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Agricultural Application of Synthesized ZnS Nanoparticles for the Development of Tomato Crop

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Abstract: Nanoparticles (NPs) are playing a significant role in the development of modern agriculture. Among other metal nanoparticles, ZnS NPs are important due to their utilization in agriculture. Zinc sulfide nanoparticles have great potential to enhance agriculture production. The co-precipitation method was used to make ZnS nanoparticles, and morphological features were investigated using X-ray diffraction (XRD) and a transmission electron microscope (TEM) to determine size. The average particle was near ~3 nm calculated using XRD, close to the TEM study. Tomatoes, which belong to the Solanaceae family, are one of India's most important vegetable crops. The tomato plants were sprayed with a graded concentration of zinc sulfide nanoparticles (ZnS NPs) based nano-fertilizer four times at a 15-day interval and a control. At the flowering time, growth parameters such as plant height were measured. Nanofertilizer-treated plants showed increased weight and quality of crop yield. This paper elaborates the synthesis, characterization, properties, and application of ZnS NPs as nano-fertilizer on tomato plant growth. Developing nano-based fertilizer would be a new technique in this field, as nano-fertilizers are beneficial and less toxic to chemical fertilizer and improve soil fertility.

Keywords: zinc sulfide; nanoparticles; tomato; X-ray diffraction; TEM; characterization.

1. Introduction

To increase productivity per unit area, current agricultural cropping systems use a lot of fertilizers, insecticides, and herbicides. Yet, these chemicals and fertilizers cause a lot of problems such as soil, water, and air pollution [1]. Due to urbanization and industrialization, the world population is rapidly expanding while cultivated land decreases [2]. To feed an ever-increasing population, greater yield per unit area in per unit time is required while ensuring economic, social, and environmental sustainability [3-6]. Similar to the other difficulties, it is determined that zinc deficiency is the most widespread micronutrient deficiency in worldwide and Indian soil [7, 8]. Zinc and Sulphur are essential micronutrients that are required for metabolic reactions in the plant system, such as the synthesis of indole acetic acid, protein synthesis, chlorophyll, protein and enzyme production, pollen germination, and pollen development, as well as metabolic processes [9, 10]. As a result, nano fertilizers are preferred to increase nutrient use efficiency because nano nutrient particles easily penetrate the plant from the applied surface, require fewer doses, and provide more surface area for various metabolic reactions in the plant system, enhancing crop growth and development [11, 12]. Nano fertilizers are now being utilized for site-specific nutrient management to lower fertilizer doses, lower nutrient management costs, and boost yield and nutrient usage efficiency [13-15]. Due to human activity on farmlands and societal lifestyle changes, farmlands lose their fertility. This invariably affects food output and may result in famine and starvation; thus, deliberate attempts to modify plants for increased production are required [16-18]. Nanotechnology is the most recent advancement in precision agriculture, allowing for the formulation and implementation of strategies to fulfill the growing food demands of the world's population [19,20]. There is a shift away from outdated crop production methods toward technologies that can increase agricultural yields with required nutrients while ensuring nutrient security, increasing the value of production, boosting farmer's economies, delivering the agri-value chain to rural consumers, and supporting a pollution-free environment [21]. Nanotechnology is a multidisciplinary discipline that has gained traction in industries such as textiles, cosmetics, health, electronics, food processing, and hydraulics [22, 23]. In plants, zinc plays an important role in enzymatic activation for protein synthesis. It is classified as an essential microelement since it is required in small amounts but is also necessary for vegetative growth [3].

Zinc sulfide (or zinc sulfide) is a white color, soluble in water, an inorganic compound with a chemical formula of ZnS [24]. It is well-studied that ZnS is a non-toxic and non-oxide semiconductor presenting excellent properties [25]. This is the most common form of zinc found in nature, which is found primarily in the mineral sphalerite. The pure material is white, and it is widely used as a pigment, despite the fact that it is usually black due to various impurities [26]. In its synthetic form, zinc sulfide can be transparent, and it is used as a window for visible optics and infrared optics [27]. Nano-fertilizers are synthetic or modified forms of traditional fertilizers, bulk material, or derived from various plant vegetative or reproductive portions using various chemical, physical, biological, and nanotechnology methods to improve soil fertility, productivity, and crop yields quality [28, 29]. Therefore, in this study, we synthesized and characterized ZnS nanoparticles by XRD and TEM were analyzed.

The effects of ZnS nano fertilizer on the growth of tomatoes were also determined. The tomato (*Lycopersicon esculentum* Mill.) is a member of the Solanaceae family. It is one of the most significant vegetable crops, and it is consumed fresh or processed into a variety of products, such as tomato puree and catchup. It is an antibiotic and a good source of vitamins A, B, C and minerals such as potassium folate and simple sugars and insoluble fibers [30].

2. Materials and Methods

2.1. Synthesis of zinc sulfide (ZnS) nanoparticles.

The co-precipitation approach was used to make ZnS nanoparticles. In this method, ZnS (sodium sulfide and zinc acetate) can be synthesized using a molar concentration 1:3 ratio. Sodium sulfide (Na_2S) is dissolved in 200mL distilled water and kept under steady stirring for 30 minutes to ensure complete dissolution and added dropwise to the other solution containing zinc acetate in 200mL of distilled water with constant stirring for 15 minutes to facilitate total nanoparticle production. Finally, the precipitating solution becomes hazy and white. Precipitates were centrifuged and washed 3-4 times with double distilled water. The obtained powder was dried for 12h in a vacuum oven at 60°C. The particles were de-agglomerated in pestle-mortar to obtain a very fine powder. The calcination of the obtained product was done for 2 hours at 1600°C in a hot air oven [25].

2.2. Characterization of ZnS nanoparticles.

Characterization of ZnS was done by XRD and TEM. X-ray diffraction patterns were captured on a PAN analytical X'pert PRO between 10-75° (2), with a step size of 0.02°, and matched with an ICDD card using X'pert High Score software to confirm phase formation. On the JEOL 2100 F, morphological features were also recorded (200 kV; transmission electron microscope).

2.3. Selection of plant.

The terrestrial plant tomato was selected for the following reasons: Easily available in plenty. Tomato has more species that are useful for the environment and medicinal purposes. Fruits are used as a vegetable, salad, and manufacturing of tomato sauce.

2.4. Sample collection.

In the present study, Tomato (Heem Shona) seedlings plant was collected from the nursery, Karnal 2020. Before taking seedlings, the zonation & varieties of the plant was noted. The sample was collected from the randomly selected spot of seedling bed preparation from the nursery. Stem was plucked from freshly collected seedlings & the roots were dipped in distilled water overnight.

2.5. Land preparation for the tomato plant.

The field should be plowed properly before transplanting to eliminate debris and soil clods. Organic manures should be incorporated at the time of the last plowing and flatbed with appropriate size (3ft) width & (5ft) length is formed after leveling.

2.6. Transplanting of tomato seedlings.

Before planting, seedlings should be dipped in water for 2 hrs. The optimum spacing is 60cm between the rows and 50cm from plant to plant. Proper care should be taken while selecting seedlings for transplanting. Over and under-aged seedlings should be avoided for better establishment.

2.7. Preparation of ZnS nanofertilizer suspension.

Bulk cheated for the Zn source; a ZnS nano-fertilizer was utilized; the produced materials were suspended directly in deionized water and sprayed on the plant for 30 minutes. Different concentrations of solutions (0.5, 1.0, 1.5, and 2.0 g/l) were produced. To avoid particle aggregation, magnetic bars were put in the suspensions for stirring. As expected, the nanoscale suspensions also appeared as clear solutions. All of the prepared suspensions had a pH range of 6.8-7.0. A control corresponding to pure water was also maintained.

2.8. Foliar exposure of the plant to ZnS nano fertilizer.

The effects of foliar sprays of zinc sulfide nano-fertilizer (ZnS NPs) at four different concentrations on tomato plants were measured at 15-day intervals (Figure 3). In this study, the variety of tomato (Heem Shona) was selected and transplanted into plowed soil, and after two weeks; the foliar spray at 0.5 g/l concentration was done on15 Feb 2020, followed by a second foliar spray on 2nd March 2020 at 1.0 g/L, third foliar spray at 1.5 g/L on 17th March, 2020 and the fourth spray at 2.0 g/L on t12 April 2020 respectively.

2.9. Physical parameter of soil.

Various physical parameters of soil such as pH, moisture content, electric conductivity, and heavy metals were analyzed according to standard protocol by Flame photometer AAS.

2.10. Harvesting of tomatoes.

Harvesting of tomato fruits was done at the crop's maturity after ZnS nano fertilizer application quantity, and quality of tomatoes were assessed.

3. Results and Discussion

3.1. Results.

3.1.1 Characterization of ZnS nanoparticles.

Morphological characterization of ZnS nanoparticles was analyzed by X-ray Diffraction Spectroscopy, TEM studies, and particle size distribution.

3.1.2. X-ray diffraction spectroscopy.

Figure 1 shows the XRD spectra of the as-prepared ZnS nanocrystalline. XRD spectrum of pristine ZnS thin films shows three broad peaks at 2θ = 28.69°, 48.23°, and 56.72° indicating the formation of the nanostructure. These XRD peaks corresponding to the (111), (220), and (311) planes of ZnS suggest cubic zinc blende phase [JCPDS card no. 5–0566]. The size of the particle has been computed from the width of the first peak using Debye–Scherrer formula [24] given below

$$d = \frac{k\lambda}{\beta Cos\theta}$$

where K is constant (K = 0.9), λ the wavelength of X-ray, by the full width at half maximum, and h is Bragg angle. The particle sizes obtained from XRD were in the range of 2–3 nm [26, 27]**.**

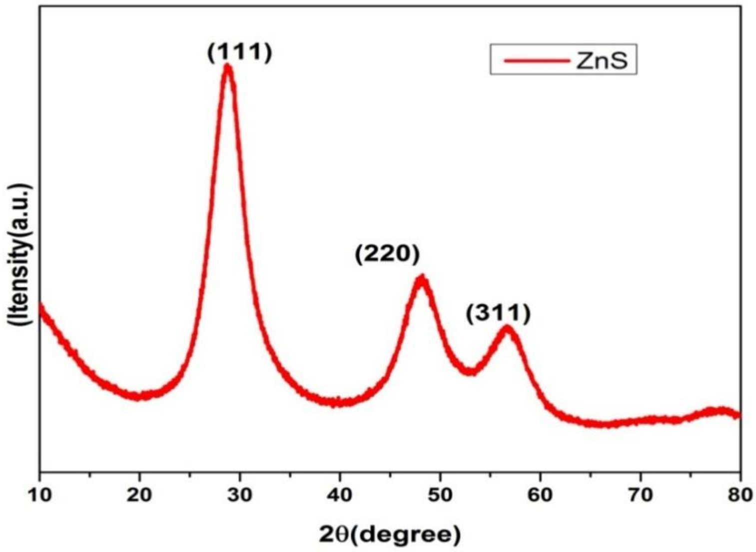
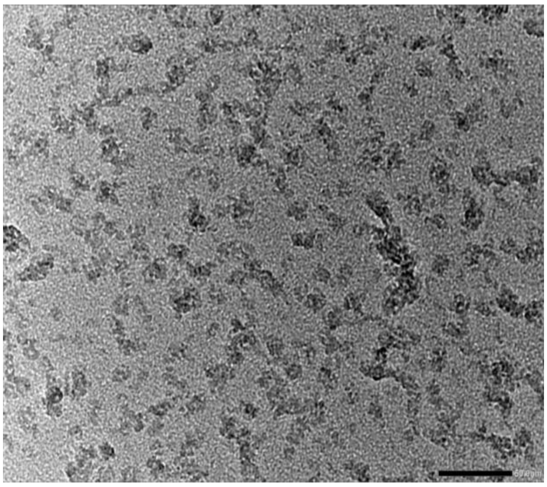


Figure 1. X-ray diffraction of ZnS nanoparticles.

3.1.3. TEM studies and particle size distribution.

A typical HRTEM image of ZnS nanoparticles is shown in Figure 2. The particle size determined by HRTEM is in the 3 nm range. The XRD results support this value. The particle size distribution is shown in Figure 2. The average size of the particle is 3.89 nm using gauss fit [28].



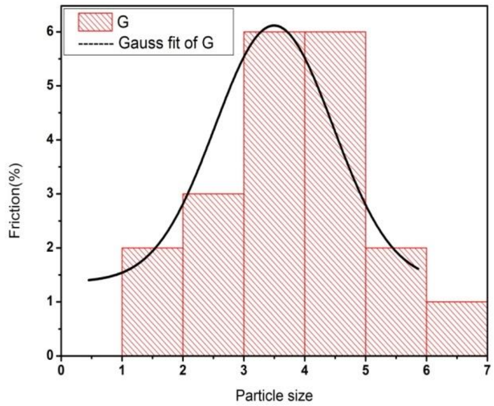


Figure 2. TEM image of ZnS nanoparticles and particle size distribution of ZnS nanoparticles.

This research focuses on the chemical synthesis of ZnS nanoparticles for eco-friendly. The Tomato (Heem Shona) seedlings were transplanted in the soil, and foliar spray should be done 15 days intervals at four different concentrations of nanoparticles. In the tomato crop, nanoparticles were applied to the plants to check the efficiency of nano-fertilizer. The soil collected from plants' roots is a good type of soil that prevents root disease. Total growth (13>10cm.), (17 >11cm.), (12 >19cm.) and (22 >13cm.) were observed after the sprays of ZnS nanoparticles on respective dates as compared to control (Table 1). The application of ZnS nanoparticles significantly improved the growth, yield, and yield-attributing characters in tomatoes. In the soil, the pH value is mostly around 7 means acidic in nature. Moisture content is also present around 50% in soil which is necessary to maintain the level of moisture in plants (Table 2).

Table 1. Effect of ZnS Nano-fertilizer on Tomato plant growth.

Type	**Total height of plant (cm) after spray**				
	Seedling planted (cm) (1 st February, 2021)	**1st spray (15th February, 2021)**	**2nd spray (2nd March 2021)**	**3rd spray (17th March, 2021)**	**4th spray (12th April, 2021)**
Control	10-14 (12)	9-11 (10)	10-12 (11)	11-13 (12)	12-14 (13)
ZnS Nano-Fertilizer	11-14 (13)	12-15 (13)	15-19 (17)	17-22 (19)	19-24 (22)

3.1.4. Harvesting of tomatoes.

After fruits development and growth, the harvesting of tomato after ZnS nano fertilizer application quantity and quality of tomato were increased (Figure 4).

Table 2. Observation of physical parameters of soil.

Soil Sample	**pH**	**Electric conductivity (Siemens)**	**Moisture %**
Tomato control	5.8	0.20 S/m	1.43 %
Tomato Nano-fertilizer	6.94	0.85 S/m	1.38 %

The conductivity of water: 4.56 S/m.

(A) Tomatos in Control **(B)** Tomatos after ZnS Nano-fertilizer

Figure 4. Qualitative and quantitative effect of ZnS Nano-fertilizer on tomato growth. (**A**) Control and (**B**) Nano-fertilizer treated**.**

3.2. Discussion.

Nano-fertilizer is any product that is made with nanoparticles or uses nanotechnology to improve nutrient efficiency [29, 31]. In comparison to the control (780 g/m^2), foliar spraying of Nano-Gro® boosted the early yield of tomato fruit (983 g/m^2) [32]. The effect of chelated micronutrients (including Zn) supplemented liquid organic fertilizer on red pepper growth and investigated yield [33]. The effect of organically chelated micronutrients (including Zn) on okra growth and productivity was investigated, and chelated micronutrient fertilizer was found to boost growth and yield [34]. Because of their nano size and reduced water solubility, ZnO NPs have a better bioavailability in peanuts [35]. The influence of ZnO NPs on onion seed germination and seedling growth was investigated, and it was discovered that seed germination increased at lower concentrations of ZnO NPs but decreased at higher concentrations [36]. The effect of a liquid organic fertilizer supplemented with organically chelated micronutrients (Zn, Cu, Fe) on seed germination and early seedling growth in red pepper and tomato plants was investigated and found that it had a positive impact on seed germination and early seedling growth. They attributed this to the availability of micronutrients to seed during seed germination. The Foliar application of zinc oxide nanoparticles promotes drought stress tolerance in eggplant (*Solanum melongena* L.) [37]. Also, the foliar application of nano-ZnO and bulk Zn-fertilizer in red acidic soil improves the rice yield [38]. Zinc improves the roots' cation-exchange capacity, which improves nutrient absorption, particularly nitrogen, responsible for higher protein composition. These findings suggest that Zn availability to seed or a high Zn content inside seeds during seed germination plays a critical role in seed germination and early seedling growth.

This research focuses on the eco-friendly synthesis of ZnS nanoparticles and their foliar application on tomato (Heem sohna) seedlings transplanted in the tilth-free soil. The foliar spray is done after 15 days with four different concentrations of nanoparticles (0.5, 1.0, 1.5, and 2.0 g/l). The nanoparticles were applied in the plants to check the efficiency of the nano-fertilizer. The elongation of the plant's root, shoot, and seedling was compared. In the soil, the pH value is mostly around 7 means acidic in nature. Moisture content is also present around 50% in soil which is necessary to maintain the level of moisture in plants [30]. Under a nano calcium treatment of 0.5g/l concentration, tomato fruit output and nutritional status were dramatically increased. That's why nano-fertilizer is a beneficial and natural product, less toxic to chemical fertilizer, and improves soil fertility at a large scale.

4. Conclusions

Due to their various properties and applications, ZnS Nanoparticles stand out as one of the most adaptable materials. When it comes to the production of ZnS Nanoparticles, they can be made via a chemical process, and nanoparticles play a vital role in agriculture. Crops that are treated with these nanoparticles grow faster and produce more. As the world's population grows, so does the need for food. As a result, staple food crop yields are falling. As a result, commercializing metal nanoparticles for sustainable agriculture is urgently needed. This study confirmed the potential of foliar application of Zinc Sulfide Nanofertilizer for growth of tomato up to optimum applied concentration. If the concentration is higher than the optimal, they have an inhibitory impact on agricultural plants, reducing crop growth and production. Society should be more concerned about the use of nano-fertilizer in agriculture.

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Conflicts of Interest

The authors claim no conflicts of interest because no financial support was received from any government, non-government agency, or organization to conduct this research work.

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