GREEN SYNTHESIS OF ZnO NANOPARTICLES AND ITS APPLICATION AS NANO-FERTILIZERS

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***Abstract*:** Zinc oxide nanoparticles are one of the multifunctional and versatile materials having diverse properties and applications in numerous fields. In the present work, zinc oxide nanoparticles are synthesized utilizing the bio-components of Hibiscus rosa-sinensis leaves which act as the reducing agents. The synthesized nanoparticles were characterized by particle size analyser, UV-Visible spectroscopy and Infra-Red (FTIR) spectra were studied to analyse the bonding pattern present in the formed nanoparticles. The synthesized Zinc oxide particles were utilized as nano-fertilizers for *Triticum aestivum* (Wheat) plant. The nano-fertilizers were given on weekly basis in form of foliar spraying and the growth was recorded periodically. The plants treated with zinc oxide nanoparticles showed significant growth against the non-treated plants. Among the various zinc oxide precursors, the nanoparticles formed from the zinc carbonate showed highest growth.

Keywords: *zinc oxide, nanoparticles, green synthesis, foliar spraying.*

1. Introduction

The unusual and fascinating properties of nanoparticles are strongly influenced by their size, morphology and structure. The traditional chemical method of nanoparticle synthesis uses range of chemical precursors and process conditions like time, temperature, pH, concentration, etc. Any variation in these process parameters or chemical precursors leads to significant change in shape and size of the nanoparticles. [1]

One of the drawbacks of conventional solid state or chemical synthesis methods is that the developed nanoparticles may have some adsorbed toxic species on the highly reactive surface which may have adverse or sometimes negative effects in its application. The green synthesis of nanoparticles utilizing biological components such as plant extracts or micro-organisms is a better alternative to chemical methods due to its cost effective and environment friendly approach. [2]

Synthesis of nanoparticles is basically a reduction process which is carried out by chemical or biological reducing agents. The biological components like plants contain several organic compounds such as flavonoids, terpenoids and polyphenols which acts as reducing agents and helps in synthesis and stabilization of nanoparticles. [3]

Among various potential applications, soil science is one such area which can be benefitted by the introduction of nanotechnology. Micronutrients deficiency in soil is a major problem in a developing country like India. Among the various micronutrients, zinc deficiency is the most common in Indian soils. The effectiveness of zinc fertilizers is determined by various factors, among which solubility and particle size are the major ones. Since surface area directly affects the dissolution process, it can be expected that nano particles have greater rate and extent of dissolution then micro sized or bulk materials. [4-6]

The zinc fertilizers can be conventionally applied to the soil or in form of foliar spraying. Foliar feeding is a technique in which liquid fertilizers are directly applied to the plant leaves in the form of fine spray. In foliar spraying, the nutrients applied are absorbed and transported from the point of application to the point where it is utilized. However, the absorption and transportation mechanism of foliar feeding of zinc nanoparticles are yet to be understood. [7]

In the present approach, leaves of Hibiscus rosa-sinensis are used as biological reducing agent to obtain Zinc oxide nanoparticles from three different inorganic salts of zinc. The zinc oxide nanoparticles obtained were utilized as nano-fertilizers for *Triticum aestivum* (Wheat) plant. The nano-fertilizers were feeded weekly in form of foliar spraying and the growth was recorded periodically.

2. Materials and Methods

The whole work is divided into two parts. First part is green synthesis of ZnO nanoparticles and its characterization. In the second part, the nano oxide particles were used as nano fertilizers given in form of foliar spraying to newly germinated wheat plants and the growth of the plants were recorded periodically for three weeks.

2.1 Green synthesis of ZnO nanoparticles

Chemical precursors for ZnO nanoparticles were commercially obtained and Zinc oxide nanoparticles were synthesised using bio components from leaf extract. The procedure for the synthesis was referenced from literature. The whole process of nanoparticle synthesis can be divided into two steps: Preparation of the leaf extract and synthesis of zinc oxide nanoparticles.

2.1.1. Preparation of the leaf extract

Leaves of Hibiscus rosa-sinensis plant (figure 1) were collected and washed with water to get rid of any dust particles. The leaves were then dried in oven for 2 days at 110^0C. The dried leaves were then crushed to a fine powder in a mortar pestle. The dried powder was dissolved in distilled water heated at 60^0C under continuous stirring to get a homogenous solution. This leaf extract were used in the next step for the reduction of zinc ions (Zn2+) from zinc salts to zinc nanoparticles (ZnO).

2.1.2. Preparation of zinc oxide nanoparticles

For preparation of zinc oxide nanoparticles, three different zinc salts (zinc acetate, zinc carbonate and zinc nitrate) were used as zinc precursors. Required amount of zinc salts were added in the leaf extract (50:1 ratio of leaf extract and zinc salt) under reflux condition and continuous stirring and heating was done till the colour of the solution changes to deep yellow due to reduction of zinc ions. The solution is then further heated till it converts to a thick paste.

The paste were transferred in a ceramic crucible and heated in a muffle furnace at 500^0C for 2 hrs. The heating rate was kept at 3^0C/min. After cooling the powder so formed were characterized for various properties. The synthesized zinc oxide powder samples were termed as ZA-ZnO formed from zinc acetate, ZC-ZnO formed from zinc carbonate and ZN-ZnO from zinc nitrate. The raw materials used and nomenclature of the final product is given in table 1. The flow chart for the green synthesis of zinc oxide particles are given in figure 2.

Table 1: Raw materials used in green synthesis and nomenclature of final product

S. N.	ZnO Nomenclature	Raw materials used	
1	ZA-ZnO	Zinc Acetate	Distilled water, Hibiscus rosa-sinensis plant leaves
2	ZC-ZnO	Zinc Carbonate	
3	ZN-ZnO	Zinc Nitrate	

Figure 1: *Hibiscus rosa-sinesis* plant

2.1.3. Characterization of nanoparticles:

The synthesized zinc oxide particles were characterized for their particle size and bonding nature with the help of a particle size analyser and FTIR spectroscopy respectively. The particle size distribution in the developed powder sample of zinc oxide is measured by dynamic light scattering (DLS) method in dilute condition with the help of a particle size analyser (Zetasizer zetameter, ZEN 3690, Malvern instruments, US make). The dispersant used in the measurement was distilled water.

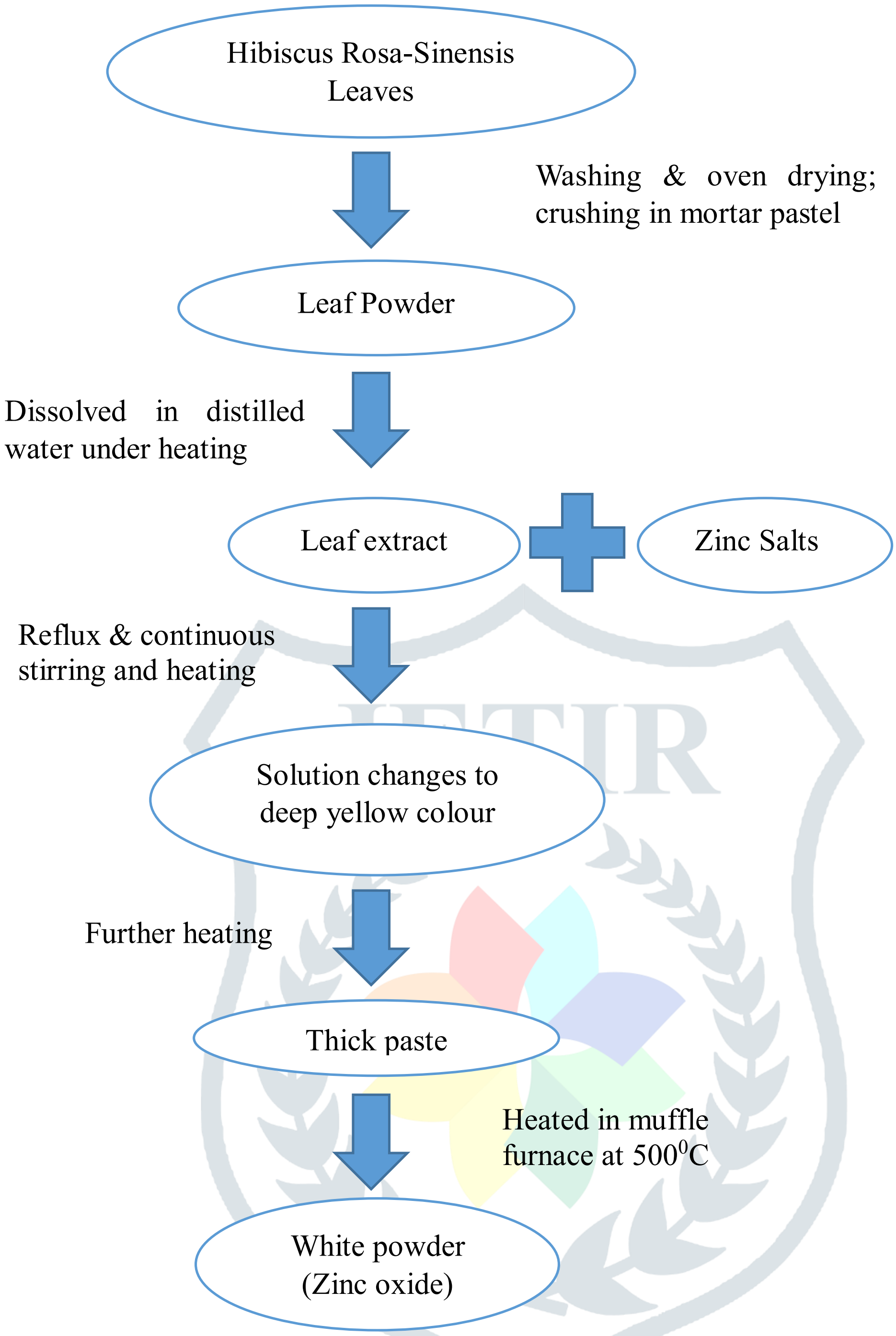


Figure 2: flow chart for Green synthesis of ZnO nanoparticles

Fourier transform infrared (FTIR) spectroscopy helps in establishing the identity of various phytochemical constituents of leaf extract involved in the reduction of Zn^{2+} ions from the zinc salts and stabilization of the formed Zn nanoparticles. FTIR spectrum for dried and powdered ZnO NPs was obtained using Bruker Alpha ll Spectrophotometer in the range of 4000–500 cm^{-1}. For the measurement of FTIR spectra, very thin pellets are prepared by mixing about 2 mg of the dried gel powder with 20 mg of IR grade potassium bromide, KBr salt and pressing the mixture at a pressure of 3 ton for 1 min. The wave number range used for absorption spectra measurement is 4000 cm^{-1} to 500 cm^{-1}.

2.2. Application as nano fertilizers: Foliar spraying to *Triticum aestivum* (wheat plant)

To study the effect of foliar spraying of the zinc oxide nanoparticles, plant species of *Triticum aestivum* (common Indian wheat) were chosen. The seeds were procured from the market and were planted in small polythene cups. To have a better and more accurate analysis, total of 12 cups were prepared, 3 for each type of zinc nanoparticles.

Soil Preparation and sowing: The work was started in the last week of October as the climate during October is suitable for wheat cultivation in India. The soil, taken from farmland, was first grounded into fine particles and then mixed with farmyard manure (cow dung) in the ratio of 3:1. No other chemical fertilizer was added in the prepared soil. Equal amount of soil was then filled in each of the polythene cups.

The seeds were soaked in water for overnight before sowing. The next day 3 seeds per cup were planted at a depth of 5-6 cm and equal amount of water was sprinkled on all the cups. The seeds started germinating in 2-3 days. After one week, the height of the plants was measured using a ruler scale. The measurement was done by measuring the longest leaves of each sample and taking average of it. The first foliar spraying was then done using a sprayer. The solution containing zinc nanoparticles was prepared by mixing 1 gram of zinc oxide powder in 100 ml of water. Care has been taken that each plant receives equal amount of zinc oxide nano particle solution. The process was repeated every week for 4 consecutive weeks and measurement was recorded and analyzed for the effect of foliar spraying of zinc oxide nanoparticle on the wheat plant.

3. Result and Discussion

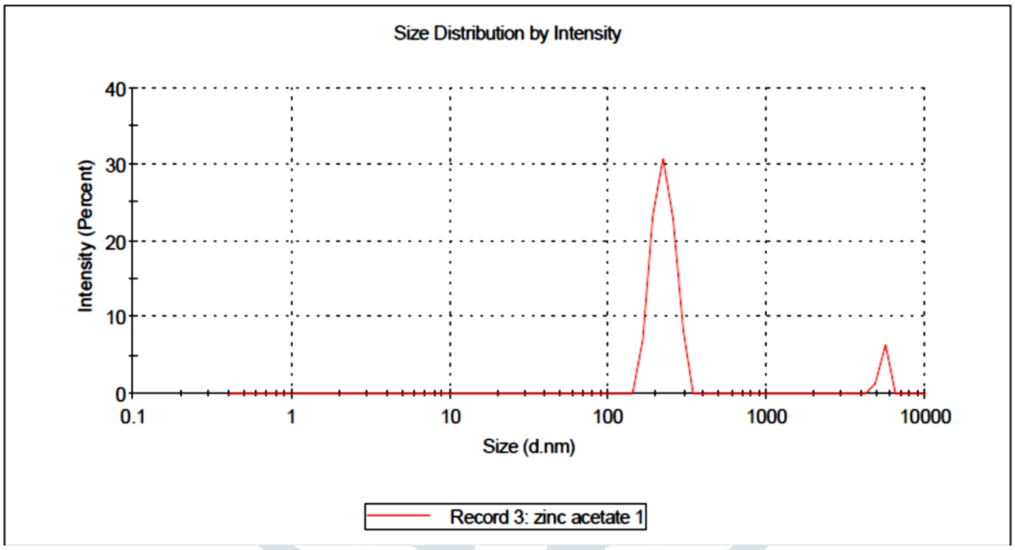
The synthesized zinc oxide particles were characterized for particle size and IR spectroscopy. And the effect of foliar spraying of zinc oxide particles were measured and the analysis were given in the below subsections.

3.1. Particle size analysis

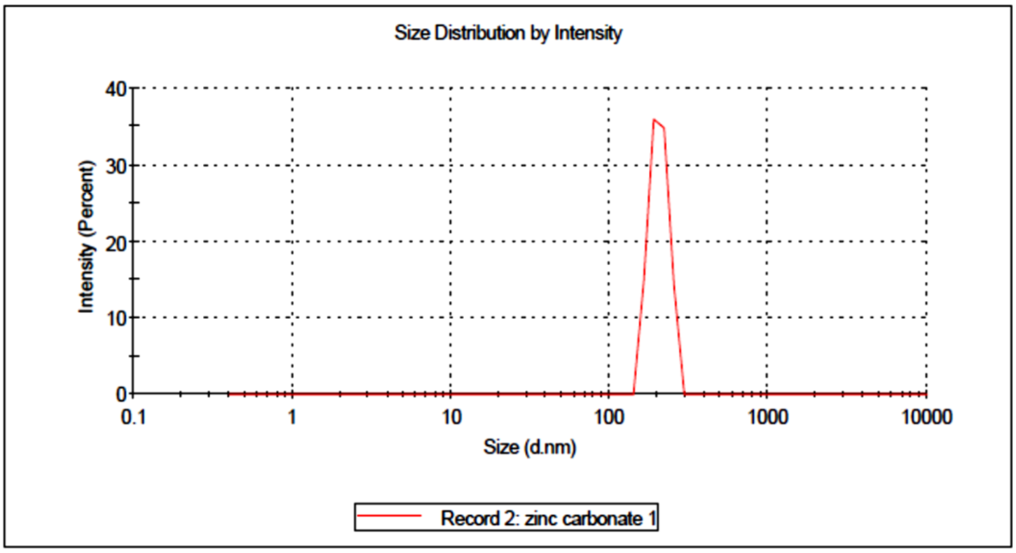
The particle size distribution (PSD) curve of the synthesized Zinc oxide particles from different zinc precursors is given in figure 3. The PSD plot for sample ZA-ZnO shows that all the particles are within the size range of 150-350 nm with a peak around 223.7 nm. For sample ZC-ZnO particles are within the size range of 150-300 nm with a peak around 206 nm and for ZN-ZnO particles are within the size range of 150-300 nm with a peak around 206 nm (Table 2). From the plots, it is clear that size range of zinc oxide particles using different precursors are on an average lies between 100- 300 nm and zinc oxide formed from zinc nitrate shows much smaller size range and average particle size. It should be noted that the powder samples were heat treated at 500^0C before size analysis. The high temperature treatment for oxide formation results in agglomeration of finer particles as well as increase in grain growth. The DLS methods of particle size analysis consider the agglomerates as a single particle. Thus this method doesn't reveal the actual particle size which is always less than the measured value.

Table 2: Particle size analysis of ZnO nanoparticles

	ZA-ZnO	ZC-ZnO	ZN-ZnO
Particle Size Range	150-350 nm	150-300 nm	120-190 nm
Particle Size (d.nm)	223.7 nm	206 nm	145.8 nm



(A)



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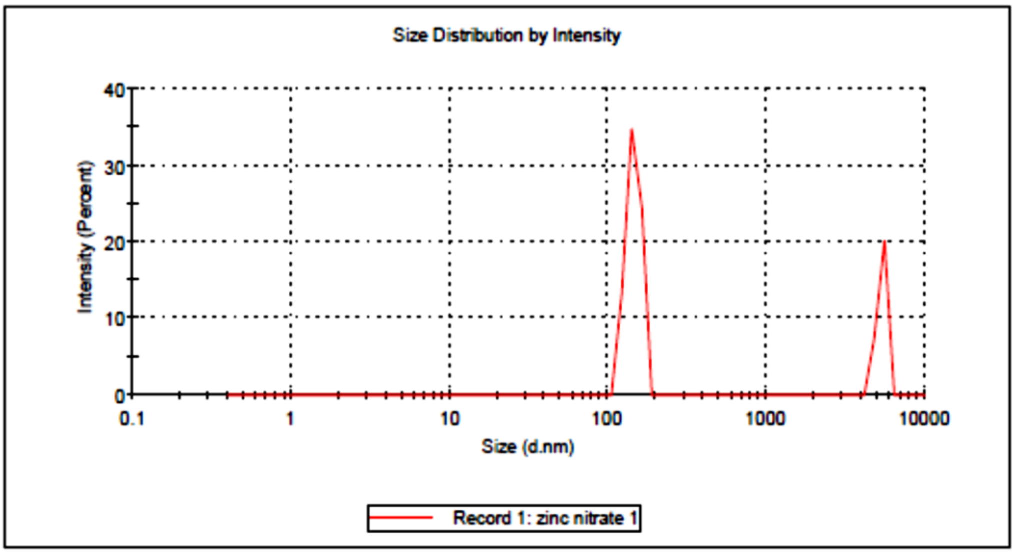

(C)

Figure 3: Particle size analysis of ZnO particles formed from (A) Zinc Acetate (B) Zinc Carbonate and (C) Zinc Nitrate

3.2. FTIR analysis

The IR studies of the ZnO formed using hibiscus leaf extract and three different Zn precursors namely zinc acetate, zinc carbonate and zinc nitrate was done. The presence of functional groups in all the three samples is nearly same, with the change in transmittance percentage from one another. The FTIR spectrum of Zinc acetate is shown as reference in figure 4 below.

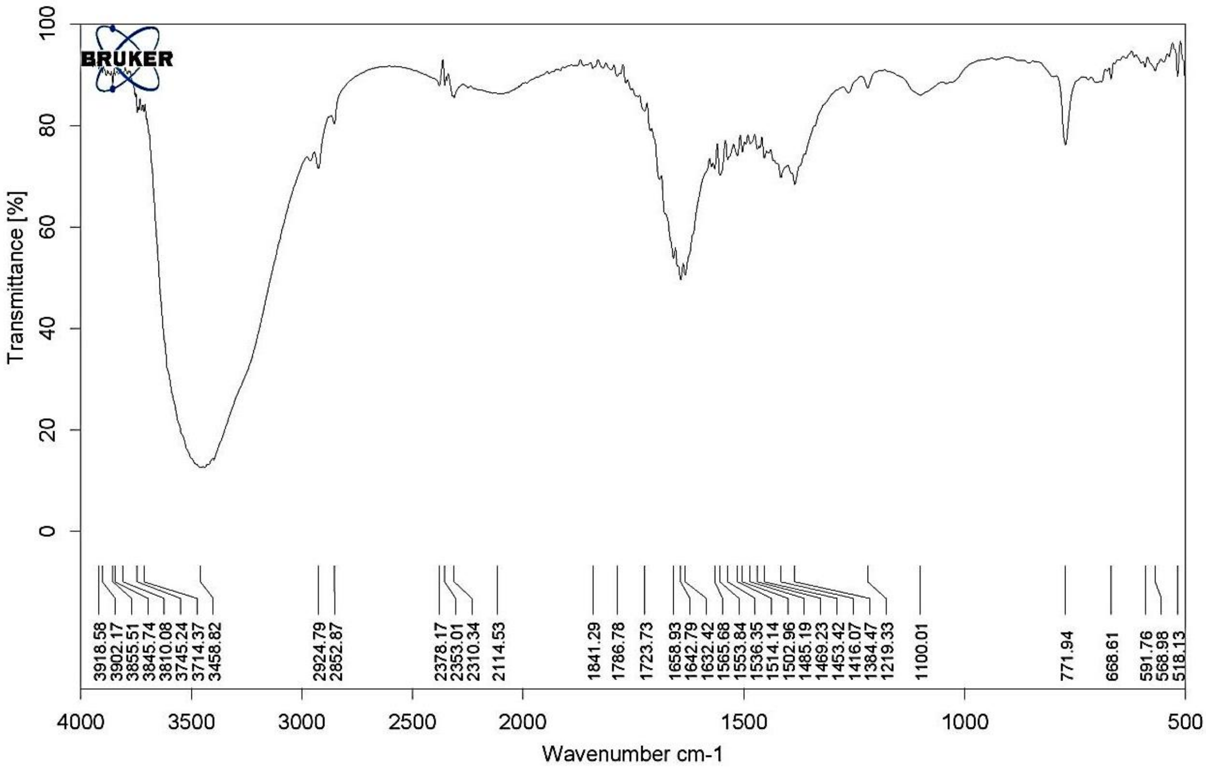

Figure 4: FTIR image of ZnO from Zinc acetate

The broad peak at 3458 cm^{-1} denoted the presence of -OH stretching vibrations. The strong absorption bands at 2924 and 2852 cm^{-1} can be ascribed to the stretching mode of C-H bonds of hibiscus leaf extract. The absorption observed at 2378, 2353 and 2310 cm^{-1} reveal the presence of C-H stretching vibration of an aromatic aldehyde. The peak at 2114 corresponds to stretching vibrations of C-C triple bond stretch of alkynes (Spectroscopy Tutorial, 2016). The peak at 1723 is due to C=O stretching vibrations in amides. The strong band at 1658, 1642, and 1632 is attributed to the C=C stretch in aromatic ring and C=O stretch in polyphenols. The band observed at 1502-1565 cm^{-1} corresponds to the carbonyl group of flavonoids. The peak at 1453 refers to the amine –NH vibration stretch in protein amide linkages. Moderate levels of absorption in the region covering 1469 -1384 cm^{-1} imply the presence of an aromatic ring. The peak at 1384 results from aromatic amine. The peak at 1100 is due to Monosubstituted Aromatic Ring. FTIR spectrum also shows the characteristic vibration band at 591, 568 and 518 cm^{-1}, which was correspond to E2 mode of hexagonal ZnO wurtzite structure. The FTIR spectrum of zinc oxide nanoparticles absorbs at 441–665 cm^{-1}.

3.3. UV-Visible spectrum analysis

The powder was suspended in deionized water to note the UV- Visible spectra. The UV-Visible spectra of the formed ZnO nanoparticles from three different precursors by green synthesis method are shown in figure 5 below. All the curves are similar in nature except their peak intensities and showing a peak at 370 nm which confirms the formation of zinc oxide particles as also reported in previous literatures.

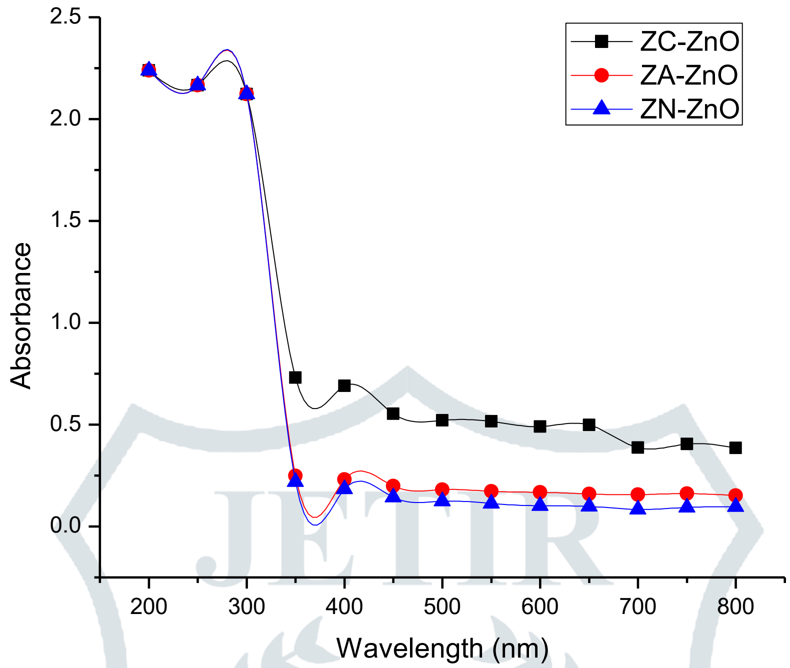

Figure 5: UV-Visible spectra of formed ZnO nano particles

3.4. Effect of foliar spraying on Plant growth

The zinc oxide nanoparticles formed from different precursors by green synthesis method were applied in form of foliar spraying to the wheat plants after one week of their germination. The spraying was done weekly for three weeks and the measurement of the plant growth is given in table 3 below. The study clearly shows that zinc oxide application in form of foliar spraying has significantly affected the plant growth. The plants sprayed with zinc oxide particles showed better average growth in comparison to the plants without foliar spraying. The images of the plants during the measurement taken, starting from week one to week four, is given in figures 6-9.

Table 3: Weekly growth analysis of *Triticum aestivum* (Wheat) Plant

Wheat Plant Height Measurement				
	Default	**ZA-ZnO**	**ZC-ZnO**	**ZN-ZnO**
1 week	38.66	39	38.66	36.66
2 week	40.66	42.33	43.66	42.5
3 week	46.66	49.33	51.75	51.33
4 week	55.33	63.33	66.66	66.33

Figure 6: Image of Wheat plant height measurement after 1st Week

[A]

[B]

[C]

[D]

Figure 7: Images of Wheat plant height measurement after 2nd Week.
(A) ZA-ZnO, (B) ZC-ZnO, (C) ZN-ZnO, and (D) Default

[A]

[B]

[C]

[D]

Figure 8: Images of Wheat plant height measurement after 3rd Week.
(A) ZA-ZnO, (B) ZC-ZnO, (C) ZN-ZnO, and (D) Default

[A]

[B]

[C]

[D]

Figure 9: Images of Wheat plant height measurement after 4th Week.
(A) ZA-ZnO, (B) ZC-ZnO, (C) ZN-ZnO, and (D) Default

4. Conclusion

Zinc Oxide crystallites have been synthesized by simple and eco-friendly method using leaf extract of hibiscus rosa-sinensis and three different zinc precursors. Characterization of particles formed shows the formation in the size range of around 100- 350 nm. The green synthesis of ZnO NPs is much safer and environment friendly compared to chemical synthesis because it does not lead to formation of toxic byproduct chemicals. The colloidal solution of ZnO NPs are used as Nano fertilizer and applied in form of foliar spraying to the species of *Triticum aestivum* i.e. common Indian wheat. Application of the nanoparticles resulted in significant increase in the growth of wheat plant. Though all the plant samples sprayed with ZnO nanoparticles showed increased growth, the one sprayed with nanoparticles formed from zinc carbonate resulted in highest growth

5. Acknowledgement

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6. References

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