmon resonance (SPR) peak around 308nm, confirming the presence of ZnS nanoparticles. Particle size could be controlled by changing the quantity of peel extract andzinc ion concentration. Results of this study revealed that ZnSNPs have the potential to enhance root and development growth of cucumber plant.

Keywords: green synthesis, zinc sulfide, *punica granatum*, seed germination.

INTRODUCTION

Znic sulfide (ZnS) is an important semiconductor material with a wide band gap 3.72 eV -3.77 eV. It has a wide range of applications such as in optical sensor, solid state solar window layers, photoconductors, phosphors and catalysts (Razykov *et al*., 2011; Pawar, 2013; Echendu & Dharmadasa, 2015; Thirumavalavan *et al*., 2015; Rao & Pennathur, 2016). It has been extensively studied with the aim of controlling the size, morphology and crystalline of ZnS nanocrystals in order to obtain desired physical properties. In recent years, zero-dimensional ZnS nanostructures has attracted much attention because it can be used for biological detection and tagging. Many routes and techniques have been used to synthesize ZnS nanomaterials such as hydrothermal method (Hoa *et al*., 2009; Rashad *et al*., 2010), precipitation method (Yin *et al*., 2016; Iranmanesh *et al*., 2015; Suresh, 2013), solvothermal and pyrolysis route (Mendil *et al*., 2016; Hrubaru *et al*., 2016), solution-Phase synthesis (Gu *et al.,* 2006), microemulsion (Xu & Li, 2003; Murugadoss, 2013), mechanochemical route (Pathak *et al*., 2013), electrochemical method (Echendu *et al*., 2013), biological method (Tian *et al*., 2016; Jayalakshmi & Rao, 2006; Mirzadeh *et al*., 2013), ultrasonic radiation method (Xu *et al*., 1998), and thermal evaporation method (Trung *et al*., 2016).

These methods and routes have many disadvantages due difficulty of scale-up the synthesis process, separation and purification of nanoparticles, high energy consumption, and toxic by-products. Developing green routes for synthesis zinc sulfide nanomaterials (ZnSNPs) are of importance and still a challenge for material researchers. This is the first work on synthesis of ZnSNPs using an ecofriendly, non-toxic aqueous extract of *Punica granatum* peel aqueous extract at ambient temperature and one single step.

MATERIALS AND METHODS

Zinc acetate dihydrate [99.99%, Zn $(CH_3COO)_2$. $2H_2O$], and sodium sulfide nonahydrate [99.99, Na_2S. $9H_2O$] were obtained from Sigma-Aldrich and used without further purifications. Cucumber seeds were purchased from National Seeds, Amman, Jordan. Double distilled water was used in all experimental work.

Pomegranate fruits were obtained from the local market, Amman, Jordan. Peels were washed three times with double distilled water to remove dust and then left to dry in shade for two weeks. 50g dried small cut pieces of peels were placed in 500ml double distilled water for 72h. Afterwards, the mixture was filtered using Whitman filter paper No. 1 to remove solid particles and then centrifuged at 1500 rpm for 10 minutes to remove biomaterials. The filtrate was kept in glass bottle with tight cover at room temperature for use in synthesis of ZnS nanoparticles.

In a typical synthetic procedure, 2.4g of sodium sulphide nanohydrate was dissolved in 100 ml double distilled water under stirring at room temperature. Afterwards, 10 ml of *Punica granatum* peel aqueous extract was added drop wise under stirring, as soon as, the peels extract comes in contact with sulfide ions spontaneous changed in mixture to yellow color. Afterwards, 10% of zinc acetate solution was added to *P. granatum*-sulfide mixture drop by drop, started the formation homogenous yellow-white suspended particles, indicating the formation of monodispersed zinc sulfide nanoparticles. The suspended zinc sulfide particles were separated by centrifugation at 1700 rpm/min for 5min and the repeatedly washed with double-distilled water to remove any biological materials. Zinc sulfide nanoparticles after purification were dried in a vacuum at 80^{o}C for SEM-EDS, XRD and FT-IR analysis.

Synthesized zinc sulfide nanoparticles were characterized by different techniques: Scanning electron microscopy (a Hitachi S-4500 SEM machine, powder X-ray diffraction (X-ray diffractometer, Shimadzu, XRD-

VOL. 12, NO. 5, MAY 2017 ISSN 1990-6145
ARPN Journal of Agricultural and Biological Science

6000), Fourier transform infrared (Shimadzu, IR-Prestige-21 spectrophotometer) and UV–vis (SPUV-26, Sco-tech spectrophotometer).

Cucumber seeds were washed twice with distilled water and immersed in 5% dimethyl sulfoxide (DMSO, C_2H_6OS, Sigma-Aldrich) for 5 min for sterilization and experimental consistency. After rinsing with double distilled water twice, seeds were soaked in nanostructured ZnS suspension at 100ppm, 200ppm, 300ppm, 400ppm, 500ppm, and 1000ppm at soaking period 6h in an incubator at 27°C. In our Laboratory (27±2°C, relative humidity 62%), one filter paper (Whatman No. 42) was put in each Petri dish. Each Petri dish contained three healthy seeds of cucumber and treated with 6ml aqueous suspension of zinc sulfide nanoparticles. Petri dishes were sealed with parafilm and placed in the dark section of our laboratory for seven days. After 7 days of treatment of cucumber seeds with ZnSNPs, seed germination was recorded. Root length and seminal were counted. First set was considered as control (0ppm ZnSNPs) for comparison with the treated ones. Each treatment was carried out with three replicates and the results were presented as a mean standard deviation (±SD).

Each treatment was conducted with three replicates and the results are presented as mean standard deviation (±SD). All treatments were compared to those controls using t-test paired two samples for means determined at a 5% confidence level ($p < 0.05$).

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) pattern of synthesized zinc sulphide nanoparticles is shown in Figure-1. XRD peaks that corresponds to (111), (220), and (311) planes of ZnSNPs which are in good agreement with those of powder ZnS obtained from the International Center of Diffraction Data card (JCPDS-05-0556) confirming the formation of a crystalline structure. No extra diffraction peaks of other phases are detected, indicating the phase purity of ZnSNPs. The average crystallite size of the synthesized ZnSNPs was calculated to be 20 nm using Debye-Scherrer equation (Tian *et al*., 2016):

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where D is the crystallite size of zinc sulphide nanosheets, λ represents wavelength of x-ray source 0.1541 nm used in XRD, β is the full width at half maximum of the diffraction peak, k is the Scherrer constant with value from 0.9 to 1 and θ is the Bragg angle.

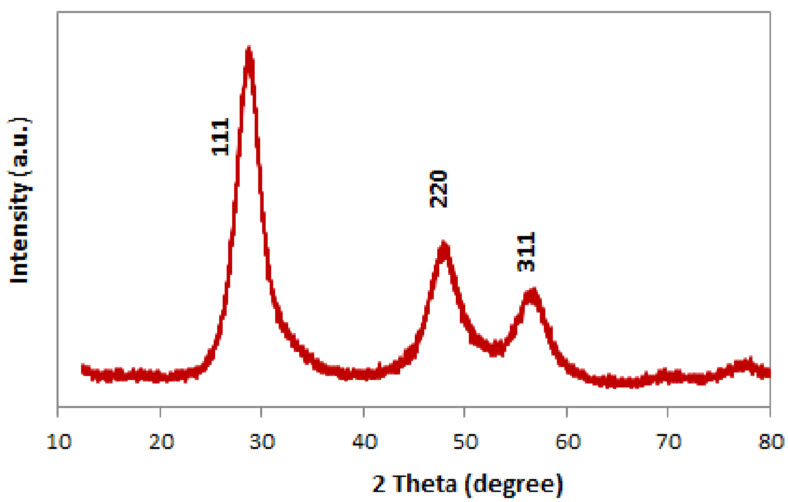

Figure-1. XRD pattern of the synthesized zinc sulphide nanoparticles.

FT-IR spectrum of *Punica granatum* peels extract is shown in Figure-2A. FT-IR spectrum showed a number of peaks thus reflecting its complex nature. Strong broad absorption band at 3407 cm^{-1} is characteristic of the alcohol/phenol - OH stretching vibration, carboxylic acid - OH stretch and N-H stretching of amides. Absorption bands at 2935 cm^{-1}can be ascribed to the stretching mode of CH_3 and CH_2. The strong peaks located at 1739 cm^{-1}could be assigned to the C=O stretching in the carboxyl or C=N bending in the amide groups. Peak at 1620 cm^{-1} is characterized to - NH stretch of primary amines. Peaks at 1523 cm^{-1}, 1456cm^{-1}, 1361 cm^{-1}, 1230 $cm^{-1}$are characterized - NH in secondary amines, aromatic - CH stretching vibrations, and C-C-N amines. Strong peak at 1061 cm^{-1} indicated the stretching vibration of (NH)–C-O group. Peaks at 897-523 cm^{-1} refers to O-C=O bending in carboxylic acids, N-C=O, and C-N-C bending mines.

FT-IR spectrum of synthesized ZnSNPs, Figure-2 B showed the strong band at 428 cm^{-1}which is attributed to the vibrations of elongation and of deformation of vibratory ZnS. The strong absorption peak at 3443 cm^{-1} corresponds to O-H stretching mode arising from the absorption of water on the surface of ZnSNPs. The structural changes in FT-IR spectra indicated that the capping and stabilization of zinc sulfide nanoparticles via the coordination with OH, -NH, C=O, C=N. The

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physicochemical properties of *Punica granatum* peel extract act as capping agent and prevents the nanoparticles formed from aggregation.

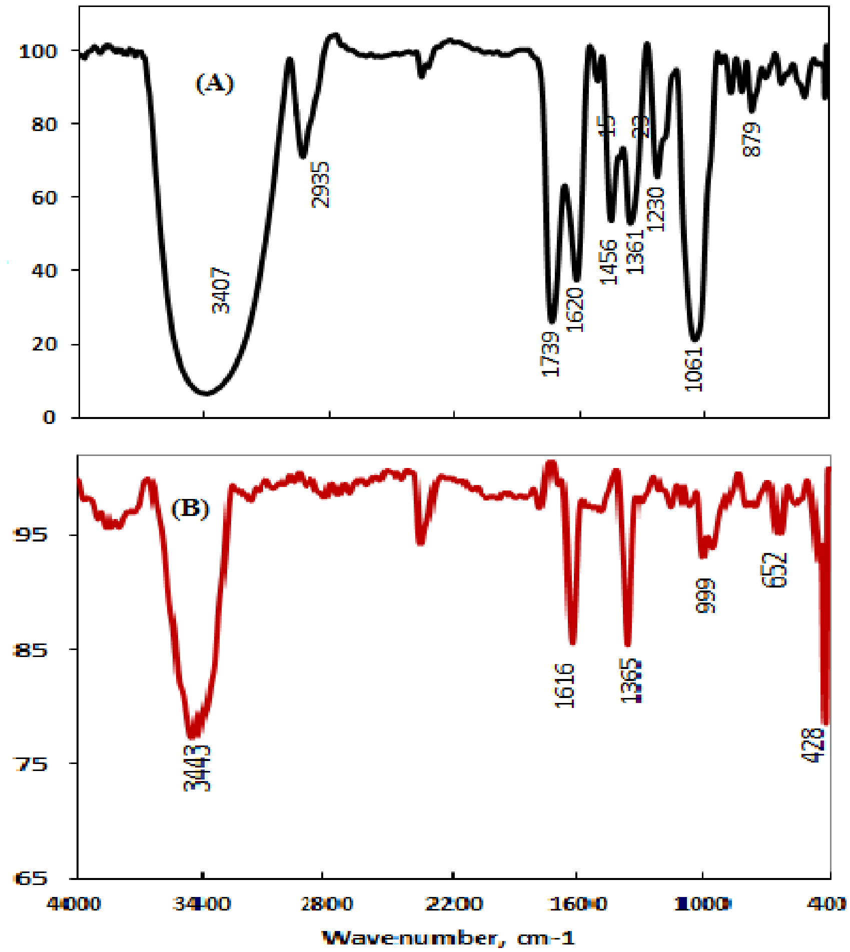

Figure-2. FT-IR spectrum (A) of *Punica granatum* peels extract and (B) of zinc sulfide nanoparticles synthesized.

Scanning electron microscopy (SEM) image and energy-dispersive spectroscopy (EDS) analysis of ZnSNPs synthesized by the green route is shown in Figure-3. The SEM analysis has showed agglomeration of the ZnSNPs nanoparticles as platelets-like. Each of the platelets has nanoparticles with an average particle size 20nm agreed with the calculated from XRD. EDS analysis showed the high purity of synthesized ZnSNPs, which composed mainly from zinc and sulfur.

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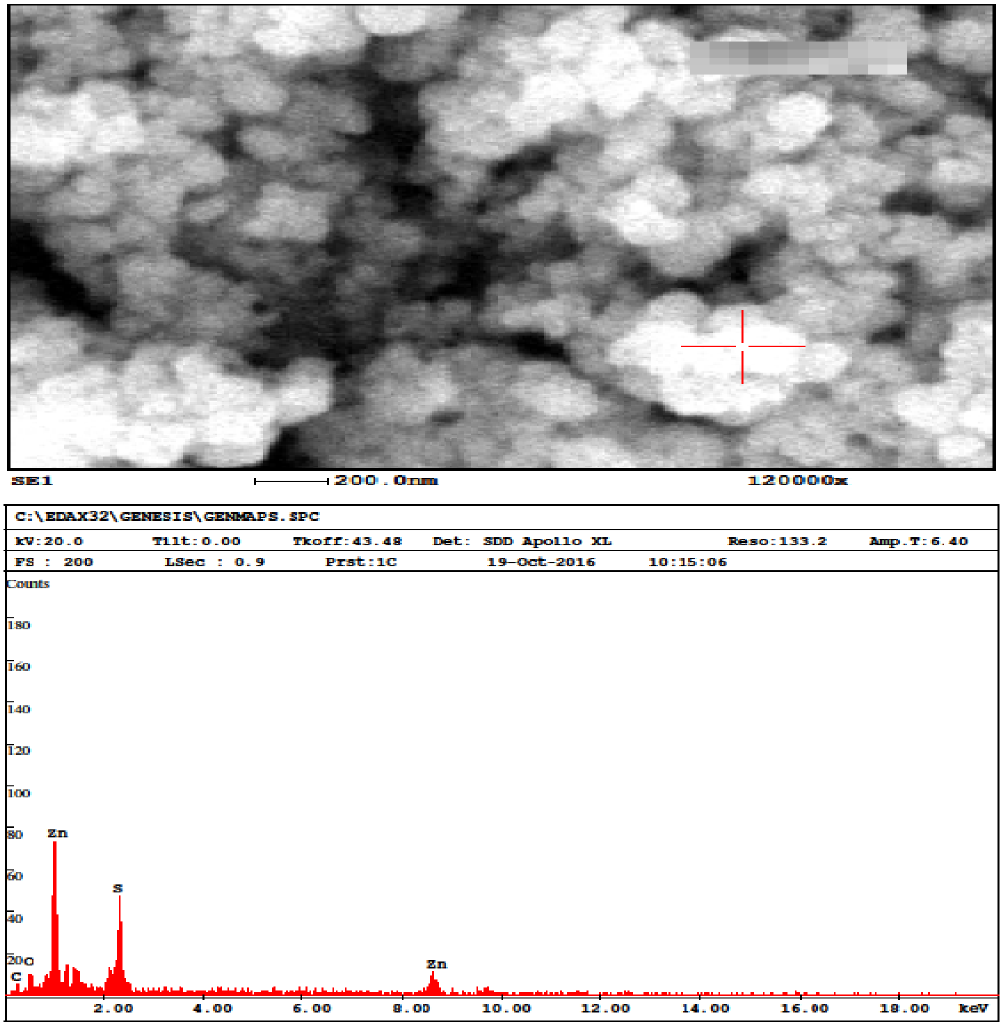

Figure-3. SEM image and EDS of synthesized ZnSNPs.

The optical absorption spectrum of the synthesized zinc sulfide nanoparticles (ZnSNPs) dispersed in deionized water was monitored after 24h of synthesis. The optical absorption spectra have been observed by UV-Visible spectrophotometer shown in Figure-4. From the optical absorption spectra ZnS nanoparticles it is clear that optical absorption spectra of ZnS nanoparticles in the range of 305-310 nm this peak position reflects the band gap of particles. There is no absorption peak at visible region.

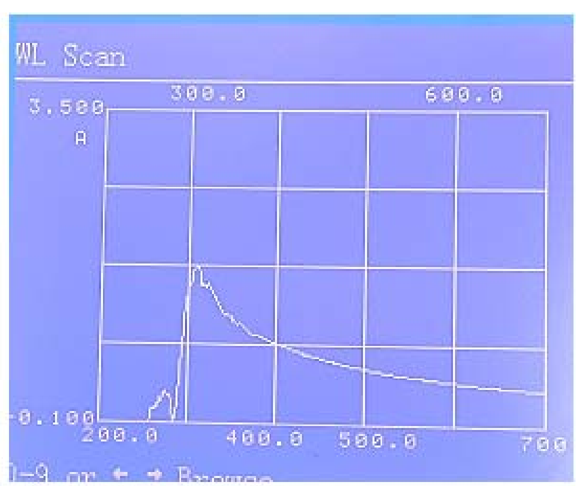

Figure-4. UV-vis spectrum of synthesized ZnS nanoparticles.

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Effect of zinc sulfide nanoparticles on germinations and seminal roots are presented in Table-1. Different concentrations of ZnSNPs (100ppm, 200ppm, 300ppm, 400ppm, 500ppm, and 1000ppm) have a different impact on seed germination of cucumber. Authors knowledge, there is no information reported in the literature on the effect of ZnSNPs on cucumber seed germination. Analysis of the obtained data indicated that different concentrations of zinc sulfide nanoparticles (400ppm-1000ppm) significantly influence germination percentage, root length and number of seminal routes of cucumber seed in comparison to control. It was observed that higher concentrations of zinc sulfide nanoparticles (>400ppm) lowered germination percentage, root length and number of seminal roots. A digital photograph, Figure-5 showed the effect of different concentrations of ZnSNPs on cucumber seeds in comparison to control (0ppm ZnSNPs). Figure-6 showed the enhancement of root growth of cucumber by 300 ppm ZnSNPs in comparison with control after 12 days.

Table-1. Effect of ZnSNPs on germinations and number of seminal roots.

ZnSNPs (ppm)	**G** (%)	**Root length** (cm)	**Seminal root number**
Control	79.6a*	4.5cd	8.2e
100	846a	5.2cd	9.3e
200	96.4a	8.1c	14.8d
300	98.8a	14.9b	30.7a
400	97.8a	11.4a	23.3b
500	90.1b	10.8ab	22.8b
1000	86.3c	9.3ab	21.1c

*Means sharing similar letters do not differ significantly at 5% probability level

Figure-5. Photograph showed the effect of different concentrations of ZnS NPs on root growth of cucumber after 7 days.

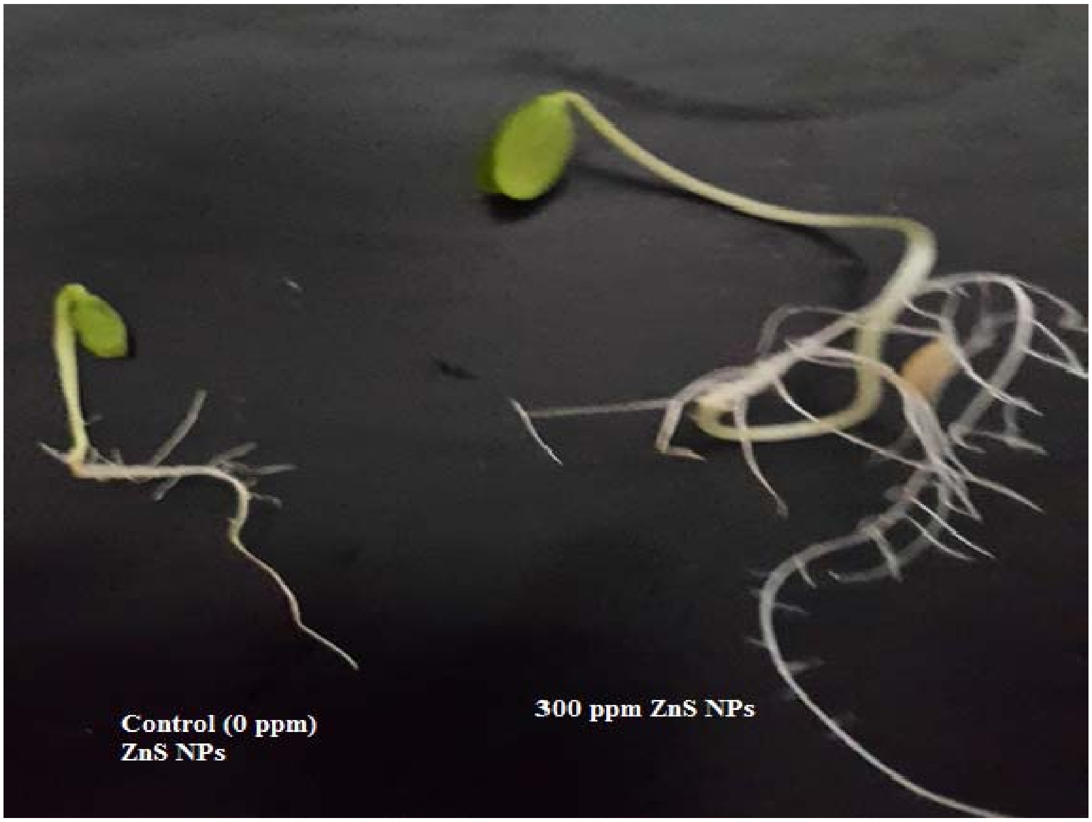

Figure-6. Photograph showed the effect of 300 ppm ZnSNPs on the root growth of cucumber after 12 days.

CONCLUSIONS

In the present work, we first report an eco-friendly and simple method for the synthesis of zinc sulfide nanoparticles using *Punica granatum* peels aqueous extract. Synthesized ZnSNPs were characterized by different techniques for determining crystalline size and morphology. This study demonstrated that different concentration of ZnSNPs (100ppm-1000ppm) had a clear effect on enhancing the cucumber germination percentage, root length and number of seminal roots. Applied 400ppm zinc sulfide nanoparticles to cucumber seeds had highly favorable growth promoting effects on cucumber growth. A comprehensive experimentation is carried out on the effect of ZnSNPs on cucumber growth in greenhouse and field. The method of the present study offers several important advantageous features. First, the synthesis route is economical and environmentally friendly, because it involves inexpensive and non-toxic materials for second, large scale synthesis.

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