SIZE DEPENDENT EFFECTS OF NANOSCALE ZINC OXIDE ON PRODUCTIVITY OF GROUNDNUT IN ALFISOLS

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BY

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DECLARATION

I, **Ms. B. JAYASREE,** hereby declare that the thesis entitled **"SIZE DEPENDENT EFFECTS OF NANOSCALE ZINC OXIDE ON PRODUCTIVITY OF GROUNDNUT IN ALFISOLS"** submitted to the **Acharya N.G. Ranga Agricultural University** for the degree of **MASTER OF SCIENCE** is a result of original research work done by me. I also declare that no material contained in the thesis has been published earlier in any manner.

Date :

Place : Tirupati

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I.D. No.: TAM/2017-043

CERTIFICATE

Ms. B. JAYASREE has satisfactorily prosecuted the course of research and that thesis entitled **“SIZE DEPENDENT EFFECTS OF NANOSCALE ZINC OXIDE ON PRODUCTIVITY OF GROUNDNUT IN ALFISOLS”** submitted is the result of original research work and is of sufficiently high standard to warrant its presentation to the examination. I also certify that neither the thesis nor its part thereof has been previously submitted by her for a degree of any University.

Date:

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CERTIFICATE

This is to certify that the thesis entitled **“SIZE DEPENDENT EFFECTS OF NANOSCALE ZINC OXIDE ON PRODUCTIVITY OF GROUNDNUT IN ALFISOLS”** submitted in partial fulfillment of the requirements for the degree of **‘Master of Science in Agriculture’** of the Acharya N. G. Ranga Agricultural University, Guntur, is a record of the bonafide research work carried out by **Ms. B. JAYASREE** under our guidance and supervision.

No part of the thesis has been submitted by the student for any other degree or diploma. The published part and all assistance received during the course of investigations have been duly acknowledged by the author of the thesis.

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B. Jayasree…✍

LIST OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF PLATES

LIST OF ABBREVIATIONS AND SYMBOLS

%	:	Per cent
@	:	At the rate of
°C	:	Degree Celsius
µ L	:	Microlitre
cm	:	centimetre
cm^2	:	Square centimetre
DAS	:	Days After Sowing
DLS	:	Dynamic Light Scattering
dSm^{-1}	:	Deci Siemen per metre
EC	:	Electrical Conductivity
et al.	:	and others
etc.	:	and so on
Fig.	:	Figure
FT-IR	:	Fourier Transform Infrared spectrophotometer
g	:	gram
$kg\ ha^{-1}$	:	Kilogram per hectare
$mg\ kg^{-1}$	:	Milligram per kilogram
$ml\ L^{-1}$	:	Millilitre per litre
mm	:	Millimeter
$mm\ day^{-1}$	:	Millimeter per day
nm	:	Nanometer
NS	:	Non-significant
n-ZnO	:	Zinc Oxide nanoparticles
pH	:	Potential of Hydrogen ion concentration
ppm	:	Parts per million
SEM	:	Scanning Electron Microscopy
SEm±	:	Standard error of mean

TEM : Transmission Electron Microscopy

viz., : Namely

XRD : X-ray Diffractometry

ABSTRACT

Name of the Author : **B. JAYASREE**
Title of the thesis : **SIZE DEPENDENT EFFECTS OF NANOSCALE ZINC OXIDE ON PRODUCTIVITY OF GROUNDNUT IN ALFISOLS**
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Nanotechnology deals with the matter at the nanoscale (1-100 nm) in at least one dimension. The development of nanomaterials could open up new applications in agriculture and allied sciences. Evaluation of the effects of nanoscale materials on agricultural crops is currently under exploitation. The present investigation was initiated considering the micronutrient deficiencies in the food crops especially the zinc. From the human health point of view, the enrichment of oilseeds with zinc is a desired outcome and in recent days there is an increasing interest in making the oilseeds with optimum zinc concentration. In the present study, groundnut was selected as a test crop. Nano ZnO particles were prepared using a modified oxalate decomposition method.

The prepared ZnO nanoparticles were characterized using the techniques *viz.*, UV-Vis spectrophotometer, Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and zeta potential analyzer. The mean size of the particles was found to be 20, 25, 30 nm with concentrations of 150, 200 and 400 ppm. The experiment was laid in twelve treatments and three replications to know the effect of nano zinc oxide particles on the growth and development, yield and yield attributes of groundnut along with the bulk $ZnSO_4$ and control. Morphological and physiological characters, yield attributes have shown significant effect by the application of nanoscale zinc oxide particles of different sizes and concentrations. The maximum pod yield was recorded in the treatment n- ZnO particles of size 25 nm @ 150 ppm which is 25 % more than control, 15.5 % more

than bulk $ZnSO_4$ @ 2000 ppm and on a par with treatment n- ZnO particles of size 20 nm @ 150 ppm. Highest accumulation of Zn in leaves was observed in treatment n- ZnO of size 20 nm @ 150 ppm which is 53.4 % more than control and 50 % more than bulk $ZnSO_4$ @ 2000 ppm. However, the accumulation of Zn in kernels was more with the application of n-ZnO particles of size 30 nm @ 200 ppm which is 21.6 % more than control and 11.8 % more than bulk $ZnSO_4$ @ 2000 ppm. These results indicate that the nano ZnO particles have significant effect on the growth, development and yield enhancement of agricultural crops, especially in groundnut.

CHAPTER I

INTRODUCTION

Chapter I

INTRODUCTION

Micronutrient malnutrition is a growing concern in the developing world, resulting in diverse health and social problems, such as mental retardations, impairments of the immune system and overall poor health. In recent years, the zinc (Zn) deficiency problem has drawn increasing attention and appears to be the most serious micronutrient deficiency together with vitamin A deficiency. On the other hand, zinc deficiency is particularly widespread among children and represents a major cause of child death in the world. Zinc deficiency is the most extensive micronutrient problem in Indian soils as almost 40.0% of the soils are deficient in Zn availability (Shukla *et al.* 2016). Because the concentration of Zn in crops is inherently very low, growing crops on potentially Zn-deficient soils further decreases grain Zn concentrations. Zinc has been considered as an essential micronutrient for metabolic activities in plants. It regulates the various enzyme activities and required in biochemical reactions leading to formations of chlorophyll and carbohydrates. The crop yield and quality of production can be affected by the deficiency of Zn. Micronutrient fertilizers can increase the tolerance of plants to environmental stresses like drought and salinity.

Groundnut (*Arachis hypogaea* L.) is an important oilseed and supplementary food crop of the world. It is the fourth most important source of edible oil and the third most important source of vegetable protein. Globally, groundnut is raised on 26.4 million hectares with a total production of 37.1 million MT. The average productivity is 1400 kg ha $^{-1}$ (IOPEPC *Kharif*-2017 Survey of Groundnut Crop). Globally, with annual all-season coverage of about 70 lakh hectares, India ranks first in acreage and with an output of about 85 lakh MT of in shell groundnuts, second in production. Micronutrients, particularly Zn plays an important role in the growth and productivity of groundnut. In a field experiment, the yield losses due to Zn deficiency were found to be 13.3 per cent to 20 per cent (Singh *et al.*, 2004). The soil application of zinc sulfate showed a positive response with good germination, yield attributes, pod number, pod yield and oil content (Singh *et al.*, 2004). Seed dressing with zinc oxide increased the pod yield (Gopala Gowda *et al.*, 1994).

The major factor that is shaping or changing modern agriculture is the improvement in agricultural technology. Among the innovative technologies currently, nanotechnology occupies a prominent role in transforming agriculture and food production. Nanotechnologies have been already revolutionized the healthcare, textile industry, information and communication technology and energy sectors but its applications are still at infancy stage in agriculture. Nanotechnology includes designing and synthesis of materials whose size is less than 100 nm in at least one dimension. The EU (European Commission, 2011) defines nanomaterial as a natural, incidental or manufactured material containing particles in an unbound state or as agglomerate and where 50% or more of the particles in the number size distribution, one or more external dimension is in the size range 1–100 nm.

Nanotechnology plays a vital role in improving soil health, nutrient management, weed management, pest and disease control, through the new scientific approaches to increase production and productivity of crops. It helps to introduce new techniques through enabling slow and controlled release of nutrients from fertilizers, efficient and targeted delivery of fertilizers coupled with enabling resistance, effective processing, storage and packing.

Nanoparticles have smaller particle sizes, higher specific surface area and an increased proportion of reactive surface atoms as compared to bulk particles (Wigginton *et al.*, 2007). Zinc nano-particle is used in various agricultural experiments to understand its effect on growth, germination, and various other properties. Most of the farmers are using either zinc sulfate or EDTA-Zn chelate for soil and foliar applications, however, the efficacy, the retention time of Zn in the plant system is low and hence, the bioavailability of Zn for a long period is not sure with the use of $ZnSO_4$ fertilizer. Under high temperature conditions, $ZnSO_4$ has a large salt index and it may show burning injury if the plants are succulant or sensitive (Kisan *et al*, 2015).

The new area of research on application of nanoscale materials in agriculture as nutrients is catching up in agricultural universities and ICAR institutes that will help to understand further processes of nanoscale fertilizer/nutrient transformations and availability in soil-cropping systems as well as their mechanisms of uptake, translocation and utilization in plants.

Only limited studies have been reported on the promotory effects of nanoparticles on plants at low concentrations. In the recent past, the positive effects of nanoscale nutrients on germination, growth, nutrient absorption, nutrient use efficiency and yield have been studied in various crops under controlled and field conditions. **However, studies on the size dependent effects of nanoscale materials on agricultural crops in either of the methods are scant.** Keeping in view of the importance of the size dependent properties of the particles, an experiment entitled "**Size dependent effects of nanoscale zinc oxide on productivity of groundnut in Alfisols**" is planned with the following objectives.

1. To synthesize different sizes (20, 25 and 30 nm) of nanoscale zinc oxide particles using sol-gel method.

2. To characterize nanoscale zinc oxide particles using the techniques such as UV-VIS spectroscopy, Dynamic Light Scattering (DLS), High Resolution Transmission Electron Microscopy (HRTEM) / Scanning Electron Microscopy (SEM) and X-ray Diffractometry (XRD).

3. To quantify the effects of size-dependent nanoparticulate delivery of zinc on the productivity of groundnut at a field level.

CHAPTER II

REVIEW OF LITERATURE

Chapter II

REVIEW OF LITERATURE

Nanotechnology is a multidisciplinary and rapidly growing science and technology which involves the manufacture, processing, and application of nanoscale materials. Nanomaterials are generally defined as materials with at least one dimension less than 100 nm (Powers *et al.* 2006). Due to their small size and greater surface activity, they possess unique physical and chemical characteristics which deviate vastly from those of individual atoms or molecules and also the same material at bulk scale. Therefore, their reactivity enables them to have novel applications in different sectors (Banfield and Zhang, 2001).

There are only a few studies about the fate of nanomaterials in the environment. The limited available reports suggest that ZnO nanoparticles are found to be of great importance in enhancing plant growth and yield. In a lower dose of foliar application, the effects are significantly productive. Therefore, nanoscale ZnO with small size and large surface area are expected to be the ideal material to use as a Zn fertilizer in plants. The available literature on the effect of nanoscale nutrients on the physiological and biochemical parameters is limited. Hence the effects of bulk nutrients on the plant growth and development were also reviewed apart from the nanoscale material's effect in order to have a comprehensive understanding. In this chapter, the literature pertaining to the objectives are reviewed under the following subheadings.

2.1 SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLES

There are a wide variety of methods that are used to synthesize nanoscale zinc oxide particles (n-ZnO). But the fundamental approaches in nanoparticle fabrication can be categorized into two groups:

2.1.1 Top-down approach
2.1.2 Bottom-up approach

2.1.1 Top Down Approach

In top-down method macroscopic particles are reduced to nano-size scale by different physical methods like high energy ball milling, mechano-chemical processing, etching, electro explosion, sonication, sputtering or laser-ablation (Luther, 2004). However, these methods usually are not suitable for generating uniformly shaped nanoparticles (Schmid, 2001).

Shen *et al.* (2006) reported the controlled mechano-chemical synthesis of ZnO nanoparticles in the presence of oxalic acid and zinc acetate. The initial reactant mixture of zinc acetate and oxalic acid was milled from 30 min to 4 hours and thermally treated at 450 °C for 30 minutes. Uniform ZnO nanoparticles with a size range of 20 - 40 nm can be easily achieved.

Zhi *et al*. (2006) reported one step rapid synthesis of ZnO nanoparticles using zinc acetate, CTAB and NaOH at room temperature. In a typical synthesis, zinc acetate dihydrate, CTAB and sodium hydroxide were mixed (molar ratio 1:0.4:3) and ground together in an agate mortar for 50 min at room temperature. ZnO nano-rods with diameters of 10–30 nm can be synthesized conveniently with this method.

2.1.2 Bottom Up Approach

In bottom-up approach, nanoparticles are prepared by a build-up of material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. This method is more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape, and distribution.

A study by Ni *et al.* (2005) resulted that ZnO nanorods with the mean size of 50 nm to 250 nm were successfully synthesized *via* a hydrothermal synthesis route in the presence of Cetyl Trimethyl Ammonium Bromide (CTAB) at a reaction temperature of 120 °C for 5 hours in the presence of $ZnCl_2$ and KOH.

In another study, Liu *et al*. (2007) followed sol-gel route using zinc acetate and NaOH for the synthesis of ZnO NPs with an average diameter of about 20 nm. In a similar manner, Tang *et al*. (2008) also reported the uniform synthesis of ZnO NPs using urea, zinc nitrate and sodium dodecyl sulfonate (anionic surfactant) to block the growth of ZnO with size range of 20-25 nm.

Yong *et al*. (2008) reported the synthesis of ZnO nanoparticles by a hydrothermal method where ZnO nanoparticles with an average particle size of 20-30 nm were readily synthesized by the reaction between zinc acetate and oxalic acid under hydrothermal conditions. In another strategy, Sridevi and Rajendran (2009) synthesized nano ZnO particles by using low-temperature CTAB assisted hydrothermal method for the synthesis of ZnO NPs (range: 25 nm) where the size is controlled by CTAB molecule.

Pandey *et al*. (2010) synthesized the nano zinc particles by hydrothermal method by using zinc acetate dihydrate $Zn(CH_3COO)_2$ $2H_2O$ (98%) and sodium hydroxide (NaOH). Zak *et al*. (2011) reported the synthesis of ZnO nanoparticles by sol-gel route; wherein the precursor molecules were Zinc acetate and Tri-ethanol amine (TEA). Here, TEA molecule was used to control the growth of ZnO. The average size obtained was in the range of 33 nm.

Prasad *et al.* (2012) reported the synthesis of nano ZnO particles by using the oxalate decomposition technique. Zinc oxalate was prepared by mixing equimolar (0.2 M) solutions of zinc acetate and oxalic acid. The resultant precipitate was collected and rinsed extensively with double deionized water (DI-water) and dried in air. The oxalate was then ground and decomposed in air by placing it in a pre-heated furnace for 45 minutes at $50^{0\circ}$C.

Saleem *et al.* (2012) prepared nano-crystalline ZnO thin films by multi-step sol-gel method using spin coating technique in which zinc acetate dihydrate, 2-methoxyethanol and mono ethanolamine were used as a starting material, solvent and stabilizer, respectively.

Moezzi *et al.* (2012) prepared nano ZnO by pyrometallurgical methods (e.g. the indirect process, the direct process, or spray pyrolysis) by hydrometallurgical methods. Zinc oxide can also be produced as a by-product of some chemical reactions such as in the production of sodium dithionite.

Raut *et al.* (2013) reported the biosynthesis of nano ZnO particles by using leaves of *Ocimum Tenuiflorum* plant as reducing agent with zinc nitrate. Tarafdar *et al*. (2014) reported the biosynthesis of zinc nano fertilizers by using the fungi, *R. bataticola* TFR-6 (NCBI GenBank Accession number JQ675307) was grown-up in 250-mL Erlenmeyer flask containing 100-mL PD broth medium. The extracellular synthesis of zinc nanoparticles was carried out by exposure of a precursor salt aqueous zinc oxide solution of 0.1 mM concentration to fungal cell-free filtrate obtained by incubating the fungus *R. bataticola* TFR-6 in an aqueous solution. The reaction was carried out for 62 h.

Shyla *et al*. (2014) synthesized Zinc oxide (ZnO), Silver (Ag) and Titanium dioxide (TiO_2) nanoparticles using template-free aqueous solution based on a simple chemical method. ZnO NPs were synthesized by preparing 0.45 M aqueous solution of zinc nitrate ($Zn(NO_3)_2 .4H_2 O$) and 0.9 M aqueous solution of sodium hydroxide (NaOH). The Ag NPs were prepared based on the chemical reduction method by using $AgNO_3$. TiO_2 NPs were synthesized by using TiO_2 pellets and NaOH solution.

Jayarambabu and Sivakumari (2015) biologically synthesized nano ZnO particles of 20 nm size by using Curcurm longa tubers, 0.5 M of zinc acetate, acetone, ethanol, and distilled water.

Javed *et al*. (2016) synthesized nano ZnO particles by using the coprecipitation method (Kumar *et al*., 2013). It involved the addition of 1 M NaOH solution to 0.06 M zinc acetate dihydrate [Zn $(CH_3COO)_2$ $2H_2O$; 99.5%] solution in a drop wise manner under continuous stirring at room temperature. A milky white solution was obtained at pH 12, and subsequently filtered, washed and then heated for 2 days at 100^0C. Furthermore, the powdered material was subjected to calcination at 350^0C for 4 h. In a study, Hasnidawani *et al.* (2016) synthesized ZnO NPs *via* sol-gel method using zinc acetate dehydrate $(Zn(CH_3COO)_2.2H_2O)$ as a precursor and ethanol as a solvent, while, NaOH and distilled water were used as a medium.

Anandaraj *et al.* (2017) synthesized Zinc oxide (ZnO), Silver (Ag), Copper oxide (CuO) and Titanium oxide (TiO2) nanoparticles by using a simple chemical route. Nano ZnO particles prepared by using 0.45 M aqueous solution of zinc nitrate $(Zn(NO_3)_2.4H_2O)$ and 0.9 M aqueous solution of sodium hydroxide (NaOH). The Ag NPs were prepared by using a chemical reduction method. CuO NPs were synthesised using copper nitrate trihydrate $(CuN_2O_6.3H_2O)$, and sodium hydroxide anhydrous pellets (NaOH) in the presence of polyvinyl alcohol (PVA) as starting precursor. TiO_2 NPs were synthesized by dissolving 0.5 g TiO_2 pellets in 30 ml of NaOH solution.

Recently, Ramapuram *et al.* (2018) synthesized nano ZnO particles by using modified oxalate decomposition technique or modified sol-gel method (Prasad *et al*.2012). Zinc oxalate was prepared by mixing equimolar (0.2 M) solutions each of zinc acetate and oxalic acid. In another study Upadhyaya *et al.* (2018) used mehendi extract (*Lawsonia inermis*) for phytosynthesis of ZnO nanoparticles using 0.1 M $Zn(NO_3)_2$ as precursor under alkaline condition using NaOH with vigorous stirring for 2 h.

2.1.3 Characterization of Nano ZnO Particles

Aneesh *et al.* (2007) studied the characterization of ZnO nanoparticles by using x-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies. The average particle size have been found to be about 7-24 nm and the compositional analysis is done with inductively coupled plasma atomic emission spectroscopy (ICP-AES). Diffuse reflectance spectroscopy (DRS) results shows that the band gap of ZnO nanoparticles is blue shifted with a decrease in particle size.

Yong *et al*. (2008) performed the X-ray powder diffraction (XRD) of nano ZnO particles on a Rigaku (Japan) D/max- X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm) at a scanning rate of $0.02^{\circ}\ s^{-1}$ in the 2θ range from 10° to 70°. Transmission electron microscopy (TEM) micrographs were taken on a JEM- 200CX, JEOL Transmission Electron Microscope, employing an accelerating voltage of 200 kV. UV–vis spectra were recorded on a Hitachi U-3010 spectrophotometer (Tokyo, Japan). The fluorescence spectra were measured with an F-4500 spectrofluorometer (Hitachi) with a quartz cell of 1cm.

Sridevi and Rajendran (2009) characterized the samples by powder X-ray diffractometer XPERT PRO with Cukα X-ray radiation (λ=0.15496nm). The composition of elements like ZnO are confirmed by Energy Dispersive X-ray spectra (EDX). The surface morphology of the samples is observed by Scanning Electron Microscopy (SEM, JEOL, JSM-67001). The room temperature photoluminescence (PL) spectra of ZnO nanostructures are recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at excitation wavelength (λex=325nm)

Pandey *et al.* (2010) characterized the hydrothermally prepared nano zinc particles by using X-ray diffraction and field emission scanning electron microscopy (FE-SEM) for the study of crystal structure and morphology/size.

FE-SEM image revealed that ZnO NPs are spherical in shape with a diameter of 20–30 nm.

Prasad *et al*. (2012) reported the characterization of the samples by transmission electron microscopy (HRTEM, JEOL 3010; Jeol Ltd, Peabody, MA, USA), scanning electron microscopy (SEM, FEI Quanta 200; FEI, Malvern, UK) and energy dispersive analysis of X-rays (EDAX, FEI Quanta 200; FEI). The TEM samples were prepared by drop casting the suspensions on carbon coated Cu grids.

Saleem *et al*. (2012) reported the XRD results as-deposited films exhibited a hexagonal wurtzite structure with (002) preferential orientation after annealing at 400˚C in air ambiance for 1 hour. The XRD pattern consists of a single (002) peak which occurred due to ZnO crystals and grows along the c-axis. The grain size and thickness of the films are estimated to be 16 nm and 266 nm. SEM micrograph of ZnO thin film showed that the small grains made a smooth and transparent surface.

Raut *et al.* (2013) characterized nano ZnO particles that are prepared by green synthesis by using XRD, SEM, FTIR, The size and structure of nanoparticles is confirmed with the XRD technique. The synthesized ZnO average particle size is calculated as 13.86 nm by using Scherrer's Formula. The SEM image showed hexagonal shape nanoparticle formed with diameter range of 11-25 nm.

Tarafdar *et al.* (2014) determined the Particle size of biotransformed zinc nanoparticles by DLS using particle size analyzer. Histogram of number distribution shows the average particle size of 18.5 nm. The polydispersity index was 0.219 which indicates high monodispersity of the particle. The TEM measurements were used to determine the size, shape, and morphological study of zinc nanoparticles. The micrograph showed the well distribution of zinc nanoparticles, which was encapsulated by a thin layer of protein at the measurement scale bar of 50 nm with 100 kV applied voltage.it has shown that nanoparticles were spherical with a clear edge of crystal and lattice structure which proved the crystalline nature of zinc nanoparticles. Elemental analysis confirms the purity of zinc metal, which was carried out by EDS (Electron Dispersive X-ray Spectroscopy) attached with TEM.

Jayarambabu and Sivakumari (2015) characterized nano ZnO particles that are prepared by green synthesis by using XRD, PSA, FTIR, SEM and TG-DTA. Javed *et al*. (2016) characterized prepared ZnO nanoparticles by using X-ray diffraction (XRD) analysis and it is performed on a PANalytical Empyrean diffractometer using Cu Kα radiation The Fourier-transform infra-red (FTIR) spectra were recorded at a resolution of 1 cm^{-1} and ranged 4000-500 cm^{-1}.

Hasnidawani *et al.* (2016) showed that EDX characterization of ZnO NPs has good purity (Zn: 55.38% and O_2: 44.62%). While, XRD result spectrum displayed mainly O_2 and Zn peaks, which indicate the crystallinity in nature as exhibited. The FESEM micrographs shows that synthesized ZnO have a rod-like structure. The obtained ZnO NPs are homogenous and consistent in size which corresponds to the XRD result that exhibits good crystallinity. Through this method, ZnO NPs were successfully synthesized in nano-size range within 81.28 nm to 84.98 nm.

Narendhran *et al.* (2016) characterized ZnO nanoparticles were confirmed with Ultra Violet-visible spectroscopy (UV-vis), Fourier transform infrared spectrometer (FTIR), Energy dispersive X-ray spectrometer (EDX), X-ray diffractometer (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and High-Resolution Transmission Electron Microscopy (HR-TEM).

Anandaraj *et al.* (2017) characterised nano Zinc oxide (ZnO), Silver (Ag), Copper oxide (CuO) and Titanium oxide (TiO_2) nanoparticles by using

ScanningElectron Microscope (SEM), Transmission Electron Microscope (TEM), Particle Size Analyzer and Raman Spectroscopy.

Ramapuram *et al*. (2018) reported the characterization of ZnO, CaO and MgO nanoscale particles by using electron microscopy (TEM & SEM), X-Ray Diffraction (XRD) and Dynamic Light Scattering (DLS). Average size (25 nm, 53.7 nm, 53.5 nm) and zeta potentials (-10.9mV, - 28.2mV, -16.2 mV) of n-ZnO, n-CaO and n-MgO were measured respectively. x-ray diffraction (XRD) analysis was performed on a diffractometer (Shimadzu, 108 xrd 700) using Cukα radiation for all analyses at 40 kv and 30 ma in order to identify the 109 phases of the powders. SEM is used to study the surface morphological characters of nanoscale nutrients and also to measure the size and shape of nano nutrients. Further they are subjected to HR-TEM for surface morphological studies.

Upadhyaya *et al.* (2018) characterized ZnO NP by using UV-Vis spectroscopy, SEM, TEM and XRD. The morphology was investigated using field emission scanning electron microscopy. Uv-Vis spectroscopy of the sample was done using Biospectrometer (Eppendorf) in which 10 mg of ZnO NP was resuspended in 15 ml distilled water and sonicated for 10 min after which the sample was scanned from wavelength 300 - 700nm. X-Ray diffraction of the sample powder was carried out in a PANalytical X-PERT PRO applying a monochromator.

Recently, the effects of nano-ZnO and nano-SiO_2 on the properties of PVA/xylan composite films were investigated and the obtained results revealed that nano-ZnO and nano-SiO_2 could effectively improve the mechanical strength, moisture, and oxygen barrier properties and the surface hydrophobic property of the composite films. Moreover, the results of FTIR and XRD indicated the interaction of hydrogen bonds between nanoparticles and PVA and xylan (Liu *et al.* 2019).

2.2 EFFECT OF NANOPARTICLES ON CROP GROWTH AND YIELD

2.2.1 Plant Height

Prasad *et al*. (2012) conducted an experiment on the effect of nanoscale zinc oxide particles on growth parameters of groundnut. They concluded that highest plant height (43.80 cm) recorded with NPK+ZnO (nano) @ 2g 15 L^{-1} when compared to bulk $ZnSO_4$ and control i.e 37.10 cm and 36.50 cm respectively.

Singh *et al*. (2013) conducted an experiment on zinc oxide nanoparticles as a fertilizer for germination, growth and metabolism of vegetable crops and they revealed that bulk zinc oxide and a lower concentration of zinc oxide NPs did not affect seedling height in *Brassica oleracea* var. Capitata. But, the seedling height increased for treatments with higher concentrations of ZnO NPs.

Laware *et al.* (2014) conducted an experiment on influence of zinc oxide nanoparticles on growth and seed productivity in onion and they concluded that maximum plant height was increased by 3.93 % (32.24 cm) in 20 µg ml^{-1} concentrations of -ZnO NPs over control and it was decreased by 0.45 % (30.88 cm) in 40 µg ml^{-1} concentration of ZnO NPs as against 31.02 cm in control.

Shyla *et al*. (2014) characterized Zinc oxide (ZnO), Silver (Ag) and Titanium dioxide (TiO_2) nanoparticles by the techniques such as SEM, TEM and X-ray diffraction.

Benzon *et al.* (2015) reported the effect of nano fertilizer effects on growth, development chemical properties of rice and they concluded that use of a full dose of the recommended rate of conventional and nanofertilizer enhanced the plant height by 3.6 % over other treatments.

Subbaiah *et al.* (2016) did experiment on novel effects of nanoscale ZnO on growth of maize. The plant height at 30 DAS did not differ significantly because the treatments were not applied at this stage. However, there was a significant difference in the plant height of maize plants at 60 DAS. Among the treatments, application of 400 ppm of ZnO-nanoparticulates had shown a significant increase in plant height (167.50 cm) (25% increment over control and 11% increment over bulk $ZnSO_4$ of 2000 ppm, and at 90 DAS a similar trend was observed with the same concentration 400 ppm of ZnO-nanoparticulates (187.56 cm), 19% increment over control and 8% increment over bulk $ZnSO_4$ of 2000 ppm.

Harish and Gowda (2017) conducted an experiment in groundnut on the effect of nanoscale ZnO particles and they concluded that the application of nano ZnO particles @ (1000ppm) recorded higher plant height (37.33 cm) when compared to $ZnSO_4$ @ 2000ppm + RDF (33.28cm).

Rameshraddy *et al*. (2017) conducted an experiment on seed priming and nano zinc effect on seed yield of ragi and the treatments with ZnO nano-treated plants with the combination of seed priming and foliar application resulted in higher plant height.

Saraswathi *et al*. (2017) conducted an experiment on the effect of nano ZnO on growth and the yield of finger millet (*Eleusine coracana* (L.) Garten.) and they concluded that at harvest stage the highest plant height (120.5 cm)was recorded in the treatment with the foliar application of nano ZnO @ 500 ppm and the control treatment was recorded 85 cm.

A study by Singh *et al*. (2017) reported the bio-efficacy of nano zinc sulphide (ZnS) on growth and yield of sunflower (*Helianthus annuus* L.) and nutrient status in the soil revealed that among the different concentrations of nano zinc sulphide, 400 ppm sprayed at 35 DAS recorded highest plant height (67.85

cm, 120.9 cm, 124.73 cm) at 40, 70 and harvest respectively which were on par with 500 ppm nano zinc sulphide sprayed at 55 DAS and 500 ppm nano zinc sulphide sprayed at 35 DAS.

El-Metwally *et al.* (2018) reported the response of peanut plants to different foliar applications of nano-iron, manganese and zinc under sandy soil conditions and they concluded that application of nanofertilizers have a significant effect on plant height at a concentration of 30 ppm (38.29 cm) when compared to all concentrations 10, 20,30 and 40 ppm.

2.2.2 Leaf Area Index

Jhanzab *et al.* (2015) reported the effect of Silver nano-particles enhanced the growth, yield and nutrient use efficiency of wheat and they concluded that among different treatments of SNPs greatly affected the leaf area and maximum leaf area (19.7 cm^2) was with 25 ppm of SNPs followed by 50 ppm (18.18 cm^2) SNPs, while in control it was (15.0 cm^2). Further increase in the concentration of SNPs reduced the leaf area.

Subbaiah *et al.* (2016) conducted an experiment on growth parameters of maize and concluded that there was a significant difference in the leaf area at 60 DAS, and the maximum leaf area (4533.42 cm^2) was recorded with the application of 400 ppm ZnO-nanoparticulates (64% increment over control and 31% increment over bulk $ZnSO_4$ @ 2000 ppm). The other treatments in which notable leaf area was recorded were 100 ppm of ZnO-nanoparticulates (4246.25 cm^2) and 200 ppm of ZnO-nanoparticulates (4110.22 cm^2).At 90 DAS, application of 400 ppm of ZnO-nanoparticulates had shown the maximum leaf area (5715.10 cm^2), significantly superior to control (52%) and bulk $ZnSO_4$ of 2000 ppm (19%), respectively.

Singh *et al*. (2017) reported the bio-efficacy of nano zinc sulphide (ZnS) on growth and yield of sunflower and they concluded that, 400 ppm nano zinc sulphide sprayed 35 DAS recorded significantly higher leaf area (356.00, 698.83, 537.67 cm^2 $plant^{-1}$), leaf area index (0.197, 0.365, 0.289) at 40, 70 DAS and harvest respectively which were on par with 500 ppm nano zinc sulphide sprayed at 35 and 55 DAS.

Jyothi *et al.* (2017) reported a review on the effect of nanofertilizers on growth and yield of selected cereals and they concluded that the ZnO nanoparticles increased the leaf area index by 69.7% in mineral poor soils.

2.2.3 Dry Matter Production

Subbaiah *et al.* (2016) conducted an experiment on yield parameters of maize and concluded that there is a significant difference in dry weight recorded at 60 DAS was 105.56 g $plant^{-1}$ with the application of 400 ppm of ZnO-nanoparticulates and at 90 DAS 145.30 g $plant^{-1}$ dry weight was recorded with the application of 400 ppm of ZnO-nanoparticulates (34% increment over control and 16% increment over bulk $ZnSO_4$ of 2000 ppm).

Jyothi *et al.* (2017) reported a review on effect of nanofertilizers on growth and yield of selected cereals and concluded that TiO_2 nanoparticles has shown a significant effect on maize dry weight (2396.35 kg ha^{-1}).

Saraswathi *et al*. (2017) conducted an experiment on Effect of nano ZnO on growth and yield of finger millet and the highest dry matter weight (15.87 gm $plant^{-1}$) was recorded in the treatment receiving nano ZnO @ 500 ppm and lowest were in control (11.25 gm $plant^{-1}$).

2.2.4 Number of Nodules

Moll *et al*. (2016) reported the effects of titanium dioxide nanoparticles on red clover and its rhizobial symbiont. In this study, the nitrogen-fixing bacterium *Rhizobium trifolii* and red clover were exposed to two TiO_2 NPs, i.e., P25, E171 and a non-nanomaterial TiO_2. At a concentration of 23 and 18 mg l^{-1} of E171 and non-nanomaterial TiO_2 decreased the growth rate of *R. trifolii* by 43 and 23% respectively, P25 did not cause effects and they concluded that at higher concentrations certain TiO_2 NPs impaired *R. trifolii* as well as red clover growth and their symbiosis in the hydroponic systems.

Moghaddam *et al* (2017) reported the impact of ZnO and silver nanoparticles on legume- *sinorhizobium* symbiosis and they evaluated the effect of silver and ZnO NPs on *Sinorhizobium meliloti* and alfalfa symbiosis. The number of nodules were seemed to be unaffected at lower concentrations and by increasing the concentration of NPs (1.25 to 10 μg ml^{-1} of AgNPs and 12.5 to 100 mg ml^{-1} of ZnO NPs) nodules number decreased.

2.2.5 Number of Pods Plant^{-1} and Number of Filled Pods Plant^{-1}

Prasad *et al.* (2012) reported the effect of nanoscale zinc oxide particles on yield parameters of groundnut and concluded that the number of pods plant^{-1} (16.8) and number of filled pods plant^{-1} (15.0) were significantly highest when treated with NPK+ZnO (nano) @ 2g 15 L^{-1} compared to bulk $ZnSO_4$ and control.

Armin *et al.* (2014) reported the effect of time and concentration of nano Fe foliar application on yield and yield components of wheat and they concluded that the foliar applications of nano Fe at tillering and stem elongation stage has significant effect on the number of fertile tillers as 4.82 % increase was observed compared to control but the Fe concentration had no significant effect on tiller number. Nano-Fe fertilizer application at tillering + stem elongation did increase the number of seeds spike^{-1}, whereas early application of Fe fertilizer decreased the number of seeds spike^{-1}. But, when the Nano-Fe concentration was increased to 6 per cent there was an increase of seeds spike^{-1} (41.08 %) compared to the control.

Benzon *et al.* (2015) reported the nano fertilizer effects on growth, development chemical properties of rice and they concluded that use of a full dose of recommended rate of conventional and nanofertilizer improved the number of reproductive tillers, panicles and spikelets by 2.72%, 9.10% and 15.42% respectively.

Farnia *et al*. (2015) reported the effect of nano-zinc chelate and nano-biofertilizer on yield and yield components of maize (*Zea mays* L.) under water stress condition and they have concluded that interaction between water stress and nano biofertilizer showed that 7 day irrigation period treatment with the use of nano-biofertilizer had the highest number of rows per cob^{-1} (17) and grains cob^{-1} (520) while 21 day irrigation period treatment without use of nano-biofertilizer had the lowest (12) number of rows cob^{-1} and the number of grains cob^{-1} (280).

Subbaiah *et al.* (2016) conducted an experiment in maize and they concluded that the number of cobs plant^{-1} recorded was the same in all treatments but application of ZnO nanoparticulates of 400 ppm resulted in the production of more number of rows cob^{-1} (15), which was significantly higher than control (11%) and bulk $ZnSO_4$ of 2000 ppm (8%). More grains row^{-1} (38.5) were produced with the application of 400 ppm of ZnO nanoparticulates and was significantly different from control (36%) and bulk $ZnSO_4$ of 2000 ppm (27%). However, the application of ZnO-nanoparticulates of 100 and 200 ppm recorded notable grains row^{-1} of 34.9 and 33.2, respectively.

Janmohammadi *et al*. (2016) conducted an experiment on the impact of foliar application of nano micronutrient fertilizers (Fe & Zn) on yield components of barley and stated that foliar application of the Fe and Zn improved grain number up to 11 % and 13 %, respectively, compared to control.

Ewais *et al*. (2017) conducted an experiment on yield of *phaseolus vulgaris* (L.) plants in response to the application of biologically-synthesized zinc oxide nanoparticles and zinc sulfate. They concluded that the most significant increase in no of pods plant^{-1} and number of seeds were recorded with the plants treated with the interaction of ZnONPs 50 ppm + Zn 50 ppm in comparison to control. Weights of seeds are the same in ZnONPs 200 ppm and ZnONPs 50 ppm + Zn 50 ppm. Whereas 100-seed weight recorded to be the highest in case of application of ZnONPs @ 50 ppm.

Jyothi *et al*. (2017) reported a review on effect of nanofertilizers on growth and yield of selected cereals and concluded that the full recommended rate of conventional and nanofertilizer (FRR-CF+FRR-NF) enhanced the number of reproductive tillers, panicles, and spikelets in rice. The magnitudes of increase over the FRR-CF were 9.10 %, 9.10 %, and 15.42 %, respectively.

EI-Metwally *et al*. (2018) reported the response of peanut plants to different foliar applications of nano-iron, manganese and zinc under sandy soil conditions and they concluded that application of 10, 20, 30, 40 ppm nano fertilizers gave higher values of the number of pods plant^{-1} when compared to control (11).

2.2.6 Test weight (100 Pod Weight and 100 Kernel Weight)

Benzon *et al*. (2015) reported the effects of nano fertilizer effects on growth, development and chemical properties of rice and they concluded that use of a full dose of recommended rate of conventional and nanofertilizer improved the total grain weight (unpolished 17.5%, polished 20.7%). And the highest seed weight per umbel (2.34 g and 2.33 g) was recorded from the 20 and 30 µg ml^{-1}concentration of NPs respectively, while the lowest seed weight (1.94 g) was obtained from the control plants. Whereas the highest 1000-seed weight (3.52 g) was obtained in 30 µg ml^{-1}concentrations of NPs and in control plants as 3.18 g.

Prasad *et al*. (2012) conducted an experiment on the effect of nanoscale zinc oxide particles on yield parameters of groundnut during *rabi* 2009 and 2010 and they concluded that highest 100 pod weight (83.90 g, 117.80 g) and 100 kernal weight (36.25 g, 47.91 g) respectively in treatments with NPK+ZnO (nano) @ 2g 15 L^{-1} when compared to bulk $ZnSO_4$ and control.

Laware *et al.* (2014) conducted an experiment on the influence of zinc oxide nanoparticles on growth and seed productivity in onion. This study revealed that the 30 µg ml^{-1} concentration of ZnO NPs produced the highest number (228.68) of seeded fruits $umbel^{-1}$, whereas the least 220.14 was recorded from 40 µg ml^{-1} concentration of NPs.

Armin *et al*. (2014) reported the effect of time and concentration of nano Fe foliar application on yield and yield components of wheat and they concluded that foliar application of nano-Fe at tillering+stem elongation and tillering stages had increased 1000 grain weight followed by application at the stem elongation stage.

Farnia *et al*. (2015) reported the effect of nano-zinc chelate and nano-biofertilizer on yield and yield components of maize (*Zea mays* L.) under water stress condition and they have concluded that interaction between water stress and nano biofertilizer showed that 7 day irrigation period treatment with the use of nano-biofertilizer had the highest 100-grain weight (27 g) and 21 day irrigation period treatment without nano biofertilizer and nano-Zn had the lowest (16 g).

Bakhtiari *et al.* (2015) reported the effect of iron nanoparticles on spraying time and concentration in wheat and the results proved that spraying time and concentration significantly affected all measured traits. However, the effect of the interaction of the two factors was not significant. The comparison of the spraying times indicated that the highest values of spike weight (614.88 g), 1000 grain weight (36.10 g) were achieved in first spraying. Among the Fe concentrations, the highest values of spike weight (666.96 g), 1000 grain weight (37.96 g) were obtained with 0.04% Fe concentration.

Subbaiah *et al.* (2016) conducted an experiment in maize and the highest test weight 35.2 g was recorded with the application of ZnO-nanoparticulates of 400 ppm which was significantly higher than control and bulk $ZnSO_4$ of 2000 ppm (16 % over control and 11 % increment over bulk).

Janmohammadi *et al.* (2016) conducted an experiment on the impact of foliar application of nano micronutrient fertilizers (Fe & Zn) on yield components of barley. Thousand grain weight and grain weight plant^{-1} highest in the application of zinc nano-fertilizer increased the grain weight up to 6 % over control.

Rameshraddy *et al.* (2017) conducted an experiment on seed priming and nano zinc effect on seed yield of ragi and test weight (1000 seed weight) is 3.21g in case of ZnO nano particles which are comparable with seed priming + foliar spray (3.02 g) and control (3.09 g).

EI-Metwally *et al.* (2018) reported the response of peanut plants to different foliar applications of nano-iron, manganese, and zinc under sandy soil conditions and they concluded that application of 10, 20, 30, 40 ppm nano fertilizers gave higher values of pods weight plant^{-1} (28.97, 48.05, 51.53, 62.86) compared to control (22.43), 100 seed weight of peanut (55.99, 61.33, 66.78, 62.35 g respectively) than control (53.46 g).

2.2.7 Shelling Percentage

Prasad *et al.* (2012) conducted an experiment on the effect of nanoscale zinc oxide particles on yield parameters of groundnut during *rabi* seasons of 2009 and 2010 and higher shelling percentage (67.50, 69.30) recorded with NPK+ZnO (nano) @ 2g 15 L^{-1} compared to bulk $ZnSO_4$ and control.

Adhikari *et al*. (2014) conducted an experiment on utilization of nano rock phosphate by maize (*Zea mays* L.) crop in a *Vertisols* of central India and they concluded that shelling percentage (61.47 %) were obtained from Udaipur nano RP (34 % P_2O_5) treated plants after SSP treatment whereas the lowest was in control.

2.2.8 Pod Yield

Prasad *et al.* (2012) conducted an experiment on the effect of nanoscale zinc oxide particles on yield parameters of groundnut during *rabi* seasons of 2009 and 2010 and they concluded that highest pod yield 3121 kg ha^{-1}, 3763 kg ha^{-1} respectively obtained with the application of NPK+ZnO (nano) @ 2g 15 L^{-1} when compared to bulk $ZnSO_4$ and control.

Afshar *et al.* (2014) reported the comparison of the effects of spraying different amounts of nano zinc oxide and zinc oxide on wheat and they concluded that maximum yield rate of 95/401 grams $meter^{-2}$ of treated nano zinc oxide i.e 60 g ha^{-1} and the lowest yield rate of 28/267 grams $meter^{-2}$ was observed when compared to the control.

Armin *et al*. (2014) reported the effect of time and concentration of nano Fe foliar application on yield and yield components of wheat and they concluded that foliar application of nano-Fe at tillering+stem elongation and tillering had 9.17 % and 5.19 % more grain yield compared with foliar application of Nanc at stem elongation and the grain yield obtained by 2 %, 4 % and 6 % foliar application of nano-Fe resulted in an increase of 12 %, 22.09 % and 19.07 % of grain yield over the control but there is no significant difference observed in between the treatments.

Tarafdar *et al.* (2014) conducted an experiment on the effect of zinc nanofertilizer to enhance crop production in pearl millet (*Pennisetum americanum*) and they reported that grain yield at crop maturity was improved by 37.7 % due to the application of zinc nanofertilizer.

Farnia *et al*. (2015) reported the effect of nano-zinc chelate and nano-biofertilizer on yield and yield components of maize (*Zea mays* L.) Under Water Stress Condition and they have concluded that interaction between water stress and nano biofertilizer showed that 7 day irrigation period treatment with use of nano-biofertilizer had the highest grain yield (11.5 t ha^{-1}) and non-application of nano biofertilizer in 21 day irrigation period treatment had the lowest yield 3.2 t ha^{-1}.

Bakhtiari *et al.* (2015) reported the effect of iron nanoparticles spraying time and concentration on wheat and the results proved that spraying time and concentration significantly affected all measured traits. However, the effect of interaction of the two factors was not significant. The comparison of the spraying times indicated that the grain yield 3639.5 kg ha^{-1} obtained at first spraying. Among the Fe concentrations grain yield 3776.5 kg ha^{-1} obtained with 0.04 % Fe concentration.

Subbaiah *et al.* (2016) conducted experiment in maize and reported that the highest grain yield of 3298 kg ha^{-1} was recorded with the application of ZnO-nanoparticulates of 400 ppm which was significantly higher (42 %) compared to control (1884 kg ha^{-1}) and 15 % higher compared to 2000 ppm of bulk ZnSO$_4$ (2787 kg ha^{-1}). The next best treatments were application of 100 ppm of ZnC 23 nanoparticulates (3182 kg ha^{-1}) and 200 ppm of ZnO-nanoparticulates (3120 kg ha^{-1}), followed by 50 ppm of ZnO-nanoparticulates.

Janmohammadi *et al.* (2016) conducted an experiment on impact of foliar application of nano micronutrient fertilizers (Fe & Zn) on yield components of barley and stated that foliar utilization of micronutrients improved and grain yield up to 7 % and 16 % over to control.

Harish and Gowda (2017) conducted an experiment in groundnut and reported that application of nanoscale ZnO particles of 25 nm @ 1000 ppm recorded highest pod yield 26.69 per cent and 19.8 per cent when compared to RDF during 2015 and 2016 respectively.

Rameshraddy *et al.* (2017) conducted an experiment on seed priming and nano zinc effect on seed yield of ragi and the revealed that ZnO nano particles have shown pod yield of 21.5 g $plant^{-1}$ which is not significantly different with seed priming + foliar spray and control.

Saraswathi *et al.* (2017) conducted an experiment on effect of nano ZnO on growth and yield of finger millet and found that with the application of nano ZnO as foliar spray has recorded highest grain yield (9.60 g $plant^{-1}$) and least in control i.e without application of fertilizers(7.00 g $plant^{-1}$)

Singh *et al.* (2017) reported the effect of nano zinc sulphide (ZnS) on growth and yield of sunflower and results stated that among different concentration of nano zinc sulphide, 500 ppm nano-ZnS sprayed at 55 DAS recorded significantly higher yield (5.27 g $plant^{-1}$) which was on par with nano ZnS 400 ppm (4.87 g $plant^{-1}$) at 35 DAS.

EI-Metwally *et al.* (2018) reported the response of peanut plants to different foliar applications of nano- iron, manganese and zinc under sandy soil conditions and they concluded that application of 10, 20, 30, 40 ppm nano fertilizers gave higher values of seed yield significantly obtained over the untreated plants by 19.4, 40.6, 52.7 and 51.7 % respectively.

2.2.9 Haulm yield

Bakhtiari *et al.* (2015) reported the effect of iron nanoparticles spraying time and concentration on wheat and they proved that the effect of the interaction of two factors was not significant. The comparison of the spraying times indicated that the biological yield of 8830 kg ha^{-1} was obtained at first spraying. Among the Fe concentrations biologic yield (8895.0 kg ha^{-1}) obtained with 0.04 % Fe concentration.

Farnia *et al*. (2015) reported the effect of nano-zinc chelate and nano-biofertilizer on yield and yield components of maize (*Zea mays* L.) under water stress condition and they have concluded that interaction between Zn nanofertilizer and nano biofertilizer on biomass yield were significant nanofertilizer and nano biofertilizer treatment had the highest (17000 kg ha^{-1}) biomass yield and the lowest is control treatment (11000 kg ha^{-1}).

Janmohammadi *et al.* (2016) conducted an experiment on the impact of foliar application of nano micronutrient fertilizers (Fe & Zn) on yield components of barley and stated that foliar utilization of micronutrients shown that foliar utilization of micronutrients improved straw yield and 7 % over to Control.

2.2.10 Harvest Index

Benzon *et al*. (2015) reported the effect of nano fertilizer effect on growth, development of chemical properties of rice and they concluded that use of a full dose of recommended rate of conventional and nanofertilizer increased the harvest index by 2.9%.

Farnia *et al*. (2015) reported the effect of nano-zinc chelate and nano-biofertilizer maize (*Zea mays* L.) under water stress condition and they have concluded that interaction between water stress and nano biofertilizer showed that 7 day irrigation period treatment with use of nano-biofertilizer had the highest harvest index (51 %) and 21 day irrigation period treatment without nano biofertilizer and nano-Zn had the lowest (28%).

Janmohammadi *et al.* (2016) conducted an experiment on impact of foliar application of nano micronutrient fertilizers (Fe & Zn) on yield components of barley and stated that foliar utilization of micronutrients shown higher harvest index (30.77, 32.46 respectively) which is on par with control (29.92).

2.3 EFFECT OF NANOPARTICLES ON NUTRIENT UPTAKE AND SOIL NUTRIENTS LIKE N, P, K, Cu, Mn, Fe AND Zn AFTER HARVEST

Yuvaraj and Subramanian (2014b) found that the soil application of Zn-fortified with manganese hollow core-shell in rice (*Oryza sativa* L.), the plants fertilized or encapsulated with a Zn-fortified manganese hollow core shell had resulted in higher Zn uptake of 5.66 and 3.47 mg hill^{-1} under submerged and aerobic moisture regimes, respectively.

Mazaherinia *et al.* (2010) reported that there is an increment in plant Fe, Zn, Cu concentrations with the application of nano iron oxide in wheat compared to the application of bulk iron oxide.

Kim *et al*. (2011) conducted an experiment on effect of Zn and ZnO nanoparticles and Zn^{2+} on soil enzyme activity and bioaccumulation of Zn in *Cucumis sativus* and results shown that there was no significant difference in the amount of Zn in plants or soil between the Zn and ZnO NP treatments. The concentration of Zn in plant organs increased in response to Zn^{2+}, whereas the soil Zn concentration decreased.

Prasad *et al*. (2012) conducted an experiment on the effect of nanoscale zinc oxide particles on yield parameters of groundnut during *rabi* seasons 2009 and 2010 and there is significant increment in zinc content in leaves (42 %, 29 %) and kernels (42 %, 36.6 %) when supplied with nanoscale ZnO compared to chelated $ZnSO_4$ and control.

Afshar *et al*. (2012) reported the effect of nano-iron foliar application on qualitative and quantitative characteristics of cowpea under end season drought stress and they concluded that the highest rate of seed nitrogen was obtained in irrigation disruption after the first harvest and 1.5 per 1000 Nano-iron. The greatest leaf nitrogen content was achieved from nano-iron treatment of 1 per 1000 and irrigation disruption after the first harvest. The highest amount of leaf potassium was observed in the iron treatment of 0.5 per 1000 and irrigation disruption after 80% of pod formation. But the treatments did not affect leaf phosphorus rate and seed Fe content significantly.

A study by Dhoke *et al.* (2013) reported the effect of nanoparticles (nano-ZnO, nano-FeO and nano-ZnCuFe-oxide) suspension on the growth of mung (*vigna radiata*) seedlings by foliar spray method. And they concluded that the nanoparticle suspensions of ZnO, FeO and ZnFeCu-oxide were able to affect the development and growth processes and bioaccumulation in a plant by foliar spray. In nano-ZnO (20 ppm) sprayed plants shown 6.59 mg L^{-1} of Zn concentration for nano- FeO (50 ppm) sprayed plants, 11.49 mg L^{-1} of Fe concentration was observed. And for nano- ZnFeCu-Oxide (50 ppm) sprayed plants, 0.54 mg L^{-1} of Zn, 4.23 mg L^{-1} of Fe and 6.66 mg L^{-1} of Cu concentrations were observed.

Tarafdar *et al.* (2014) conducted an experiment on effect of zinc nanofertilizer to enhance crop production in pearl millet. They reported that plant zinc concentration obtained was 10.4 % over control obtained when applied with nano zinc fertilizer.

Subbaiah *et al.* (2016) conducted experiment on effect of nano ZnO particles on post-harvest nutrients concentration in maize. They concluded that highest zinc concentration of 22 ppm was recorded in leaf at 2000 ppm of ZnO nanoparticulates which is significantly higher than that of control (53%) and bulk zinc sulfate of 2000 ppm (50%). Application of 2000 ppm of ZnO-nanoparticulates also resulted in higher zinc accumulation in maize cobs (47.6 ppm) compared to control (21.4 ppm) and 2000 ppm of bulk zinc sulfate (31.3 ppm). The highest grain zinc content of 35.96 ppm was recorded with the application of 100 ppm of ZnO-nanoparticulates and was significantly higher (37 %) over control and bulk zinc sulfate of 2000 ppm (29 %).

The zinc concentration in soils was estimated and greater content of zinc of 24.3 ppm of soil was found in the treatment with ZnO-nanoparticulates of 1000 ppm indicating the translocation of zinc from the leaves to the soil through the plant body system and accumulation in the soils.

Singh *et al*. (2017) reported the effect of nano zinc sulphide (ZnS) on uptake of primary nutrients (N, P, K, S and Zn) and available nutrient status (N, P_2O_5, K_2O, S and Zn) in soil after the harvest of sunflower plants and there is a marked increase in the nitrogen (418.30 and 398.76 mg plant^{-1}), phosphorus (92.51 and 91.68 mg^{-1}) and potassium (357.14 mg and 336.3 mg plant^{-1}) uptake was recorded with the application of 400 ppm of nano ZnS sprayed at 35 DAS and 500 ppm nano ZnS spray at 55 DAS respectively and uptake of sulphur and zinc observed to be the highest in 500 ppm nanoZnS sprayed at 55 DAS followed by 400 ppm nano-ZnS sprayed at 35 DAS.

EI-Metwally *et al.* (2018) reported the response of peanut plants to different foliar applications of nano-iron, manganese and zinc under sandy soil conditions and they concluded that nano fertilizers treatments have a significant effect on macronutrients (N, K and P) and micronutrients (Fe, Mn and Zn) in seeds and shoot of peanut plants at harvest. Application of 30 ppm nano fertilizers gave the highest values of macronutrients (N, P and K) while, 40 ppm gave the greatest values of micronutrients (Fe, Mn and Zn) in seeds of peanut.

CHAPTER III

MATERIAL AND METHODS

Chapter III

MATERIAL AND METHODS

Synthesis and part of the characterization of the as-prepared ZnO nanoparticles (n-ZnO) was done at Nanotechnology Laboratory, Institute of Frontier Technology, Regional Agricultural Research Station, Acharya N G Ranga Agricultural University, Tirupati, Andhra Pradesh and consequently a field experiment was conducted in the farmland to study the '**Size dependent effects of nanoscale zinc oxide on productivity of groundnut in Alfisols**" during *Kharif*, 2018. The material used and the methods employed during the course of the investigation are presented in this chapter.

3.1 SYNTHESIS AND CHARACTERIZATION OF ZnO NANOPARTICLES

3.1.1 Synthesis of ZnO Nanoparticles

ZnO nanoparticles (mean size 20, 25, 30 nm) used in this study were prepared by using the oxalate decomposition technique (sol-gel method). Zinc oxalate was prepared by mixing equimolar (0.2 M) solutions of zinc acetate and oxalic acid. The resultant precipitate was collected and rinsed extensively with double deionized water and dried in air. The oxalate was then ground and decomposed in the air by placing it in a pre-heated furnace for 45 minutes at 500^0C.

3.1.2 Characterization of ZnO Nanoparticles

After the preparation of n-ZnO particles, different characterization techniques were used to investigate their structure and optical properties. The equipment, materials and methods used for the characterization of synthesized n-ZnO particles are described below.

3.1.2.1 Transmission Electron Microscopy (TEM)

The characterization of the sample was done by transmission electron microscopy (HRTEM, JEOL 3010). The TEM samples were prepared by drop casting the suspensions on carbon-coated Cu grids.

3.1.2.2 Dynamic Light Scattering (DLS)

The hydrodynamic diameter (Size of the hydrosol) of the ZnO nanoparticles was measured using Particle size analyzer or Dynamic Light Scattering (DLS) (Nanopartica SZ-100, Horiba Scientific). This apparatus works on the principles of laser diffraction. The sample holder temperature was maintained at 25^{o}C. Using this apparatus, the measurable particle size range is 0.3nm – 8μm. Depending on the configuration and application, the system can also be used to measure zeta potential. Zeta potential is widely used to denote the magnitude of the electrical charge surrounding the particles. The sample was prepared by centrifuging the ZnO nanoparticles suspension at 10,000 rpm for about 10 minutes and then the size (hydrodynamic diameter) and zeta potential of ZnO nanoparticles were measured.

3.1.2.3 UV-VIS Spectroscopic Analysis

ZnO nanoparticles were characterized by UV-visible spectrophotometer (UV-2450, Shimadzu) is used to record the absorption spectrum of ZnO nanoparticles which shows the characteristic absorption spectra of nano ZnO.

3.1.2.4 Fourier Transform Infrared spectroscopic analysis (FT-IR)

When Infrared Radiation (IR) passed through a sample, some radiation is absorbed by the sample and some transmitted. It measures the absorption of IR by the sample material versus wave length. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibration frequencies in the infra-red range. The FTIR spectrum has taken in the mid-IR region of 400–4000 cm^{-1}. The spectrum recorded using ATR (Attenuated Total Reflectance) technique. The dried sample was mixed with the KBr (1:200) crystal, and the spectrum was recorded in the transmittance mode (Tensor 27, BRUKER). It is a powerful tool for isolating and characterizing organic contamination.

3.1.2.5 X-ray diffraction analysis (XRD)

The crystal-phase structure and the crystallite size of the n-ZnO particles were determined using X-ray diffractometer (Philips X'Pert MPD, Japan) using monochromatic CuKa1 radiation of wavelength k = 1.5418Å from a fixed source operated at 40 kV and 30 mA in the 2θ scan range of 20–80°. The ZnO NP crystallite size was calculated using the Scherrer equation.

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

Where, k is the Scherrer constant (k=0.89), λ is the X-ray wavelength, β is full width of the peak at half maximum (FWHM) intensity (in radians) and θ is the Bragg's diffraction angle.

3.2 LOCATION OF THE EXPERIMENTAL SITE

The experiment was conducted in field No.50, College farm, S. V. Agricultural College, Tirupati, Acharya N.G. Ranga Agricultural University, which is geographically situated at 13.5°N latitude and 79.5°E longitude, with an altitude of 182.9 m above the mean sea level in the Southern Agro-Climatic Zone of Andhra Pradesh.

3.3 WEATHER DURING THE CROP PERIOD

Weather data during the crop period (02-7-2018 to 27-10-2018) recorded at the S.V. Agricultural College Meteorological Observatory, Tirupati is presented in Table 3.1 and depicted in Fig. 3.1.

A total rainfall of 367.8 mm was received in 23 rainy days during the crop growth period. The weekly mean maximum temperature during the crop period ranged from 32 to 37.2^{o}C. The weekly mean minimum temperature during the crop growth period varied from 20 to 28^{o}C. The weekly mean bright sunshine hours day^{-1} during the crop growth period ranged from 0.3 to 7.6 with an average of 4.54 hr.

The weekly mean relative humidity during the crop growth period ranged from 50 to 73.6 percent, with an average of 60.8 percent and the weekly mean evaporation (USWB Class-A Open Pan evaporimeter) ranged from 3.7 to 7 mm day^{-1}, with an average of 5.59 mm day^{-1}.

3.4 SOIL CHARACTERS OF THE EXPERIMENTAL SITE

The field experiment was conducted in field no.50 College farm, S. V. Agricultural College, Tirupati. The composite soil sample was collected randomly at 0-15 cm soil depth and analyzed for different physico-chemical properties prior to start of the experiment. The particulars of the physico-chemical properties and methods employed for each of them are presented in Table 3.2.

Table 3.1. Standard week wise meteorological data during the crop growth period of groundnut (01.07.2018 - 26.10.2018)

Standard week	Date and Month	Temperature (°C)		Mean relative humidity (%)	Rainfall (mm)	Number of rainy days	Mean evaporation (mm day^{-1})	Mean bright sunshine (hours day^{-1})
		Maximum	Minimum					
27	01 July - 07 July	34.6	25.2	58.10	30.4	1	5.5	3.2
28	08 July - 14 July	34.4	26.3	55.6	5.2	2	5.9	0.3
29	15 July - 21 July	36.5	26.7	53	0.0	0	7.0	3.8
30	22 July - 28 July	36.7	27.3	50.0	0.0	0	6.6	6.0
31	29 July - 04 Aug.	37.2	28.0	50.1	0.0	0	7.0	5.1
32	05 Aug. - 11 Aug.	35.7	26.0	57.7	10.6	2	6.5	2.2
33	12 Aug. - 18 Aug.	32.0	25.0	62.7	14	2	3.8	2.1
34	19 Aug. - 25 Aug.	35.8	27.1	51.0	0.0	0	6.8	3.5
35	26 Aug. - 01 Sep.	35.8	24.9	59.5	44.6	2	5.8	3.8
36	02 Sep. - 08 Sep.	36.2	25.5	55.2	12.0	1	6.4	7.6
37	09 Sep. - 15 Sep.	35.2	25.3	67.6	56.8	3	5.4	5.3
38	16 Sep. - 22 Sep.	32.0	22.8	73.0	96.6	4	3.7	2.5
39	23 Sep. - 29 Sep.	34.8	24.6	65.2	4.0	1	5.2	7.1
40	30 Sep. - 06 Oct.	32.0	24.5	73.6	16.4	2	4.2	5.3
41	07 Oct. – 13 Oct.	35.1	22.2	64.3	3.60	1	5.3	6.2
42	14 Oct. – 20 Oct.	33.3	23.2	72.2	73.6	2	4.5	6.2
43	21 Oct. – 27 Oct.	32.6	20.0	65.5	00.0	0	5.5	7.1
					367.8			

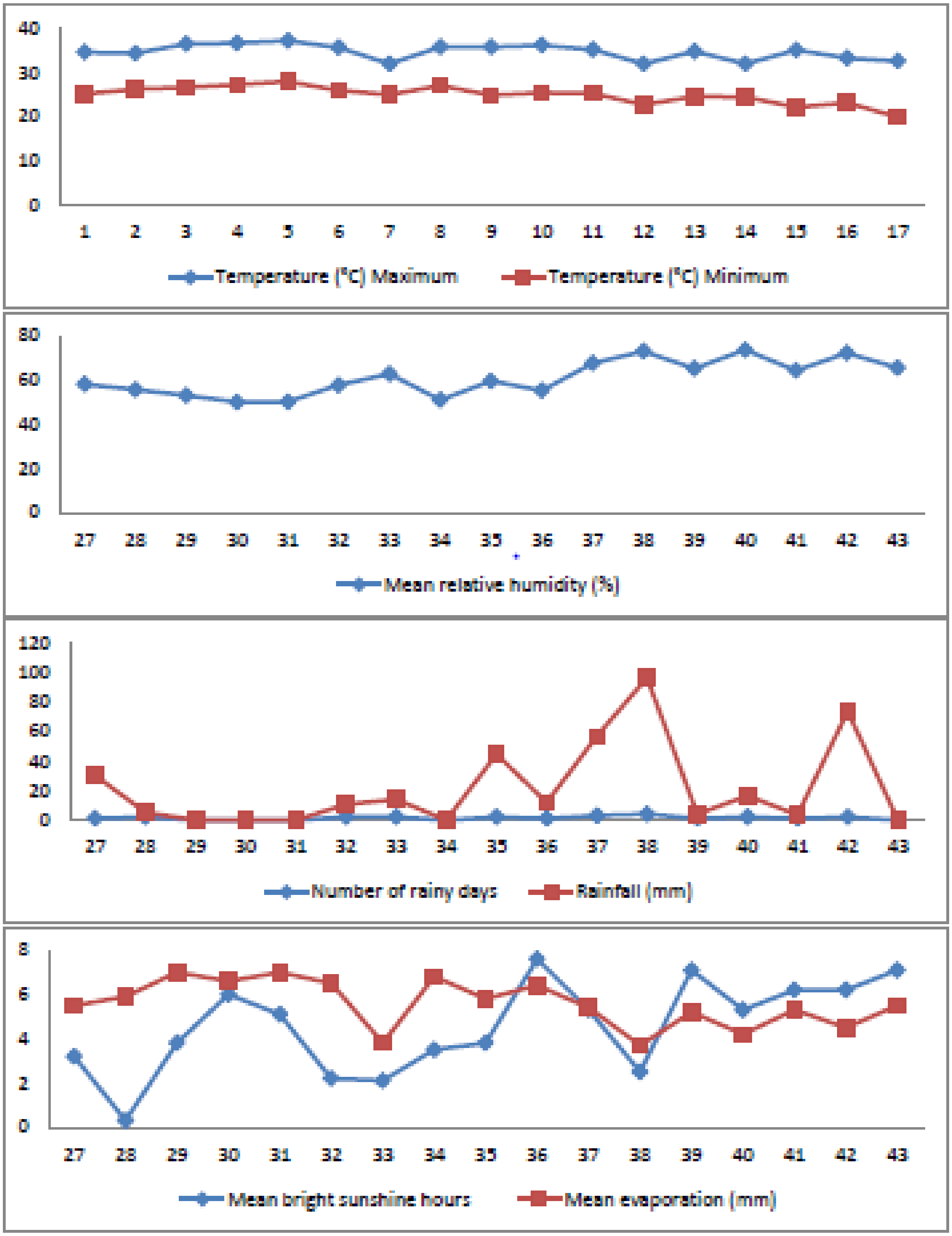


Fig. 3.1. Standard week wise meteorological data during the crop period.

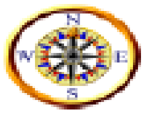
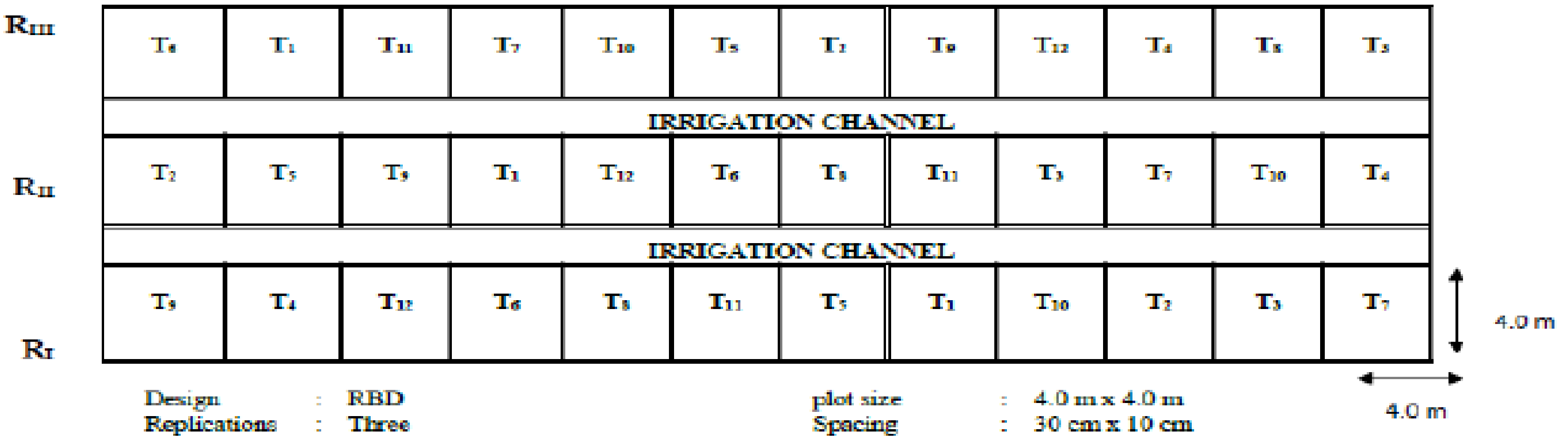


Figure 3.1 Lay-out plan of experimental filed



R_{III}	T_6	T_1	T_{11}	T_7	T_{10}	T_5	T_2	T_9	T_{12}	T_4	T_8	T_3
	IRRIGATION CHANNEL											
R_{II}	T_2	T_5	T_9	T_1	T_{12}	T_6	T_8	T_{11}	T_3	T_7	T_{10}	T_4
	IRRIGATION CHANNEL											
R_I	T_9	T_4	T_{12}	T_6	T_8	T_{11}	T_5	T_1	T_{10}	T_2	T_3	T_7

Design : RBD
Replications : Three
Treatments : Twelve

plot size : 4.0 m x 4.0 m
Spacing : 30 cm x 10 cm

T_1 :	Control (No application)	T_7 :	RDF + Nanoscale zinc oxide (25 nm) @ 400 ppm at 25 and 45 DAS
T_2 :	100% recommended dose of fertilizer (RDF)	T_8 :	RDF + Nanoscale zinc oxide (25 nm) @ 200 ppm at 25 and 45 DAS
T_3 :	RDF + Zinc sulphate @ 2000 ppm at 25 and 45 DAS	T_9 :	RDF + Nanoscale zinc oxide (25 nm) @ 150 ppm at 25 and 45 DAS
T_4 :	RDF + Nanoscale zinc oxide (20 nm) @ 400 ppm at 25 and 45 DAS	T_{10} :	RDF + Nanoscale zinc oxide (30 nm) @ 400 ppm at 25 and 45 DAS
T_5 :	RDF + Nanoscale zinc oxide (20 nm) @ 200 ppm at 25 and 45 DAS)	T_{11} :	RDF + Nanoscale zinc oxide (30 nm) @ 200 ppm at 25 and 45 DAS
T_6	RDF + Nanoscale zinc oxide (20 nm) @ 150 ppm at 25 and 45 DAS	T_{12} :	RDF + Nanoscale zinc oxide (30 nm) @ 150 ppm at 25 and 45 DAS

Table 3.2. Physico-chemical properties of soil of the experimental field

S.No.	Particulars	Result	Method adopted
1.	Soil texture	Sandy clay loam	International pipette method (Piper 1950)
2.	Soil pH (1: 2.5 soil water suspension)	6.91	Glass electrode pH meter (Jackson, 1973)
3.	Electrical Conductivity (dSm^{-1})	0.167	Conductivity bridge (Jackson, 1973)
5.	Available N ($kg\ ha^{-1}$)	191.1	Alkaline potassium permanganate method (Subbaiah and Asija, 1956)
6.	Available P_2O_5 ($kg\ ha^{-1}$)	35.5	Olsen's method (Olsen *et. al.*1954)
7.	Available K_2O ($kg\ ha^{-1}$)	187.9	Flame photometry (Jackson, 1973)
8.	Total Zn ($mg\ kg^{-1}$)	0.92	DTPA extraction (Lindsay, W.L and Norvell, W.A. 1978)
	Fe	6.76	
	Mn	25.6	
	Cu	1.1	

3.5 CROPPING HISTORY OF THE EXPERIMENTAL SITE

Cropping history of the experimental site during the three years preceding the present investigation are given below:

Year	***Kharif***	***Rabi***	**Summer**
2015-2016	Groundnut	Maize	Fallow
2016-2017	Groundnut	Redgram	Fallow
2017-2018	Groundnut	Sesamum	Fallow
2018-2019	**Groundnut (Present Experiment)**	**-**	**-**

3.6 EXPERIMENTAL DETAILS

3.6.1 Design and Layout

The experiment was laid out in a randomized block design with twelve treatments and three replications. The layout plan is furnished in the Fig.3.1.

3.6.2 Treatments

T_1 : Control (No application)
T_2 : RDF (20-40-50 kg N, P_2O_5, K_2O)
T_3 : RDF + Zinc sulphate @ 2000 ppm at 25 and 45 DAS
T_4 : RDF + Nanoscale zinc oxide (20 nm) @ 400 ppm at 25 and 45 DAS
T_5 : RDF + Nanoscale zinc oxide (20 nm) @ 200 ppm at 25 and 45 DAS
T_6 : RDF + Nanoscale zinc oxide (20 nm) @ 150 ppm at 25 and 45 DAS
T_7 : RDF + Nanoscale zinc oxide (25 nm) @ 400 ppm at 25 and 45 DAS
T_8 : RDF + Nanoscale zinc oxide (25 nm) @ 200 ppm at 25 and 45 DAS
T_9 : RDF + Nanoscale zinc oxide (25 nm) @ 150 ppm at 25 and 45 DAS
T_{10} : RDF + Nanoscale zinc oxide (30 nm) @ 400 ppm at 25 and 45 DAS
T_{11} : RDF + Nanoscale zinc oxide (30 nm) @ 200 ppm at 25 and 45 DAS

T_{12} : RDF + Nanoscale zinc oxide (30 nm) @ 150 ppm at 25 and 45 DAS

3.6.3 Plot Size and Spacing

Gross plot size : 4 m X 4 m
Spacing : 30 cm X 10 cm

3.6.4. Variety

The improved “Dharani” variety released during 2013 was used in this experiment. It is medium statured spanish bunch type, determinate with erect growth habit and an early maturing variety with 105-110 days duration, recommended for all the seasons in groundnut growing areas of Andhra Pradesh. The pod is medium bold with moderate reticulation and constriction with slight beak. The kernel size is moderate with light rose coloured testa. It has a yield potential of 2.60 t ha^{-1} and 3.30 t ha^{-1} during *kharif* and *rabi* respectively, with an average oil content of 46-48 per cent.

3.7 CULTIVATION DETAILS

3.7.1 Land Preparation

The experimental field was ploughed and prepared with tractor drawn cultivator and rotavator to bring the soil to fine tilth. The uprooted weeds and stubbles were removed. Layout was made according to the experimental design with 1.0 m spacing between the replications.

3.7.2 Fertilizer Application

Full dose of nitrogen (20 kg ha^{-1}), phosphorous (40 kg ha^{-1}) and potassium (50 kg ha^{-1}) in the form of urea (46 per cent N), single super phosphate (16 per cent P_2O_5) and muriate of potash (60 per cent K_2O) were applied as basal dose at the time of sowing in furrows made 5 cm away from the seed rows. Gypsum @ 500 kg ha^{-1} was applied at 30 DAS commonly for all the treatments.

3.7.3 Seeds and Sowing

Bold and healthy pods were selected for seeding. After shelling, the bold kernels were selected and treated with imidachloprid @ 2 ml + mancozeb 3g per Kg seed. The seeds were sown on 1st July, 2018 manually at a depth of 5 cm in the furrows which were laid with spacing of 30 cm and the intra row spacing was 10 cm.

3.7.4 Irrigation

Rainfall was received before sowing which served as a pre sowing irrigation. First irrigation was given at 4 DAS to ensure uniform germination. Total of six irrigations were given throughout the crop growth period as and when necessary through sprinkler irrigation.

3.7.5 Gap Filling

Gap filling was done within 7 days after sowing to maintain uniform plant stand in all the treatments.

3.7.6 Weeding

Pre-emergence herbicide Pendimethalin @ 2.5 to 3 L ha^{-1} was applied just immediately after sowing and one hand weeding was carried out at 25 DAS for effective weed management. Major weeds observed in the experimental field include *Commelina benghalensis*, and *Cyperus rotundus*.

3.7.7 Plant Protection

Root rot and leaf spot was controlled by the spraying Carbendazim 50% WP @ 2 g $litre^{-1}$ at 40 DAS.

3.7.8 Harvesting and Stripping

The crop was considered to be matured when more than 75 per cent of the pods of the randomly selected plants showed black streaks on the inner wall of the shell. In each plot, four rows of the crop (two rows on either side) were taken as border rows. In each plot, the border rows were first harvested followed by the plants in the plot. The pods were hand stripped and sun dried to reach constant weight. The pod yield was recorded in kg ha^{-1}. After stripping the pods, the haulm yield was also recorded after sun drying and expressed in kg ha^{-1}

3.8 OBSERVATIONS ON CROP

Observations on crop growth at 30, 60 and 90 DAS were taken from five plants, which were randomly selected and labeled in each plot.

3.8.1 Plant Height

Plant height was measured from the base of the plant to the tip of growing point at 30, 60 and 90 DAS and expressed in cm.

3.8.2 Leaf Area Index

Leaf area from five destructively samples plants was measured at 30, 60 and 90 DAS using LI-COR Model LI-3100 leaf area meter with transparent conveyor belt having electronic digital display and expressed in cm^2. Leaf area index was calculated by dividing the total number of leaves in each hill and area occupied by each hill based on the formula suggested by Watson (1952).

3.8.3 Dry matter Production

Five plants at random from the border rows leaving the extreme row were destructively sampled at harvest for the estimation of dry matter production. The plants were removed along the root system. The roots of samples were separated and shoots were sundried for 2 days and then oven dried in hot air oven at 60^0C to a constant weight and expressed in kg ha^{-1}.

3.8.4 Number of Nodules Plant^{-1}

The roots of five plants at 75 DAS used for destructive sampling were excavated gently without damaging the roots and washed under gentle stream of water so as to remove the adhering soil. Then the total number of nodules were counted.

3.8.5 Number of Pods Plant^{-1} and Filled Pods Plant^{-1}

The number of pods and filled pods plant^{-1} for five labeled plants were counted separately, averaged for each treatment and expressed as number of pods and filled pods plant^{-1} respectively.

3.8.6 Hundred Pod Weight

After thorough sun drying of pods to a constant weight, five lots of 100 pods were randomly selected and weight was recorded and the average weight of 100 pods was expressed in g.

3.8.7 Hundred Kernel Weight

A sample of pods from plot in each treatment was drawn, hand shelled and hundred kernels were counted from the sample, weighed and expressed in g.

3.8.8 Shelling Percentage (%)

Three separate random samples (250 g) of pods were drawn, shelled, kernels were separated and weights were recorded. The per cent of kernels to pods worked out for each treatment as shelling percentage.

$$\text{Shelling percentage} = \frac{\text{weight of kernals}}{\text{weight of pods}} \times 100$$

3.8.9 Pod Yield

The pods obtained from each plot area along with five sampled plants were thoroughly sun dried, cleaned and weighed. The pod yield from the sampled plants was added to plot yield and the total pod yield was weighed and expressed in kg ha^{-1}

3.8.10 Haulm Yield

The haulms obtained from each plot area along with five sampled plants were thoroughly sun dried, weighed and expressed in kg ha^{-1}.

3.8.11 Harvest Index

The harvest index for each treatment plot was calculated by using the following formula

$$\text{HI} = \frac{\text{Economic yield}}{\text{Biological yield}} \text{ X } 100$$

3.9 COLLECTION AND PROCESSING OF SOIL SAMPLES AND ANALYSIS

Initial soil samples were collected from 0-15 cm depth before planting of the crop. While collecting the samples, five pits were dug in each plot with the help of spade. The five soil samples were collected, mixed separately, dried under shade, processed to pass through 2 mm sieve and labelled. The soil samples so collected were analyzed for physico-chemical and chemical properties by using standard procedures.

3.9.1 Soil Physico-Chemical Analysis

3.9.1.1 Soil reaction (pH)

The pH of the soil was determined in 1:2.5 soil-water suspension using Elico pH meter with a glass electrode as described by Jackson (1973).

3.9.1.2 Electrical Conductivity (EC)

The electrical conductivity of the soil was determined in 1:2.5 soil water extract with the help of electrical conductivity meter as described by Jackson (1973) and was expressed as dSm^{-1}.

3.9.2. Chemical Analysis

3.9.2.1 Available nitrogen (N)

Available nitrogen was estimated by alkaline permanganate method as described by Subbiah and Asija (1956) and was expressed in kg ha^{-1}.

3.9.2.2 Available phosphorus (P)

Soil available phosphorus was extracted by using 0.5 M $NaHCO_3$ adjusted to pH 8.5 (Olsen *et al*. 1954) and colour intensity was read in spectrophotometer at 660 nm and was expressed in kg ha^{-1}.

3.9.2.3 Available potassium (K)

Soil available potassium was extracted with neutral normal ammonium acetate and the content was estimated as per procedure out lined by Jackson (1973) using flame photometer and was expressed in kg ha^{-1}.

3.9.2.4 DTPA extractable micronutrients

Twenty grams of soil was shaken with 40 ml of DTPA extract of pH 7.3 for 2 hrs, the contents were filtered and in the filtrate iron, manganese, zinc and coppper were determined by using atomic absorption spectrophotometer (Varian A A 240 FS) and were expressed in mg kg^{-1}.

3.10 COLLECTION OF PLANT SAMPLES AND METHODS OF ANALYSIS

The whole plant samples were collected at harvest stage and the samples washed in sequence with tap water, 1/10 HCl solution and distilled water and extra moisture was wiped out and dried in shade. Finally the samples were dried in hot air oven at 70°C. The dried samples were powdered in willey mill and preserved in butter paper cover for chemical analysis. The procedures adopted for the analysis of nutrients are briefly out lined below.

3.10.1 Plant Analysis

3.10.1.1 Nitrogen

The nitrogen concentration in plant samples was determined by micro kjeldahl distillation method (AOAC, 1970) and expressed in percentage.

3.10.1.2 Phosphorus

The phosphorus concentration in diacid extract was determined by Vanadomolybdo phosphoric yellow colour method by using spectrophotometer (Jasco V-530 UV visible spectrophotometer) at 470 nm wavelength (Jackson, 1973) and expressed as percentage.

3.10.1.3 Potassium

The concentration of potassium in diacid extract was determined by using flame photometer (systronics flame photometer 128) and was expressed as percentage.

3.10.1.4 Micronutrients

The diacid extract was fed to atomic absorption spectrophotometer (Varian AA 240 FS) and the concentration of Fe, Mn, Zn and Cu were determined (Lindsay and Norvell, 1978) and expressed in mg kg^{-1}.

Element	**Wavelength (mm)**	**Discharge current (m Amp)**
Fe	248.3	10.0
Mn	279.5	7.5
Zn	213.8	10.0
Cu	324.8	10.0

3.11 STATISTICAL ANALYSIS

The data recorded on various parameters of crop during the course of investigation was statistically analyzed following the analysis of variance for randomized block design as suggested by Panse and Sukhatme (1985). Statistical significance was tested with ‘F’ test at 5 per cent level of probability and compared the treatmental means with critical difference. The mean values were separated by Duncan’s Multiple Range Test (DMRT).

CHAPTER IV

RESULTS AND DISCUSSION

Chapter IV

RESULTS AND DISCUSSION

The results of the experiment entitled "Size dependent effects of nanoscale zinc oxide on productivity of groundnut in Alfisols" which was conducted on sandy clay loam soil in the field No. 50 at College farm, S. V. Agricultural college, Tirupati during *Kharif*, 2018 were presented in this chapter.

4.1 CHARACTERIZATION OF NANOPARTICLES

4.1.1 Transmission Electron Microscopy (TEM)

The zinc oxide nanoparticles used in this study were having the mean diameter of 20, 25 and 30 nm as shown by HRTEM imaging technique. Fig. 4.1 shows the image of nanoscale zinc oxide particles that appears hexagonal and slightly aggregated due to the absence of surface protecting ligands. The particles were crystalline in nature as revealed by the higher magnification HRTEM image of nanoparticles and the lattice of zinc oxide was clearly shown (Wurtzite).

4.1.2 Dynamic Light Scattering Analysis (DLS)

Fig. 4.2 represents the particle size of the synthesized sample that is 77.0 nm and Fig. 4.3 represents the zeta potential spectra for the zinc oxide nanoparticles (20 nm) which were recorded as zeta potential versus intensity spectra with zeta potential (mV) on x-axis and intensity (a. u) on y-axis. The zeta potential obtained was -42.1 mV and its electrophoretic mobility mean recorded was 0.000327cm^2 Vs^{-1}. It is evident from the zeta potential that ZnO particles are highly stable and mono dispersal.

Fig. 4.4 represents the particle size of the synthesized sample that is 87.5 nm and Fig. 4.5 represents the zeta potential spectra for the zinc oxide nanoparticles (25 nm). The zeta potential is -46.4 mV and its electrophoretic mobility mean recorded was 0.000361cm^2 Vs^{-1} for the zinc oxide nanoparticles which represents the monodispersity of the particles.

Fig. 4.6 represents the particle size of the synthesized sample that is 98.5 nm and Fig. 4.7 represents the zeta potential spectra for the zinc oxide nanoparticles (30 nm). The zeta potential is -61.3 mV and its electrophoretic mobility mean recorded was 0.000476cm^2 Vs^{-1}.

Size of nanoparticles at preparation is necessarily varied at application site. The size of nanoparticles was measured in dry mode for TEM. Whereas, in DLS mode, it is due to bulging effect (Size measured in suspension) the size of the nanoparticles increases.

4.1.3 UV Visible Spectroscopy

Fig. 4.8 shows absorption spectrum for the n-ZnO (20 nm) in the range of 200-800 nm. The spectrum showed the formation of a peak in the wavelength of 418 nm. UV-vis spectroscopy was used to determine the formation and the stability of the synthesized zinc oxide nanoparticles in aqueous solution.

Fig. 4.9 shows absorption spectrum was recorded for the ZnO (25 nm) in the range of 200-800 nm. The spectrum showed the formation of a peak in the wavelength of 593 nm.

Fig. 4.10 shows absorption spectrum was recorded for the ZnO (30 nm) in the range of 200-800 nm. The spectrum showed the formation of a peak in the wavelength of 460 nm.

4.1.1 Fourier Transform Infrared Spectroscopic Analysis (FTIR)

From the FTIR spectra of ZnO nanoparticles (20 nm) in fig. 4.11, shows a series of absorption peaks from 500 to 3500 cm^{-1}. Which arisen from the synthesis protocols. A broadband at around 3840, 3742 and 3623 cm^{-1} is assigned to the O−H group stretching mode of alcohols. The peak observed at 2357cm^{-1} indicating the stretching vibration of nitriles (C≡N), 1693cm^{-1} indicates C=O stretching vibration of α, β-unsaturated aldehydes. 1526cm^{-1} indicates N–O asymmetric stretching vibration of nitro compounds. 1390cm^{-1} indicates C–H rock stretching vibration of alkanes.

From the FTIR spectra of n-ZnO particles (25 nm) in fig. 4.12, a series of absorption peaks found from 500 to 3500 cm^{-1}. A broadband at around 3845, 3741 and 3619 cm^{-1} indicating O−H group stretching vibration of alcohols. 2359 cm^{-1} indicating C≡N stretching vibration of nitriles, 1694 cm^{-1} indicates C=O stretching vibration of α, β-unsaturated aldehydes, 1526 cm^{-1} indicates C–H rock stretching vibration of alkanes, 1250cm^{-1} indicates C−N stretching vibration of aliphatic amines, 911cm^{-1} indicates N–H primary and secondary amines.

Fig. 4.13, shows a series of FTIR absorption peaks from n-ZnO particles (30 nm) 500 to 3500cm^{-1}. A broadband at around 3854 and 3742cm^{-1} is assigned to the O−H stretching mode of alcohols, the range observed at 3616cm^{-1} indicating the stretching vibration of phenols (OH), 2360cm^{-1} indicates C≡N stretching vibration of nitriles, 1694 cm^{-1} indicates C=O stretching vibration of α, β-unsaturated aldehydes, 1522cm^{-1} indicates N–O stretching vibration of nitro compounds, 1384cm^{-1} indicates C–H rock stretching vibration of alkanes. The peak present at 921cm^{-1} indicates O–H bend stretching vibration of carboxylic acids.

4.1.4 X-ray Diffraction Analysis (XRD)

The ZnO nanoparticles size dependent XRD pattern and phase purity were investigated using powder XRD analysis as presented in Figure 4.14.

According to Standard JCPDS pattern for ZnO (file no: 043-0002), the diffraction peaks of ZnO nanoparticles with the sizes 20 (curve i), 25 nm (curve

ii) and 30 nm (curve iii) were (100), (002),(101),(102),(110),(103), and (112) corresponds to Braggs palnes and they were accountable to the characteristic diffraction peaks 2θ at 31.8, 34.3, 36.3, 47.6, 56.6, 62.9,and 67.9 S which clearly represents the wurtzite structure of nano ZnO . They were correlated with results reported by (Ramapuram *et al.*, 2018). Similar kind of diffraction peaks were identified with the ZnO nanoparticles of 20, 25 and 30 nm size. Overall, the structure of the nano ZnO was identified as wurtzite and remain unaltered with the change of sizes.

4.2 EFFECT OF ZnO NANOPARTICLES ON GROWTH AND YIELD OF GROUNDNUT

4.2.1 Plant Population

The data regarding plant population was represented in Table No. 4.1. There was no significant difference observed in initial and final plant population but the numerically higher population (30) was observed in T_{10} (n-ZnO particles of size 30 nm @ 400 ppm) compared to other treatments. All the treatments are in purity.

4.2.2 Plant Height (Cm)

Plant height of groundnut plants measured at different growth stages during the crop period *viz.*, 30, 60 and 90 DAS was presented in Table No. 4.1. From the data obtained, it has been observed that the plant height at 30, 60, 90 DAS were not significantly differed among the treatments. At 30 DAS, numerically highest plant height (19.33 cm) was observed with the application of nanoscale zinc oxide particles (n-ZnO) of size 25 nm @ 150 ppm (T_9) which was 17 % more than control and 3 % more than bulk $ZnSO_4$ @ 2000 ppm.

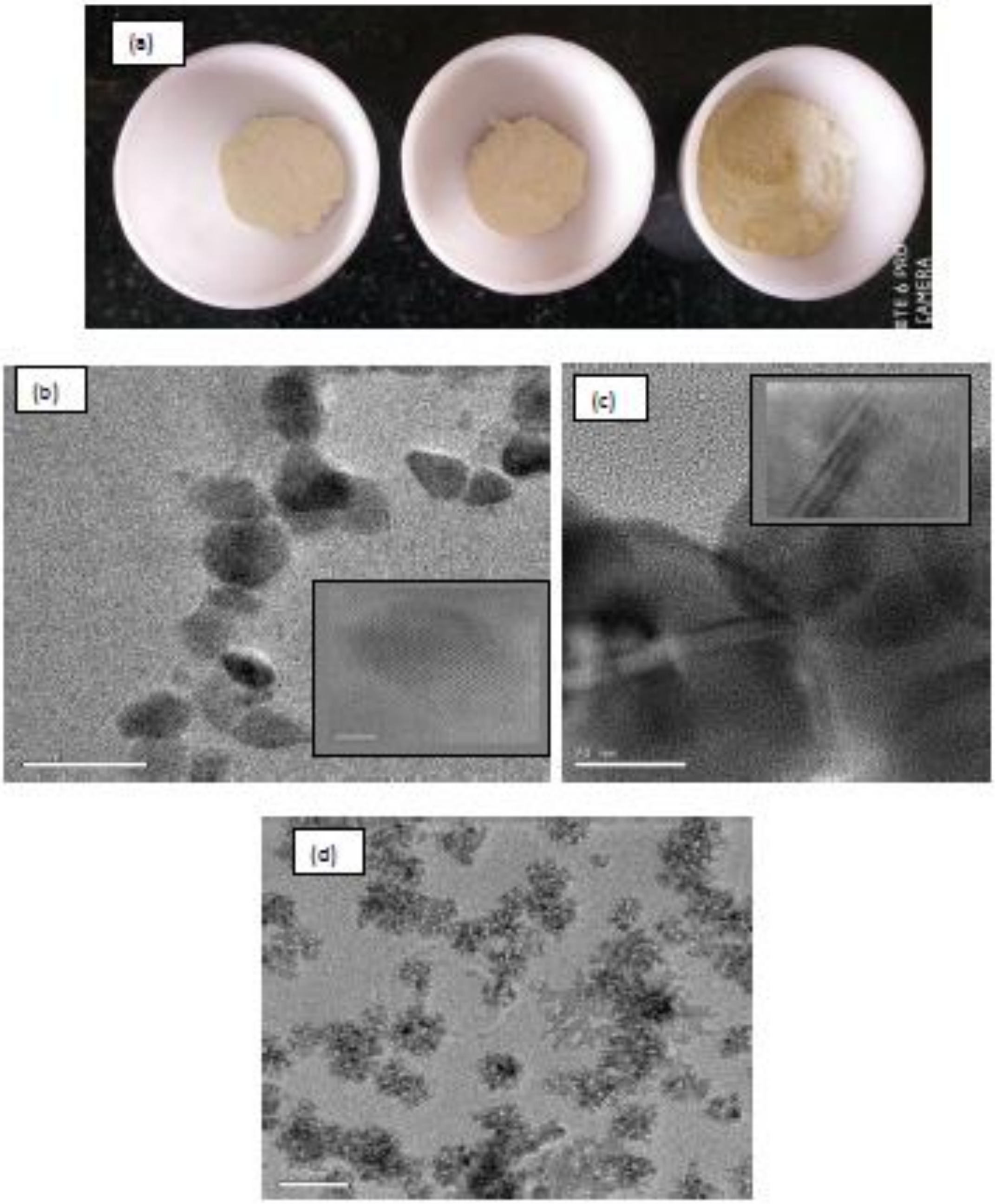


Fig. 4.1 (a) The powder form of nanoscale ZnO particles (b) TEM image of ZnO nanoparticles (at 50 nm scale) as well as a highly focused image of single ZnO nanoparticles (inset) (at 5 nm scale), (c) TEM image of ZnO nanoparticles (at 20 nm scale) showing clearly the hexagonal structure of nanoparticles as well as (inset) (at 5nm scale), (d) TEM image ZnO nanoparticles (at 20 nm scale) showing clearly the structure of nanoparticles.

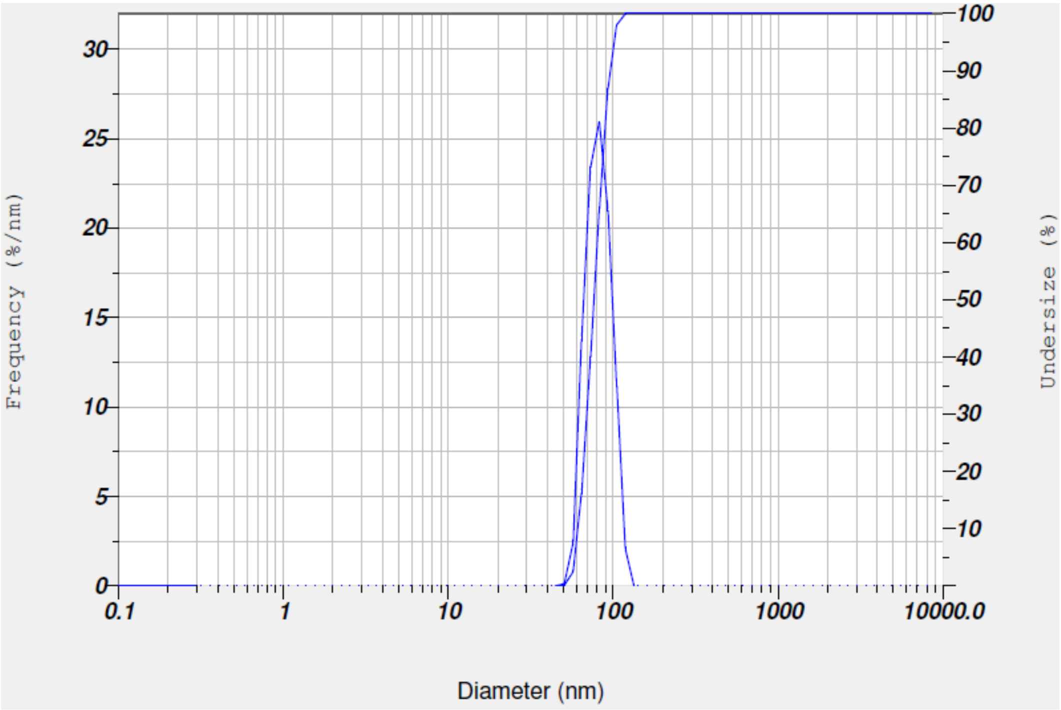


Fig. 4.2 Histogram of nanoscale ZnO particles of (mean size 77 nm) analyzed using Particle size analyzer.

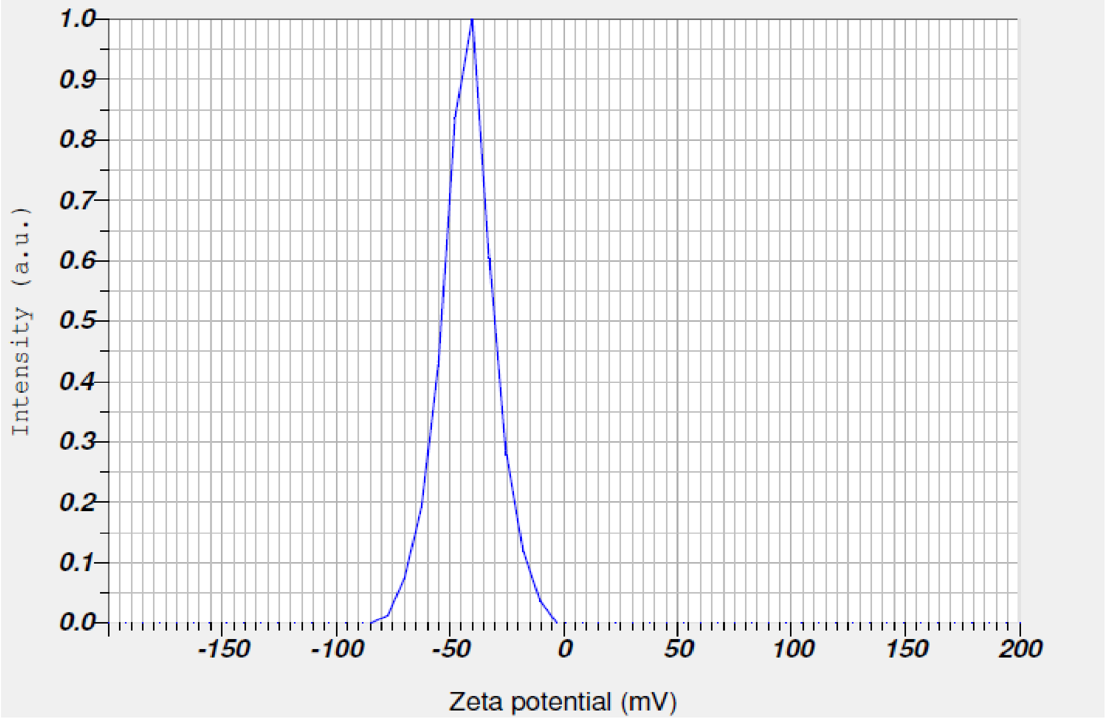


Fig. 4.3 Zeta potential of nanoscale ZnO particles (-42.1 mV) analyzed by Particle size analyzer.

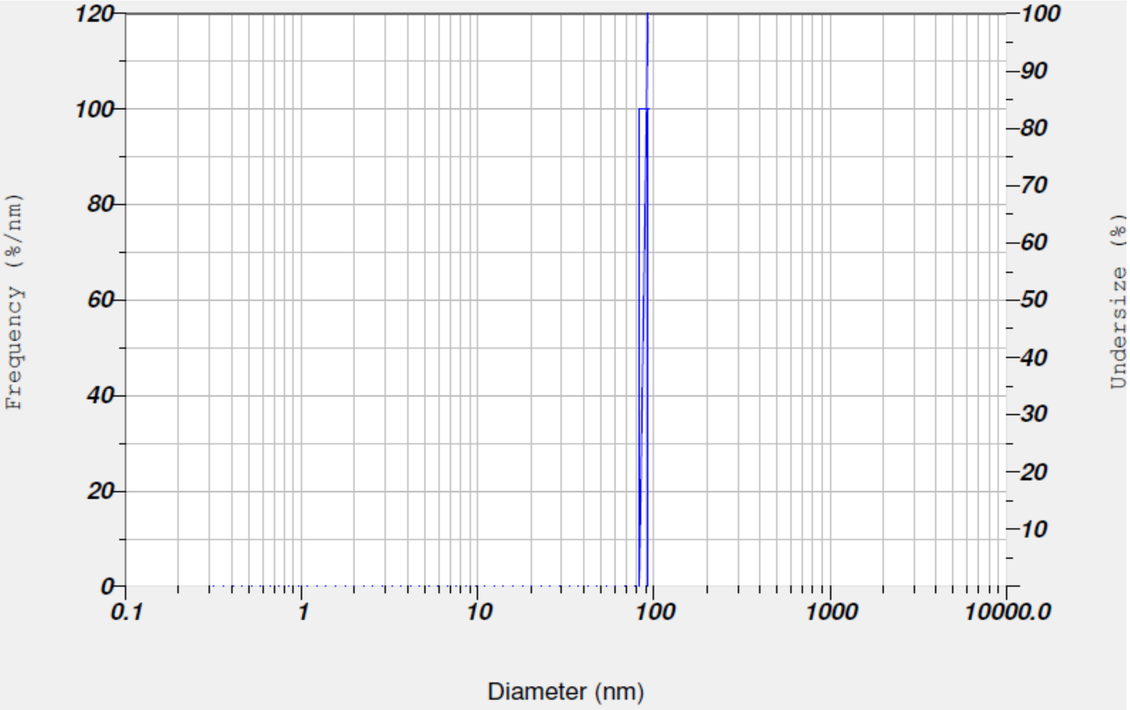


Fig. 4.4 Histogram of nanoscale ZnO particles (mean size 87.5 nm) analyzed using Particle size analyzer.

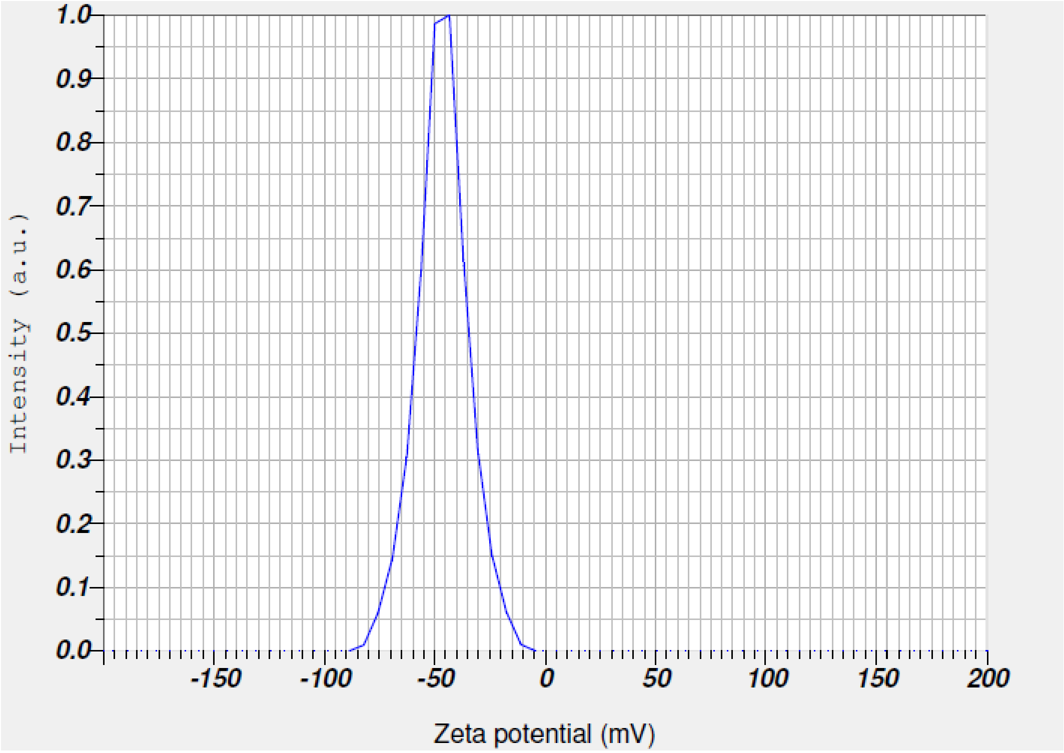


Fig. 4.5 Zeta potential of nanoscale ZnO particles (-46.4 mV) analyzed by Particle size analyzer

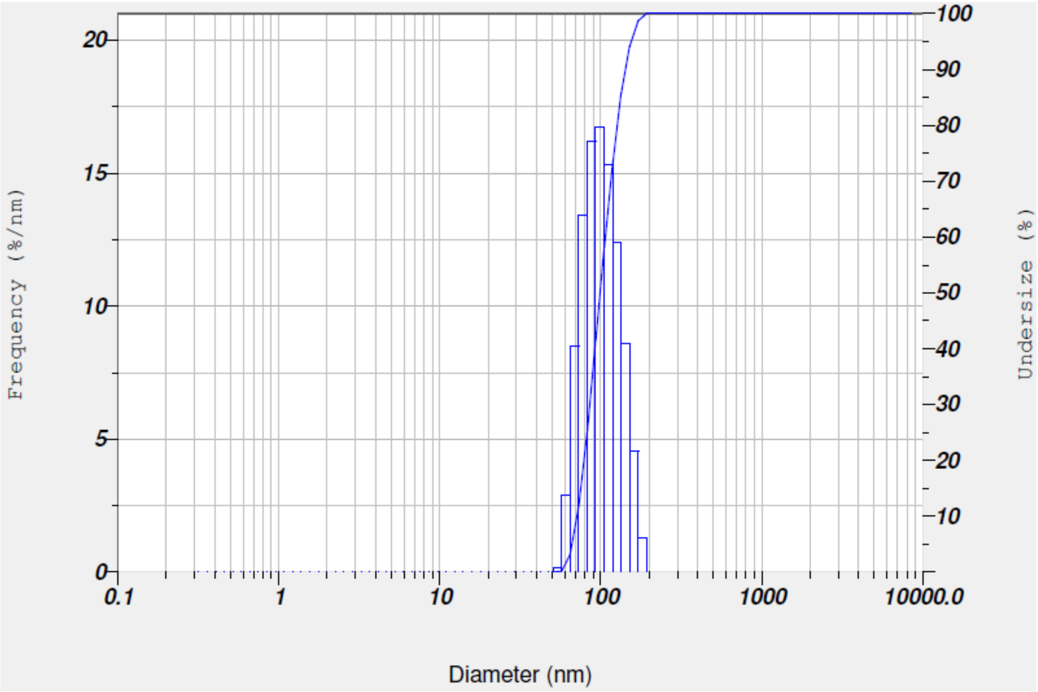


Fig. 4.6 Histogram of nanoscale ZnO particles (mean size 98.5 nm) analyzed using Particle size analyzer.

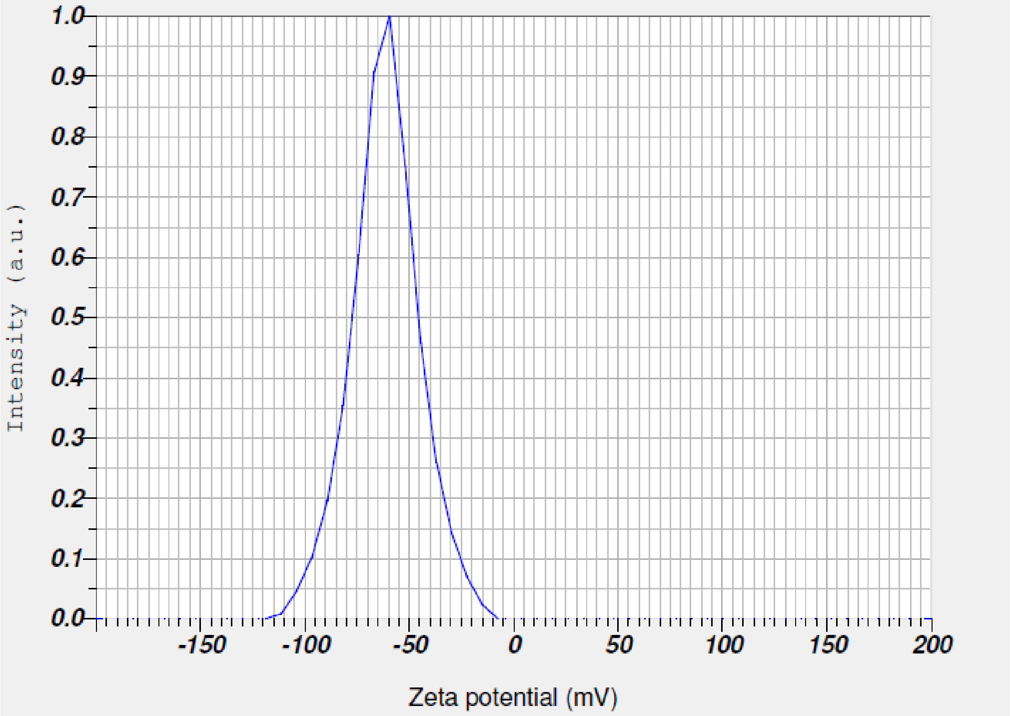


Fig. 4.7 Zeta potential of nanoscale ZnO particles (-61.3 mV) analyzed by Particle size analyzer

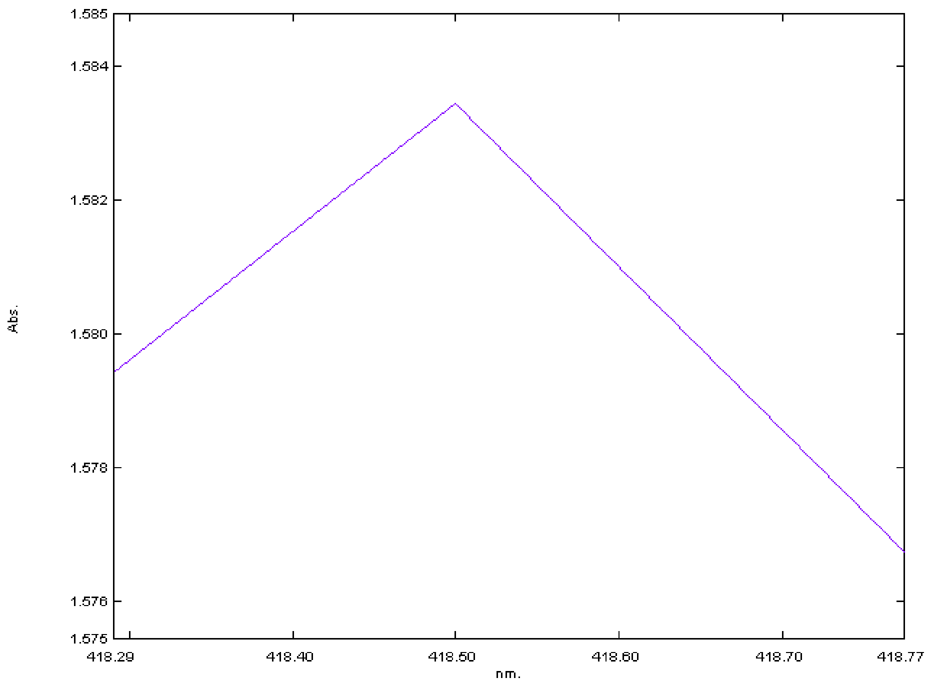


Fig. 4.8 UV-Vis absorption peak of nanoscale ZnO particles of size 20 nm at 418 nm recorded using UV-Vis spectrophotometer.

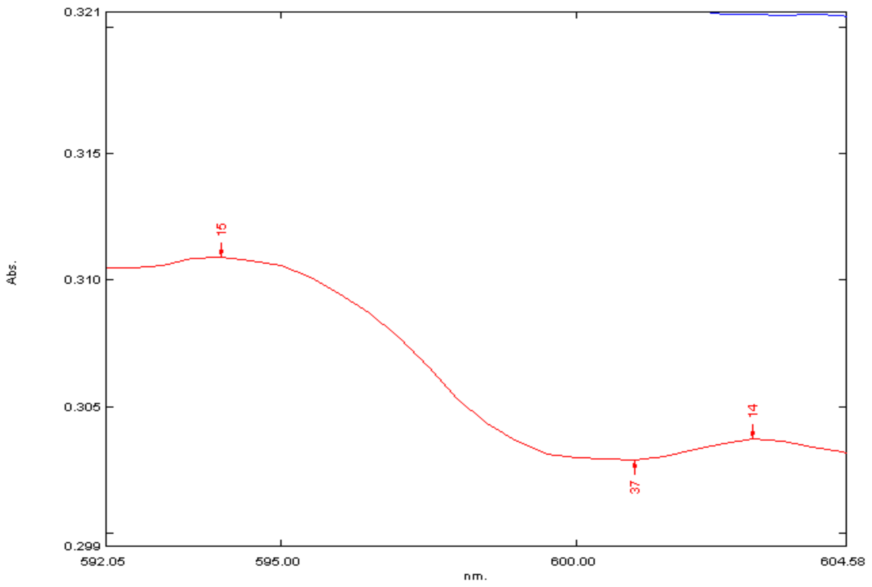


Fig. 4.9 UV-Vis absorption peak of nanoscale ZnO particles of size 25 nm at 593 nm recorded using UV-Vis spectrophotometer.

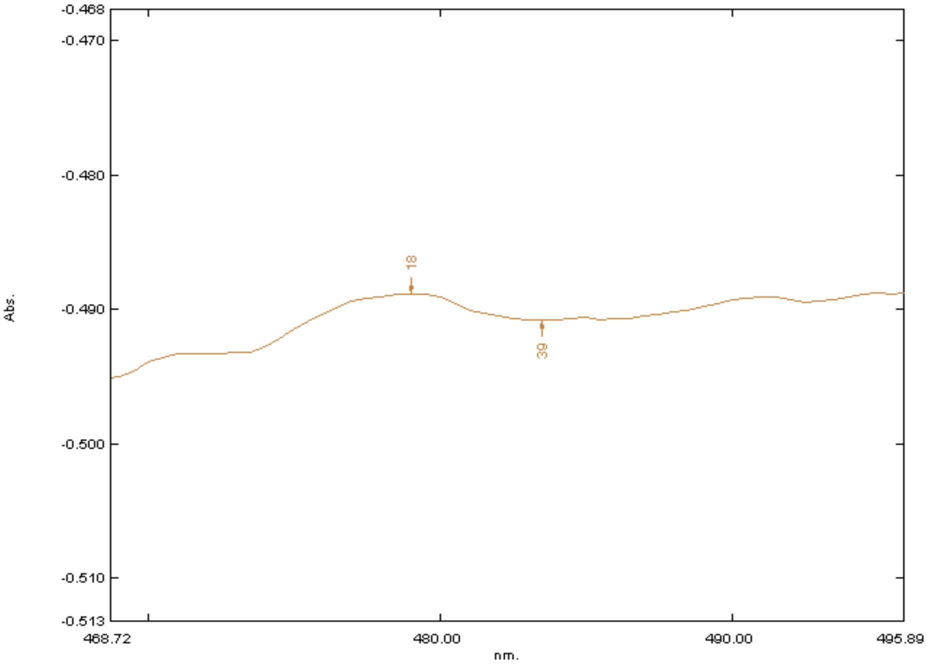


Fig. 4.10 UV-Vis absorption peak of nanoscale ZnO particles of size 30 nm at 460 nm recorded using UV-Vis spectrophotometer.

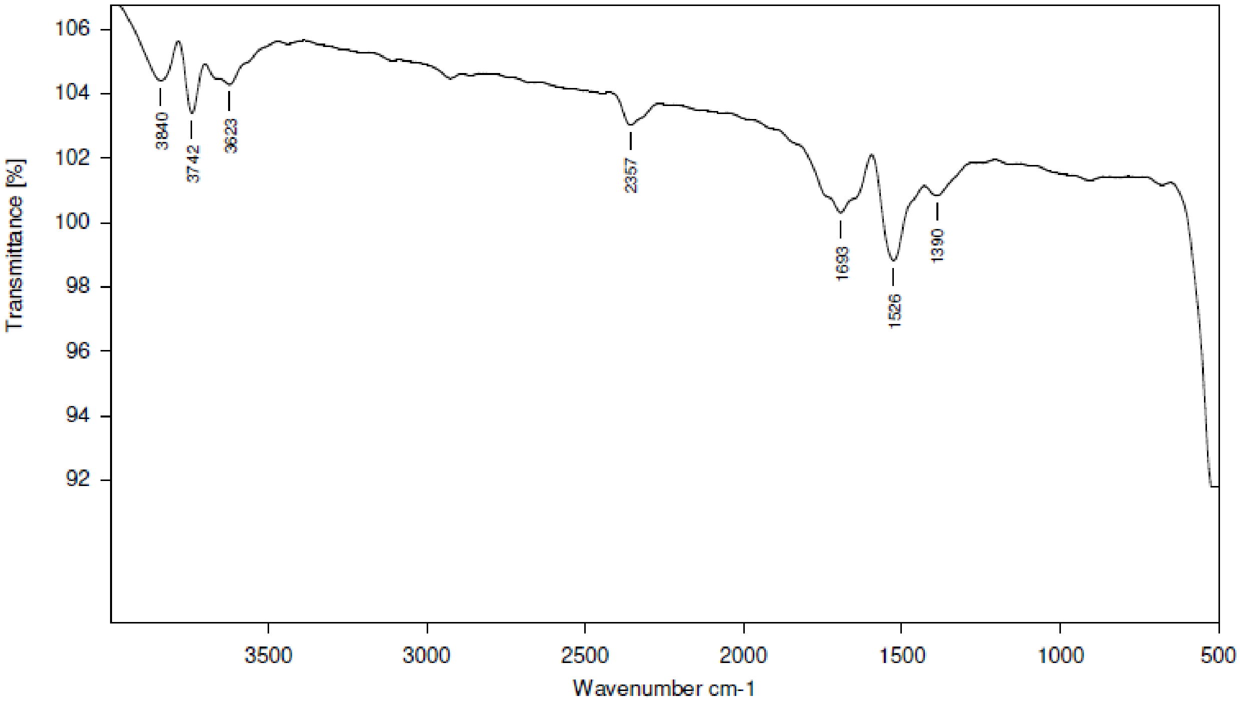


Fig. 4.11 FT-IR micrograph confirming the presence of different functional groups on the surface of the ZnO nanoparticles (20 nm)

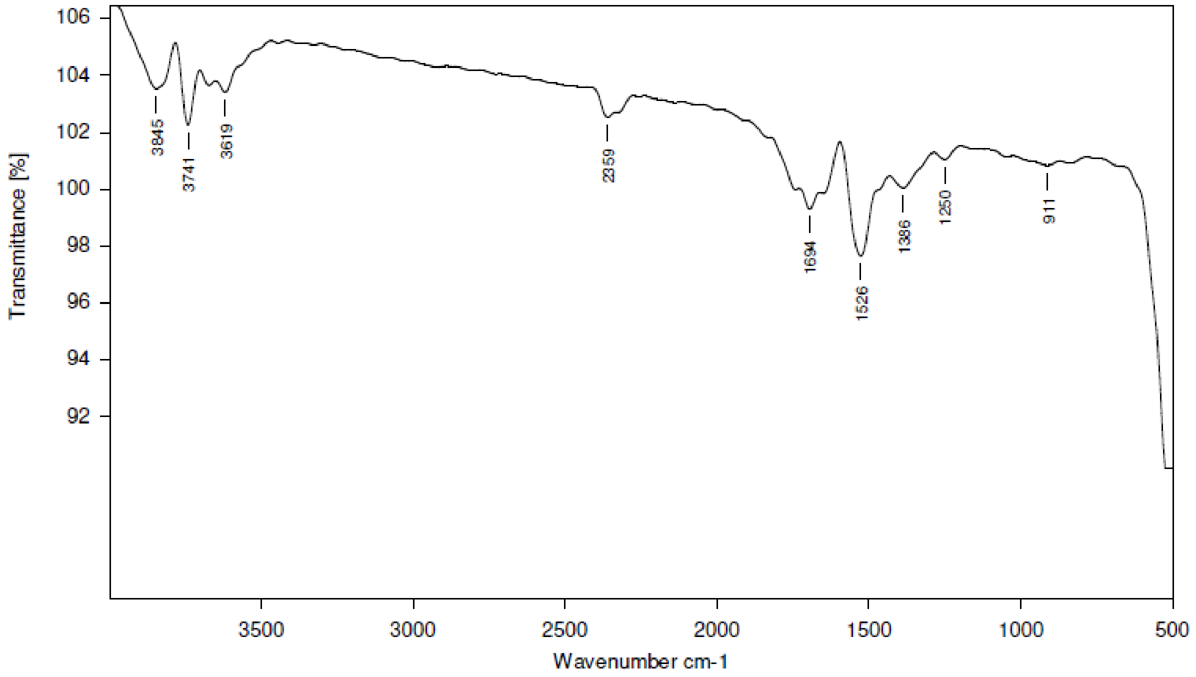


Fig. 4.12 FT-IR micrograph confirming the presence of different functional groups on the surface of the ZnO nanoparticles (25 nm)

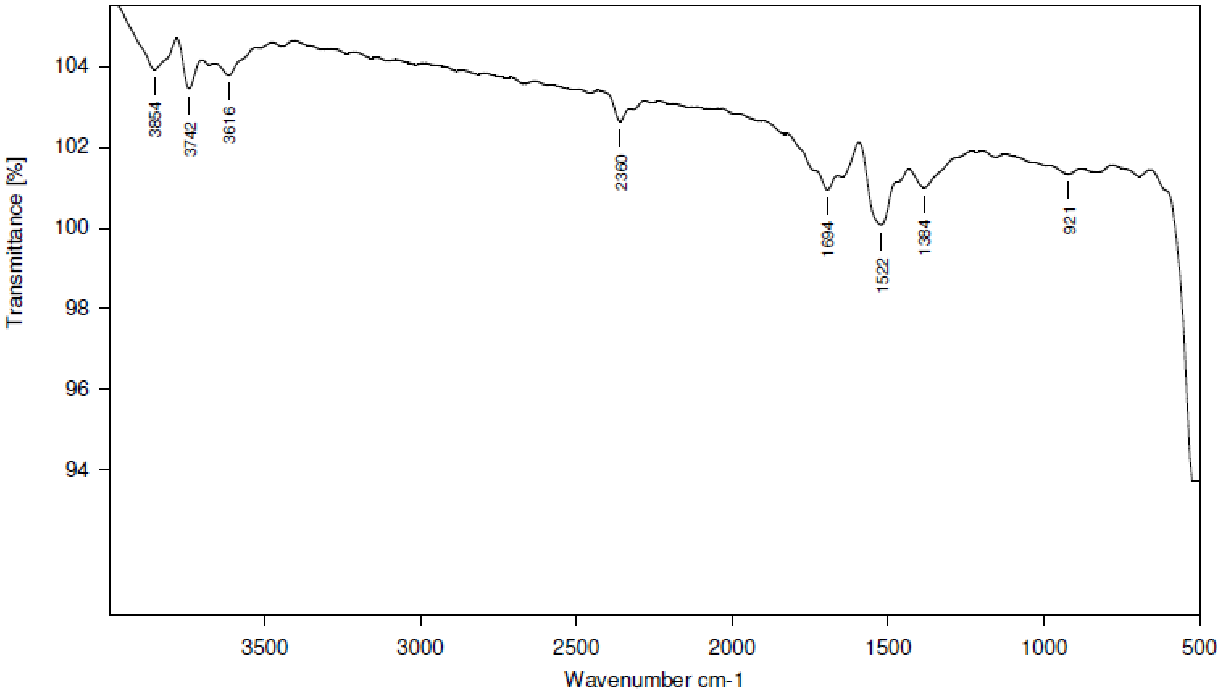


Fig. 4.13 FT-IR micrograph confirming the presence of different functional groups on the surface of the ZnO nanoparticles (30 nm)

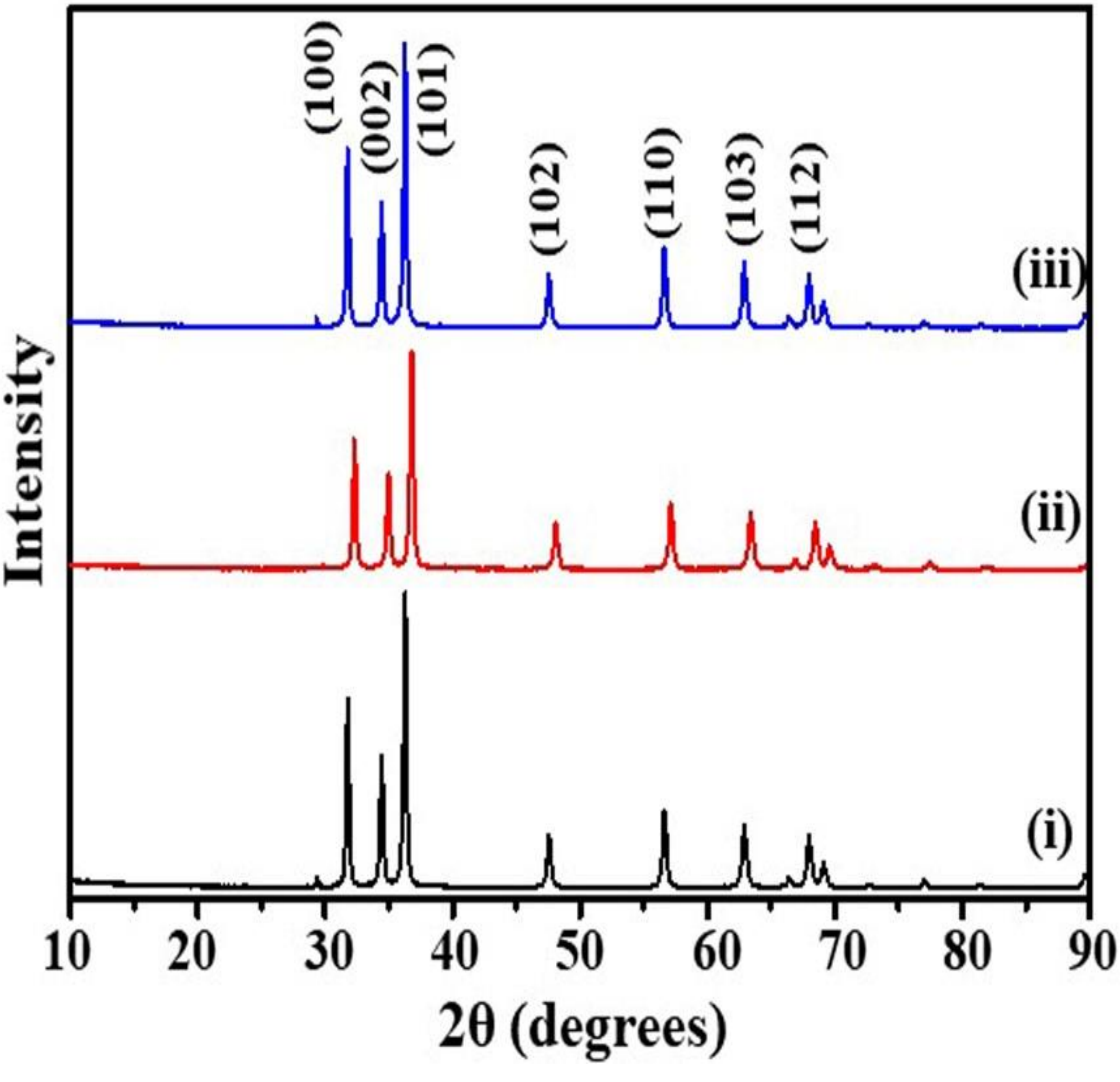


Fig. 4.14 The XRD spectra of ZnO nanoparticles with different sizes at (i) 20 (ii) 25 and (iii) 30 nm.

At 60 DAS, numerically highest plant height (39.67 cm) was observed with the application of nanoscale zinc oxide particles (n-ZnO) of size 20 nm @ 400 ppm (T_4) which was 21 % more than control and 21 % more than bulk $ZnSO_4$ @ 2000 ppm.

At 90 DAS, numerically highest plant height (43.2 cm) was observed with the application of nanoscale zinc oxide particles (n-ZnO) of size 20 nm @ 150 ppm (T_6) which was 25 % more than control and 17 % more than bulk $ZnSO_4$ @ 2000 ppm.

Zinc has a number of fundamental functions in plant systems such as synthesis of indole-acetic acid (IAA), a phyto-hormone which dramatically regulates plant growth (Cakmak, 2000). The Zinc deficiency symptoms were directly visible in the plant height as Zn deficiency reduces the internodal distance in plants and hence reduces the overall plant height. These results were in accordance with the results obtained by Prasad *et al*. (2012), Singh *et al*. (2013), Laware *et al*. (2014), Benzon *et al*. (2015), Subbaiah *et al*. (2016), Harish and Gowda (2017) and EI-Metwally *et al*. (2018).

4.2.3 Leaf area index

Leaf area index measured at different growth stages during the crop period *viz.*, 30, 60 and 90 DAS was presented in Table No. 4.1. It has been observed that at 30 DAS, there was a significant difference in leaf area index. The maximum leaf area index (1.47 m^2) was recorded with the application of n- ZnO of size 20 nm @ 200 ppm (T_5) when compared to control and bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_7 (1.37 m^2) and T_9 (1.38 m^2).

At 60 DAS, a significant difference in leaf area index (4.25 m^2) was recorded with the application of n- ZnO particles of size 20 nm @ 400 ppm (T_4) when compared to control and bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_3 (3.21 m^2) and T_6 (3.37 m^2).

At 90 DAS, significant difference in leaf area index (3.27 m^2) was recorded with the application of n- ZnO of size 20 nm @ 400 ppm (T_4) when compared to control and bulk $ZnSO_4$ @ 2000 ppm and it is on par with T_{11} (3.18 m^2), T_6 (3.16 m^2), T_{12} (3.13 m^2), T_{10} (2.92 m^2), T_3 (2.85 m^2), T_7 (2.81 m^2) treatments.

Leaves play an important role in photosynthesis. Studies indicated that zinc deficiency leads to a reduction in photosynthesis and thereby affect the rate of appearance and growth of leaves (Jezek *et al.*, 2015). Zinc is necessary for chlorophyll production which resulted in increased photosynthesis with more leaf area. When these nutrients was applied in nano form, due to their less particle size and stability and availability of nutrients at any particular time of crop requirement was more compared to bulk nutrients which resulted in higher leaf area index than bulk nutrients. These results were in good agreement with the results obtained by Subbaiah *et al.* (2016), Singh *et al.* (2017), Jyothi *et al.* (2017).

4.2.4 Dry matter production (kg ha^{-1})

The data on dry matter production was represented in Table No 4.2. There was a significant difference observed in dry matter production. Maximum dry matter production (5987 kg ha^{-1}) recorded with T_9 treatment (n- ZnO particles of size 25 nm @ 150 ppm) which is 18 % more than control and 15 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_6 (5980 kg ha^{-1}), and T_7 (5980 kg ha^{-1}). Such an increase can be ascribed to higher precursor activity of nanoscale zinc in auxin production which leads to the production of more dry matter (Kobayashi and Mizutani, 1970). The mobility of the nanoparticles is known to be very high which ensures the phloem transport and ensures the nutrient to reach all parts of the plant and thereby affecting the conversion rate of available radiation to higher dry-matter accumulation and these results were in good agreement with the results obtained by Subbaiah *et al*. (2016), Saraswathi *et al.*, (2017), Bakhtiari *et al.* (2017), Bakhtiari *et al.* (2015), Jyothi *et al*. (2017).

4.2.5 Number of nodules plant $^{-1}$

Number of nodules plant^{-1} was significantly influenced by different sizes and concentrations of n- ZnO particles and are presented in Table No 4.2. Significantly higher number of nodules plant^{-1} (63.86) was noticed with the T_9 treatment n- ZnO of size 25 nm @ 150 ppm which is 34 % more than control and 26 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_5 (58.5), T_{10} (54.7), and T_7 (54.36) and these results were in good agreement with the results obtained by Mogaddam *et al.* (2017).

4.2.6 Number of pods plant $^{-1}$

Number of pods plant^{-1} was significantly influenced by different sizes and concentrations of n-ZnO particles and the results were presented in Table No. 4.3.

A higher number of pods plant^{-1} (29.5) was recorded with the T_9 treatment (n-ZnO of size 25nm @ 150 ppm) which is 43.5 % more than control and 30.5 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_7 (27.16), T_{10} (24) and T_6 (23.66). This results were in agreement with Potarzycki and Grzebisz (2009), Prasad *et al*. (2012), Farina *et al.* (2015), Subbaiah *et al*. (2016), Janmohammadi *et al.* (2016), Ewais *et al.* (2017), Jyothi *et al*. (2017), EI-Metwally *et al*. (2018).

4.2.7 Number of filled pods plant $^{-1}$

Number of filled pods plant^{-1} was significantly influenced by different sizes and concentrations of n- ZnO particles and the results are represented in Table no. 4.3. A significantly higher number of filled pods plant^{-1} (23) was noticed with the T_7 treatment n- ZnO of size 25nm @ 400 ppm which is 45 % more than control and 31 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_{10} (20.83), T_9 (19.5), T_6 (19.16), T_{12} (19.16) and T_{11} (18.33).

The beneficial effect of application of nano nutrients resulted in higher leaf area which resulted in increased photosynthesis and production of more photosynthates leads to improved source sink relationship, with efficient translocation of photosynthates to the grains subsequently reflected in the improved number of filled grains panicle^{-1} and these results were in accordance with results obtained by Potarzycki and Grzebisz (2009), Prasad *et al*. (2012), Ewais *et al.* (2017).

4.2.8 100 Pod weight (g)

It has been observed that, there is a significant difference in 100 pod weight among the treatments and the results were represented in Table No. 4.3. The highest 100 pod weight was recorded with the T_9 treatment (n- ZnO of size 25 nm @ 150 ppm) which is 45 % more than control and 31 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_4 (108.15) and T_{10} (107.97) and these results were in good agreement with Prasad *et al*. (2012), Armin *et al.* (2014), Benzon *et al*. (2015).

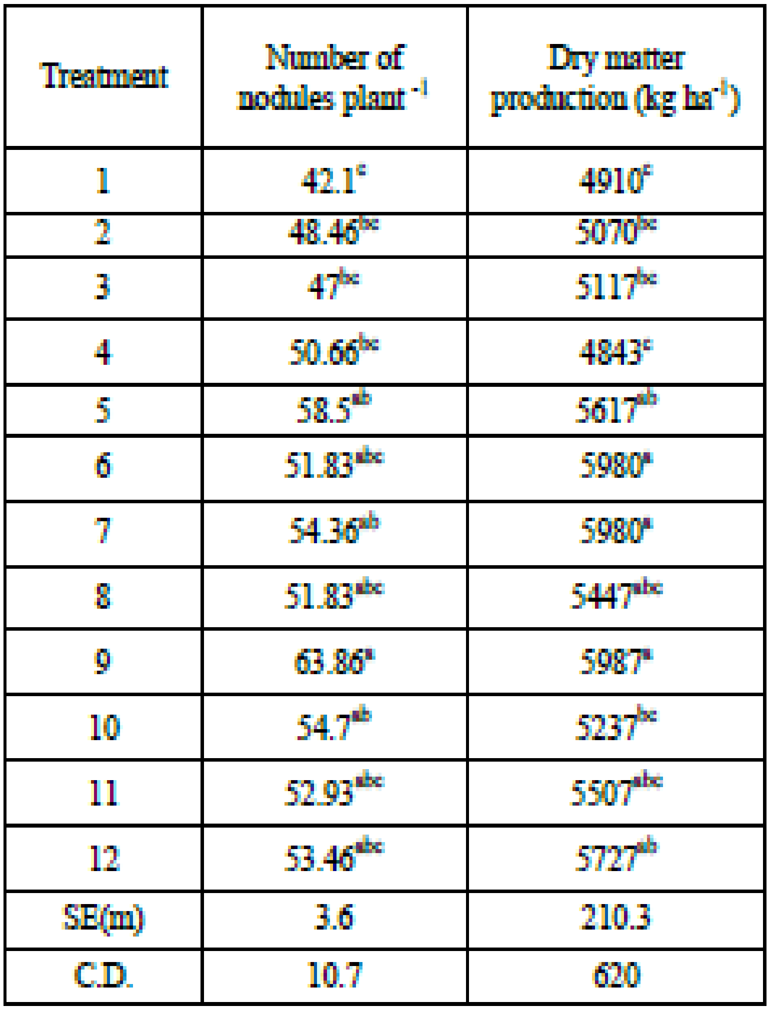
4.2.9 100 Kernel weight (g)

The test weight of 100 kernels is a variable attributes and the results were represented in Table No. 4.3. The treatments were significantly differed from each other. The highest 100 kernel weight was recorded with the T_9 treatment (n-ZnO of size 25 nm @ 150 ppm) which is 45 % more than control and 31 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_4 (42.91) and T_{10} (42.83)

Table 4.1. Effect of nanoscale ZnO particles on plant population, plant height and leaf area index of groundnut at different stages.

Treatment	Plant population		30 DAS		60DAS		90DAS	
	Initial	Final	Plant height (cm)	Leaf area index	Plant height (cm)	Leaf area index	Plant height (cm)	Leaf area index
1	30^{a}	27.33^{a}	16de	0.89^{c}	31.33^{d}	2.44^{bc}	32.42^{cd}	2.59^{ab}
2	29.3^{a}	29^{a}	16.66^{bcde}	1.04^{bcd}	34.33^{abcd}	2.24^{c}	38.21^{abcd}	2.10^{b}
3	29^{a}	27.33^{a}	18.66^{abc}	0.98^{cd}	31.33^{d}	3.21^{b}	35.75^{bcd}	2.85^{a}
4	28^{a}	27.33^{a}	17.66^{abcd}	1.09^{bcd}	39.67^{a}	4.25^{a}	39.30^{abc}	3.27^{a}
5	30.33^{a}	29.33^{a}	14.66^{e}	1.47^{a}	32^{cd}	2.92^{bc}	33.66^{bcd}	2.76^{ab}
6	31.33^{a}	29.67^{a}	18.33^{abcd}	1.05^{bcd}	39^{ab}	3.37^{b}	43.2^{a}	3.16^{a}
7	30.33^{a}	29.67^{a}	16.33^{cde}	1.37^{ab}	32.33^{cd}	2.66^{bc}	34^{bcd}	2.81^{a}
8	30.33^{a}	29.67^{a}	17.66^{abcd}	0.98^{cd}	29.67^{d}	2.99^{bc}	31.74^{d}	2.77^{ab}
9	30.67^{a}	28.33^{a}	19.33^{a}	1.38^{ab}	38^{abc}	2.9^{bc}	37.9^{abcd}	2.76^{ab}
10	30.33^{a}	30^{a}	17.33^{abcd}	1.07^{bcd}	34.67^{abcd}	2.88^{bc}	38.86^{abcd}	2.92^{a}
11	29^{a}	27.67^{a}	19^{ab}	1.31^{abc}	33.33^{bcd}	2.93^{bc}	36.62^{abcd}	3.18^{a}
12	29.33^{a}	28^{a}	18.66^{abc}	1.2^{abcd}	33.33^{bcd}	2.76^{bc}	40.55^{ab}	3.13^{a}
SE(m)	1.18	1.02	0.775	0.11	1.83	0.283	2.08	0.62
CD	NS	NS	NS	0.323	NS	0.835	NS	0.21

Table 4.2. Effect nano scale ZnO particles on number of nodules, dry matter production of groundnut



Treatment	Number of nodules plant $^{-1}$	Dry matter production (kg ha^{-1})
1	42.1^{c}	4910^{c}
2	48.46^{bc}	5070^{bc}
3	47^{bc}	5117^{bc}
4	50.66^{bc}	4843^{c}
5	58.5^{ab}	5617^{ab}
6	51.83^{abc}	5980^{a}
7	54.36^{ab}	5980^{a}
8	51.83^{abc}	5447^{abc}
9	63.86^{a}	5987^{a}
10	54.7^{ab}	5237^{bc}
11	52.93^{abc}	5507^{abc}
12	53.46^{abc}	5727^{ab}
SE(m)	3.6	210.3
C.D.	10.7	620

Zinc plays a key role as an activator of enzymes in plants and it involved in the biosynthesis of auxin, which produces more cells and dry matter that in turn will be stored in seeds as sink. Thus, the increase in kernels is more expected (Devlin and Withan 1983) and the results obtained were in good accordance with results obtained by Farina *et al.* (2015), Bhaktiari *et al.* (2015), Subbaiah *et al.* (2016), Janmohammadi *et al.* (2016), Rameshraddy *et al.* (2017).

4.2.10 Shelling percentage (%)

The data regarding shelling percentage was presented in Table No. 4.3. There was a significant difference observed in shelling percentage among the treatments. The maximum shelling percentage (71.16) was observed in T_9 treatment (n- ZnO particles of size 25 nm @ 150 ppm) which is 16 % more than control, 10 % more than bulk $ZnSO_4$ @ 2000 ppm and on a par with T_4 (70.03) n- ZnO particles of size 20 nm @ 400 ppm. The next best treatments were T_{10} (69.2) and T_7 (68.96). The results obtained were in good agreement with results obtained by Prasad *et al.* (2012), Adhikari *et al.* (2014).

4.2.11 Pod yield (kg ha^{-1})

The data pertaining to pod yield was significantly influenced by different sizes and concentrations of n- ZnO particles and the results are represented in Table No. 4.4. The maximum pod yield (2638 kg ha^{-1}) was recorded in the treatment n- ZnO particles of size 25 nm 150 ppm (T_9) which is 25 % more than control, 15.5 % more than bulk $ZnSO_4$ @ 2000 ppm and on a par with T_6 treatment (2612 kg ha^{-1}) (n- ZnO particles of size 20 nm @ 150 ppm). The next best treatments were T_{11} (2571 kg ha^{-1}) and T_7 (2552 kg ha^{-1}).

Zinc is necessary for chlorophyll production which resulted in increased photosynthesis with more leaf area and it involved in the biosynthesis of Auxins, which produces more cells and dry matter that in turn will be stored in seeds as sink. Thus, the increase in kernel yield which ultimately increased the pod yield. (Devlin and Withan 1983). These results were in good agreement with the results obtained by Prasad *et al*. (2012), Tarafdar *et al.* (2014), Subbaiah *et al.* (2016), Janmohammadi *et al.* (2016), Harish and Gowda (2017), Rameshraddy *et al.* (2017), Saraswathi *et al* (2017), Singh *et al.* (2017), Jyothi *et al*. (2017), EI-Metwally *et al*. (2018).

4.2.12 Haulm Yield (kg ha^{-1})

It has been observed that the haulm yield was significantly influenced by different sizes and concentrations of n- ZnO particles and the results were represented in Table No. 4.4. The maximum haulm yield (3425 kg ha^{-1}) was recorded with the treatment n- ZnO particles of size 25 nm 400 ppm (T_7) which is 14.5 % more than control, 19 % more than bulk $ZnSO_4$ @ 2000 ppm and on a par with T_6 (3365 kg ha^{-1}) (n- ZnO particles of size 20 nm @ 150 ppm). The next best treatment is T_5 (3204 kg ha^{-1}) followed by T_8 (3113 kg ha^{-1}), T_{12} (3009 kg ha^{-1}), T_9 (3001 kg ha^{-1}) and T_{11} (2933 kg ha^{-1}).

High dry matter accumulation ultimately in turn increased the haulm yield (Devlin and Withan 1983). These are in accordance with results obtained by Bhaktiari *et al.* (2015), Farina *et al,* (2015), Janmohammadi *et al.* (2016).

4.2.13 Harvest Index (%)

The results regarding harvest index were represented in Table No. 4.4. There was a significant difference observed in harvest index among the treatments. The maximum harvest index (46.73) was observed in T_9 treatment (n-ZnO particles of size 25 nm @ 150 ppm) which is more than control and bulk $ZnSO_4$ @ 2000 ppm. The result is on par with T_{11} (46.64) n- ZnO particles of size 30 nm @ 200 ppm and the next best treatments were T_4 (45.41) and T_{10} (45.58).

The mobility of the nanoparticles is known to be very high which ensures

Table 4.3. Effect nano scale ZnO particles on number of pods, filled pods, 100 pod weight, 100 kernel weight and shelling percentage of groundnut

Treatment	No. of pods plant^{-1}	No. of filled pods plant^{-1}	100 pod weight (g)	100 kernel weight (g)	Shelling %
1	16.66^{d}	12.66^{e}	91.52^{c}	39.46^{bc}	59.56^{e}
2	23.5^{bc}	17.83^{bcd}	89.93^{c}	40.13^{bc}	61.33^{de}
3	20.5^{cd}	15.83^{cde}	93.91^{c}	42.20^{bc}	63.96^{cd}
4	23^{bc}	18.66^{abcd}	108.15^{ab}	42.91^{b}	70.03^{a}
5	19.5^{cd}	15.83^{cde}	98.30^{bc}	39.60^{bc}	68.2^{abc}
6	23.66^{bc}	19.16^{abcd}	98.97^{bc}	41.12^{bc}	64.8^{bcd}
7	27.16^{ab}	23^{a}	101.75^{abc}	40.82^{bc}	68.96^{ab}
8	17.16^{d}	14.5^{de}	88.80^{c}	40.70^{bc}	67.06^{abc}
9	29.5^{a}	19.5^{abc}	114.58^{a}	46.46^{a}	71.16^{a}
10	24^{bc}	20.83^{ab}	107.97^{ab}	42.83^{b}	69.2^{ab}
11	21.5^{cd}	18.33^{abcd}	93.46^{c}	38.97^{c}	67.66^{abc}
12	21.83^{bcd}	19.16^{abcd}	101.63^{abc}	40.36^{bc}	67.53^{abc}
SE(m)	1.92	1.96	4.19	1.19	1.34
CD	5.91	5.79	12.4	3.5	3.97

Table 4.4. Effect nano scale ZnO particles on pod yield, haulm yield and harvest index of groundnut.

Treatment	Pod yield (kg ha^{-1})	Haulm yield (kg ha^{-1})	Harvest Index
1	1981^{d}	2927^{c}	40.36^{c}
2	2091^{cd}	2913^{bc}	41.78^{bc}
3	2228^{bcd}	2780^{bc}	44.5^{abc}
4	2193^{cd}	2642^{c}	45.41^{ab}
5	2402^{abc}	3204^{ab}	42.8^{abc}
6	2612^{a}	3365^{a}	43.7^{abc}
7	2552^{ab}	3425^{a}	42.72^{abc}
8	2314^{abcd}	3113^{abc}	42.69^{abc}
9	2638^{a}	3001^{abc}	46.73^{a}
10	2371^{abc}	2835^{bc}	45.58^{ab}
11	2571^{ab}	2933^{abc}	46.64^{a}
12	2426^{abc}	3009^{abc}	44.63^{abc}
SE(m)	103.7	131.3	1.25
CD	306.3	387	3.7

the phloem transport and ensures the nutrient to reach all parts of the plant and thereby affecting the conversion rate of available radiation to higher dry-matter accumulation which ultimately leads to increase in harvest index. The results were in good agreement with the results obtained by Benzon *et al.* (2015), Farina *et al.* (2015), Janmohammadi *et al.* (2015).

4.3 POST-HARVEST CONCENTRATION OF NUTRIENTS IN LEAF, STEM AND KERNEL AT HARVEST

The data on nutrient content (N, P, K, Cu, Fe, Mn and Zn) i. e macro and micro nutrients of groundnut at harvest as influenced by the application of nano ZnO and bulk $ZnSO_4$ are presented in the Table 4.5 and 4.6 respectively.

4.3.1 Concentration of macronutrients in leaf, stem, kernel at harvest

4.3.1.1 Nitrogen content (%)

At harvest, the concentration of nitrogen in groundnut leaves, stem was numerically higher in when compared to control and bulk $ZnSO_4$ @ 2000 ppm but they are not significantly different. Highest leaf N content (0.84 percent) was observed in treatment of 100 percent RDF (T_2) when compared to other treatments.

Highest stem N content (0.7 percent) was observed in treatment n-ZnO of size 25nm @ 400 ppm treatment (T_7) when compared to other treatments. Significantly, highest kernel N content (0.49 percent) was observed in T_{10} treatment n-ZnO of size 30 nm @ 400 ppm which is 45 % more than control and 49 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_2 (0.44), T_{12} (0.41),, T_7 (0.40), and T_9 (0.40) and these results were in good agreement with results obtained by Afsar *et al.* (2012), Singh *et al.* (2017) and EI-Metwally *et al.* (2018).

4.3.1.2 Phosphorous content (%)

At harvest, the concentration of Phosphorous in groundnut leaves, stem and kernel was significantly higher when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf P content (0.23 per cent) was observed in treatment n-ZnO of size 30 nm @ 400 ppm (T_{10}) which is 73 % more than control, 43 % more than bulk $ZnSO_4$ @ 2000 ppm and it is on par with T_{11} (0.22) n- ZnO of size 30 nm @ 400 ppm. The next best treatments were T_9 (0.17) and T_{12} (0.14).

Highest stem P content (0.27 percent) was observed in treatment T_{10} (n-ZnO of size 30 nm @ 400 ppm) which is 70 % more than control and 66.6 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_5 (0.17) and T_6 (0.16).

Highest kernel P content (0.16 per cent) was observed with T_{12} treatment (n- ZnO of size 30 nm @ 150 ppm) which is 62.5 % more than control and 44 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_8 (0.15), T_7 (0.13), T_9 (0.13), T_5 (0.12) and T_6 (0.12) and these results were in good agreement with results obtained by Afsar *et al.* (2012), Singh *et al.* (2017) and EI-Metwally *et al.* (2018).

4.3.1.3 Potassium content (%)

At harvest, the concentration of potassium in groundnut leaves, stem and kernel was significantly higher in when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf K content (1.08 per cent) was observed in treatment n-ZnO of size 20 nm @ 400 ppm (T_4) which is 20 % more than control and 23 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_9 (1.03), T_{12} (1.03) and T_8 (0.99).

Highest stem K content (1.12 per cent) was observed in treatment T_7 (n-ZnO of size 25 nm @ 400 ppm) which is 15 % more than control and 20.5 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_{12} (1.10) and T_8 (1.09).

Highest kernel K content (0.7 per cent) was observed in both T_8 and T_{11} treatments n-ZnO of size 25 nm @ 200 ppm and n- ZnO of size 30 nm @ 200 ppm respectively, which is 20 % more than control and 10 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_3 (0.63), T_4 (0.63), T_7 (0.63) and T_{12} (0.63) and these results were in good agreement with results obtained by Afsar *et al.* (2012), Singh *et al.* (2017), EI-Metwally *et al.* (2018).

Optimal levels of zinc improve the uptake of phosphorus and potassium. Zinc plays a key role in chlorophyll which increases greenness that led to increased uptake of nutrients. The increase in total N, K and Zn uptake could be attributed to the synergistic effect between N and Zn and due to the positive interaction of K and Zn, respectively. The present findings support the results of Ashoka *et al*. (2008), Morshedi and Farahbakhsh (2010). The mobility of the nanoparticles is known to be very high which ensures the phloem transport and ensures the nutrient to reach all parts of the plant thereby affecting the enzyme reactions, increased dry-matter production which led to increased nutrient uptake. This may be the reason for higher zinc content in grain and lower zinc content in dry-matter at harvest with RDF along with nanoscale nutrients in combination than bulk form of nutrient.

4.3.2 Concentration of micro nutrients in leaf, stem, kernel at harvest

4.3.2.1 Copper content (ppm)

At harvest, the concentration of copper in groundnut leaves, stem and kernel was significantly higher in when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf Cu content (7.33 ppm) was observed in n- ZnO of size 30 nm @ 150 ppm (T_{12}) which is 50 % more than control and bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_{11} (6.66) and T_{10} (5.66).

Highest stem Cu content (6 ppm) was observed with T_9 treatment (n- ZnO of size 25 nm @ 150 ppm) which is 45 % more than control and 33 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were and T_{12} (5.6), T_{11} (5), T_{10} (5) and T_7 (5). Highest kernel Cu content (8 ppm) was observed in T_{11} treatment n-ZnO of size 30 nm @ 200 ppm which is 34 % more than control and 25 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_{12} (7),

T_8 (6.6), T_9 (6.3), T_5 (6), T_3 (6) and T_7 (5.6) and these results were in good agreement with results obtained by Mazaherinia *et al.* (2010).

4.3.2.2 Manganese content (ppm)

At harvest, the concentration of manganese in groundnut leaves, stem and kernel was significantly higher in when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf Mn content (37.3 ppm) was observed in treatment n-ZnO of size 30 nm @ 200 ppm (T_{11}) which is 28.6 % more than control and 48 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_5 (34.6) and T_{12} (34).

Highest stem Mn content (24 ppm) was observed in T_{12} treatment (n- ZnO of size 25 nm @ 150 ppm) which is 29 % more than control and 10 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_4 (22.6), T_5 (22.6), T_{10} (22.6) and T_3 (21.6).

Highest kernel Mn content (18.6 ppm) was observed in T_{11} treatment (n-ZnO of size 30 nm @ 200 ppm) which is 16 % more than control and 12 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_5 (17), T_8 (17), T_3 (16.3), T_4 (16.3), T_9 (16.3), T_7 (16) and T_{12} (16), and these results were in good agreement with results obtained by EI-Metwally *et al.* (2018).

Table 4.5. Effect of nanoscale ZnO particles on concentration of macro nutrients in leaf, stem and kernel at harvest

Treatment	N concentration (%)			P concentration (%)			K concentration (%)		
	Leaf	stem	kernel	Leaf	stem	kernel	Leaf	stem	Kernel
1	0.14^{c}	0.17^{b}	0.27^{de}	0.06^{e}	0.08^{e}	0.06^{e}	0.86^{cd}	0.95^{cde}	0.56^{b}
2	0.84^{a}	0.60^{ab}	0.44^{ab}	0.1^{cde}	0.13^{bcd}	0.08^{de}	0.84^{d}	0.97^{bcde}	0.60^{b}
3	0.39^{abc}	0.26^{ab}	0.25^{e}	0.13^{bcd}	0.09^{de}	0.09^{cd}	0.83^{d}	0.89^{de}	0.63^{ab}
4	0.28^{abc}	0.38^{ab}	0.35^{bcd}	0.11^{cde}	0.12^{bcde}	0.09^{cd}	1.08^{a}	0.94^{cde}	0.63^{ab}
5	0.27^{abc}	0.23^{ab}	0.31^{cde}	0.12^{cd}	0.17^{b}	0.12^{abc}	0.94^{bcd}	0.94^{cde}	0.60^{b}
6	0.37^{abc}	0.25^{ab}	0.35^{bcd}	0.14^{bcd}	0.16^{bc}	0.12^{abc}	0.85^{d}	0.84^{e}	0.60^{b}
7	0.79^{ab}	0.70^{a}	0.40^{abc}	0.09^{de}	0.1^{de}	0.13^{abc}	0.98^{abc}	1.12^{a}	0.63^{ab}
8	0.40^{abc}	0.27^{ab}	0.35^{bcd}	0.12^{cd}	0.11^{cde}	0.15^{ab}	0.99^{ab}	1.09^{ab}	0.70^{a}
9	0.29^{abc}	0.25^{ab}	0.40^{abc}	0.17^{b}	0.14^{bcd}	0.13^{abc}	1.03^{ab}	0.95^{cde}	0.60^{b}
10	0.17^{bc}	0.23^{ab}	0.49^{a}	0.23^{a}	0.27^{a}	0.11^{bcd}	0.92^{bcd}	0.98^{bcd}	0.56^{b}
11	0.29^{abc}	0.26^{ab}	0.37^{bc}	0.22^{a}	0.11^{cde}	0.11^{bcd}	0.95^{bcd}	1.03^{abc}	0.70^{a}
12	0.29^{abc}	0.34^{ab}	0.41^{abc}	0.14^{bc}	0.11^{cde}	0.16^{a}	1.03^{ab}	1.10^{ab}	0.63^{ab}
SE(m)	0.18	0.14	0.030	0.013	0.016	0.012	0.039	0.04	0.024
CD	NS	NS	0.09	0.039	0.047	0.036	0.110	0.110	0.069

Table 4.6. Effect of nanoscale ZnO particles on concentration of micro nutrients in leaf, stem and kernel at harvest

Treatments	Leaf (ppm)				Stem (ppm)				Kernel (ppm)			
	Cu	Mn	Fe	Zn	Cu	Mn	Fe	Zn	Cu	Mn	Fe	Zn
1	3.66^{cd}	26.6^{cdef}	218.3^{bcd}	13.3^{d}	3.3^{de}	17^{cd}	173.6^{d}	13^{c}	5.3^{c}	15.6^{b}	52.6^{ab}	29^{cde}
2	3.0^{d}	26^{def}	220.6^{bcd}	13.3^{d}	2.6^{e}	18.3^{bcd}	188.3^{cd}	13^{c}	5.3^{c}	15^{b}	52.3^{ab}	27.6^{de}
3	3.66^{cd}	19.3^{f}	195^{d}	14.3^{d}	4^{cde}	21.6^{abc}	204.6^{abcd}	19^{bc}	6^{bc}	16.3^{ab}	52.3^{ab}	32.6^{abc}
4	4.66^{bcd}	27.6^{bcde}	217.6^{bcd}	17.3^{cd}	4^{cde}	22.6^{abc}	217.3^{abc}	25^{ab}	5.6^{bc}	16.3^{ab}	54.3^{ab}	32.6^{abc}
5	4.33^{cd}	34.6^{ab}	217.6^{bcd}	15.6^{d}	4.6^{abcd}	22.6^{abc}	199^{abcd}	21^{abc}	6^{bc}	17^{ab}	54.3^{ab}	31.6^{bcd}
6	2.66^{d}	27.6^{bcde}	270.6^{ab}	28.6^{a}	4.3^{bcd}	17.3^{cd}	172.6^{d}	17.6^{bc}	5.3^{c}	15^{b}	49.3^{b}	26.6^{e}
7	5^{bcd}	28.3^{bcd}	205.6^{d}	14.6^{d}	5^{abc}	18^{cde}	193.3^{bcd}	18^{bc}	5.6^{bc}	16^{ab}	51^{b}	29.3^{cde}
8	4.66^{bcd}	26^{def}	296.6^{a}	22.6^{bc}	5^{abc}	15.3^{d}	241.3^{a}	18.6^{bc}	6.6^{bc}	17^{ab}	54.3^{ab}	34^{ab}
9	4^{cd}	20.3^{ef}	220.6^{bcd}	26.6^{ab}	6^{a}	19.3^{abcd}	218.6^{abc}	22^{ab}	6.3^{bc}	16.3^{ab}	52.3^{ab}	33^{abc}
10	5.66^{abc}	24^{def}	210.6^{cd}	16^{d}	5^{abc}	22.6^{abc}	234^{ab}	29.3^{ab}	5.3^{c}	15^{b}	49.6^{b}	28.6^{cde}
11	6.66^{ab}	37.3^{a}	265.6^{abc}	18.6^{cd}	5^{abc}	16.3^{d}	211^{d}	25^{ab}	8^{a}	18.6^{a}	58.3^{a}	37^{a}
12	7.33^{a}	34^{abc}	294.3^{a}	19.6^{cd}	5.6^{ab}	24^{a}	228^{abc}	23.3^{ab}	7^{ab}	16^{ab}	49.6^{b}	33^{abc}
SE(m)	0.69	2.26	16.96	1.89	0.46	1.46	13.11	1.89	0.46	1.46	1.92	1.32
CD	2.05	6.690	50.080	5.59	1.370	4.430	38.700	5.59	1.370	4.33	NS	3.900

4.3.2.3 Iron content (ppm)

At harvest, concentration of ferrous in groundnut leaves and stem was significantly higher but kernel Fe content is significantly not different when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf Fe content (296.6 ppm) was observed in treatment n- ZnO of size 25 nm @ 200 ppm (T_8) which is 26.3 % more than control, 34 % more than bulk $ZnSO_4$ @ 2000 ppm and it is on par with T_{12} n- ZnO of size 30 nm @ 150 ppm The next best treatments were T_6 (270.6) and T_{11} (265.6).

Highest stem Fe content (241.3 ppm) was observed in T_8 treatment n- ZnO of size 25 nm @ 200 ppm which is 28 % more than control and 15 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_{10} (234), T_{12} (228), T_9 (218.6), T_4 (217.3) and T_3 (204.6).

Numerically higher kernel Fe content (58.3 ppm) was observed in T_{11} treatment n-ZnO of size 30 nm @ 200 ppm which is 9.7 % more than control and 10 % more than bulk $ZnSO_4$ @ 2000 ppm. The results were in good agreement with results obtained by Mazaherinia *et al.* (2010), Prasad et al. (2012), Dhoke *et al.* (2013), EI-Metwally *et al.* (2018).

4.3.2.4 Zinc content (ppm)

At harvest, the concentration of zinc in groundnut leaves, stem and kernel was significantly higher in when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf Zn content (28.6 ppm) was observed in treatment n- ZnO of size 20 nm @ 150 ppm (T_6) which is 53.4 % more than control and 50 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_9 (26.6) and T_8 (22.6).

Highest stem Zn content (29.3 ppm) was observed in T_{10} treatment n- ZnO of size 30 nm @ 400 ppm which is 55.6 % more than control, 35 % more than bulk $ZnSO_4$ @ 2000 ppm and it is on par with T_{11} (25), T_4 (25), T_{12} (23.3) and T_9 (22).

Highest kernel Zn content (37 ppm) was observed in T_{11} treatment n-ZnO of size 30 nm @ 200 ppm which is 21.6 % more than control and 11.8 % more than bulk $ZnSO_4$ @ 2000 ppm. The next best treatments were T_8 (34), T_9 (33), T_{12} (33), T_3 (32.6) and T_4 (32.6).

Priester *et al*. (2012) studied the effect of ZnO nanoparticles on the growth of soybean and suggested that at a higher dose of ZnO nanoparticles, the seeds accumulated more zinc as compared to control. However, they have mentioned that the plant would prefer for the uptake of zinc as ionic zinc (Zn^{+2}) and not in nanoparticle form. Similar findings were reported by Peralta-Videa *et al*. (2014) revealed that Zn accumulation was significantly enhanced in all plant tissues including pods.

Prasad *et al*. (2012) suggested that the foliar application of nano ZnO provided superior results as compared to $ZnSO_4$ because of the higher solubility of $ZnSO_4$ and lower retention time, bio-availability of ionic zinc in case of $ZnSO_4$ was reduced. Further, ZnO in nanoscale form is absorbed by leaves to a greater extent as compared to $ZnSO_4$ and thereby increased the leaf Zn content and uptake. In the present study, the effect of foliar application of ZnO nanoparticles on the growth of groundnut was evaluated.

The results were in good agreement with results obtained by Mazaherinia *et al.* (2010), Moreno *et al.* (2010), Kim *et al.* (2011), Prasad *et al.* (2012), Dhoke *et al.* (2013), Tarafdar *et al.* (2014), Yuvaraj and Subramanian (2014b), Subbaiah *et al.* (2016) and EI-Metwally (2018).

4.4 POST-HARVEST CONCENTRATION OF NUTRIENTS IN SOIL AT HARVEST

4.4.1 Concentration of macro and micronutrients in the soil after harvest

The data on nutrient content (N, P, K, Cu, Fe, Mn and Zn) after harvest of groundnut as influenced by the application of nano ZnO and bulk ZnO are presented in Table 4.7

4.4.1.1 Available nitrogen content (kg ha^{-1})

It was observed that there was no significant difference between the treatments because in all the treatments micronutrients applied through foliar spray. Numerically higher content of N (282.9 kg ha^{-1}) was observed in observed in T_8 treatment n-ZnO of size (25 nm) @ 200 ppm and all treatments were on par with each other.

4.4.1.2 Available phosphorous content (kg ha^{-1})

It was observed that there was no significant difference between the treatments. Numerically higher content of P (45.50 kg ha^{-1}) was observed in T_6 treatment n-ZnO of size (20 nm) @ 150 ppm and all treatments are on par with each other.

4.4.1.3 Available potassium content (kg ha^{-1})

The results revealed that there was no significant difference between the treatments. Numerically higher content of K (198.8 kg ha^{-1}) was observed in T_2 treatment with 100 per cent RDF and all treatments are on par with each other.

4.4.1.4 Copper content (mg kg^{-1})

It has been observed that there was no significant difference between the treatments because all the treatments are foliar applied. Numerically higher content of Cu (1.57 mg kg^{-1}) was observed in T_5 treatment n-ZnO of size (20 nm) @ 200 ppm and all treatments are on par with each other.

4.4.1.5 Manganese content (mg kg^{-1})

No significant difference was observed between the treatments. Numerically higher content of Mn (26.94 mg kg^{-1}) was observed in T_1 treatment that is control and all treatments are on par with each other.

4.4.1.6 Iron content (mg kg^{-1})

The results proved that there was no significant difference between the treatments. Numerically higher content of Fe (10.59 mg kg^{-1}) was observed in T_1 treatment that is control and all treatments are on par with each other.

4.4.1.7 Zinc content (mg kg^{-1})

It has been observed that there was no significant difference between the treatments because all the n-ZnO treatments are foliar applied. Numerically higher content of Zn was observed in (16.91 mg kg^{-1}) was observed in T_9 treatment n-ZnO of size (25 nm) @ 150 ppm which is more than initial zinc content, indicating the translocation of zinc from the leaves to the soil through the plant body system and accumulating in the soils.

The results of the present experiment suggested that there was no significant change observed in soil chemical properties amongst control and treated with ZnO nanoparticles, after harvesting of the crop. Wang *et al*. (2010) reported that ZnO nanoparticles and bulk particles have shown higher solubility in the soil environment. Similar findings were reported by Du *et al*. (2011) on the effect of ZnO nanoparticles on wheat growth and suggested that ZnO nanoparticles were no longer retained in the soil for longer period of time and dissolved in the soil and they leave no significant changes in soil chemical properties.

Table 4.7. Effect of nanoscale ZnO particles on concentration of macro and micronutrients in soil after harvest

Treatments	N (kg ha^{-1})	P (kg ha^{-1})	K (kg ha^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Fe (mg kg^{-1})	Zn (mg kg^{-1})
1	262^{a}	42.98^{a}	160.47^{a}	1.3^{ab}	26.94^{a}	10.59^{a}	15.53^{a}
2	261.5^{a}	33.28^{a}	198.80^{a}	1.08^{ab}	19.10^{a}	6.89^{ab}	13.78^{a}
3	282.3^{a}	35.59^{a}	197.03^{a}	1.07^{ab}	18.18^{a}	5.95^{ab}	11.89^{a}
4	276.3^{a}	41.58^{a}	183.13^{a}	0.89^{b}	14.55^{a}	6.73^{ab}	13.47^{a}
5	261.9^{a}	36.72^{a}	165.30^{a}	1.57^{a}	22.29^{a}	6.24^{ab}	12.47^{a}
6	258.4^{a}	45.50^{a}	173.50^{a}	1.12^{ab}	13.38^{a}	3.38^{b}	6.77^{a}
7	282^{a}	39.09^{a}	181.67^{a}	0.91^{ab}	16.8^{a}	5.06^{b}	10.14^{a}
8	282.9^{a}	39.43^{a}	181.97^{a}	1.04^{ab}	19.51^{a}	6.07^{ab}	12.15^{a}
9	273.9^{a}	33.87^{a}	192.77^{a}	1.22^{ab}	21.43^{a}	8.25^{ab}	16.51^{a}
10	272.7^{a}	34.75^{a}	172.07^{a}	1.23^{ab}	24.03^{a}	8.14^{ab}	16.27^{a}
11	272.1^{a}	39.07^{a}	153.33^{a}	1.26^{ab}	24.22^{a}	7.47^{ab}	14.93^{a}
12	275.7^{a}	37.56^{a}	196.03^{a}	1.28^{ab}	25.54^{a}	7.73^{ab}	15.46^{a}
SE(m)	8.59	4.5	15.9	0.196	4.08	1.58	3.17
CD	NS	NS	NS	NS	NS	NS	NS

CHAPTER V

SUMMARY AND CONCLUSIONS

Chapter V

SUMMARY AND CONCLUSIONS

A field experiment entitled **"Size Dependent Effects of Nanoscale Zinc Oxide on Productivity of Groundnut in Alfisols"** was conducted at College farm, S. V. Agricultural College, Acharya N.G. Ranga Agricultural University, Tirupati during *Kharif*, 2018. The experiment was laid out in a randomized block design with twelve treatments and three replications.

Twelve treatments were imposed through foliar application of different sources of zinc and the treatments were *viz.*, control *i.e.*, no application (T_1), Recommended Dose of Fertilizer RDF (T_2), RDF + Zinc sulphate @ 2000 ppm at 25 and 45 DAS (T_3), RDF + Nanoscale zinc oxide (20 nm) @ 400 ppm (T_4), , RDF + Nanoscale zinc oxide (20 nm) @ 200 ppm (T_5), RDF + Nanoscale zinc oxide (20 nm) @ 150 ppm (T_6), RDF + Nanoscale zinc oxide (25 nm) @ 400 ppm (T_7), RDF + Nanoscale zinc oxide (25 nm) @ 200 ppm (T_8), RDF + Nanoscale zinc oxide (25 nm) @ 150 ppm (T_9), RDF + Nanoscale zinc oxide (30 nm) @ 400 ppm (T_{10}), RDF + Nanoscale zinc oxide (30 nm) @ 200 ppm (T_{11}) and RDF + Nanoscale zinc oxide (30 nm) @ 150 ppm (T_{12}).

The morphological, physiological and yield attributing characters of the plants were taken into consideration during the crop growth period.

The salient findings in the present study were summarized below:

The pod yield of groundnut was significant with the application of 150 ppm of n- ZnO particles of size 25 nm and it is on par with n- ZnO particles of size 20 nm @ 150 ppm compared to control and bulk $ZnSO_4$ treatments.

The number of pods plant^{-1} were found to be significantly more with the application of n-ZnO particles of size 25nm @ 150 ppm compared to control and bulk $ZnSO_4$ at the rate of 2 grams liter^{-1} treatments.

The number of filled pods plant^{-1} were highest with the application of 400 ppm n-ZnO particles of size 25 nm compared to control and bulk $ZnSO_4$ @ 2000 ppm.

The recorded 100 pod weight was highest with the application of n- ZnO particles of size 25 nm @ 150 ppm compared to control and bulk $ZnSO_4$ treatments.

The 100 kernel weight was highest with the application of n- ZnO of size 25 nm @ 150 ppm compared to control and bulk $ZnSO_4$ treatments.

The maximum shelling percentage was obtained with the application of n-ZnO particles of size 25 nm @ 150 ppm compared to control and bulk $ZnSO_4$ treatments

Significantly highest haulm yield was recorded with the application of 400 ppm of n- ZnO particles of size 25 nm and 150 ppm of n- ZnO particles of size 20 nm compared to control and bulk $ZnSO_4$ treatments.

The harvest index was highest with the application of treatment n- ZnO particles of size 25 nm @ 150 ppm and n- ZnO particles of size 30 nm @ 200 ppm and it is significantly differed compared to control and bulk $ZnSO_4$ treatments @ 2000 ppm.

The post harvest analysis of leaves, stem and kernels were carried out to know the concentration of various macro and micronutrients and found that there was a differential effect in the concentrations of various nutrients in leaves, stem and kernels with the application of nanoscale zinc oxide particles of different sizes and concentrations compared to the rest of the treatments. Further, concentration dependent translocation of nutrients has been noticed with the application of n-ZnO.

Highest leaf Zn content (28.6 ppm) was observed in treatment n- ZnO particles of size 20 nm @ 150 ppm compared to control and bulk $ZnSO_4$ treatments.

Highest stem Zn content (29.3 ppm) was observed in T_{10} treatment n- ZnO particles of size 30 nm @ 400 ppm compared to control and bulk $ZnSO_4$ treatments.

Highest kernel Zn content (37 ppm)was observed in T_{11} treatment n-ZnO particles of size 30 nm @ 200 ppm compared to control and bulk $ZnSO_4$ treatments.

The uptake of nutrients was highly varied by the application of different sizes in different concentrations and there was a difference in the accumulation of zinc oxide particles in leaves, stem and kernels.

This differential pattern of accumulation of zinc in the kernels from that of leaves and stem may be due to the physiological barriers for the translocation of absorbed zinc from the leaves to the grains through the vascular bundles of the plant system.

Highest zinc concentration in soil was recorded with the application of n-ZnO of size (25 nm) @ 150 ppm.

No significant difference observed in all soil parameters, because all the treatments are imposed by foliar application.

The results obtained in the present investigation are discussed earlier and the salient findings from the reported work are concluded as:

1. The method of preparation and the size of nanoparticles play an important role in considering them to use in agriculture.
2. A simple and efficient method has been proposed to prepare ZnO nanoparticles by the precursors zinc acetate and oxalic acid.
3. The ZnO nanoparticles used in this study are of a specific kind and designed for agricultural applications only.
4. Foliar application of ZnO nanoparticles proved to be effective in increasing the Zn content and uptake in plants.
5. At nanoscale, ZnO particles are highly miserable in water compared to their bulk counter parts.
6. Foliar application of ZnO nanoparticles proved beneficial in increasing the pod and kernel yield over bulk $ZnSO_4$.
7. In field conditions, different parameters of groundnut crop like physiological parameters, yield and yield attributes were highly influenced by nanoscale zinc oxide particles.
8. The lowest zinc accumulation in kernel (26.6 ppm) among n-ZnO treatments is obtained with the lowest size and lowest concentration (20 nm @ 150 ppm). And it proves that, there is concentration and size dependent translocation and accumulation of ZnO nanoparticles in the plant system.
9. Concentration and size dependent biofortification of nutrients has been noticed in the present study which may lead to improving micronutrient deficiencies, malnutrition and human health.

LITERATURE CITED

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Adhikari, T., Kundu, S., Meena, V and Rao, A. 2014. Utilization of nano rock phosphate by maize (*Zea mays* l.) crop in a Vertisol of Central India. *Journal of Agricultural Science and Technology*. 4: 384-394.

Afshar, R. M., Hadi, H and Pirzad, A. 2012. Effect of nano-iron foliar application on qualitative and quantitative characteristics of cowpea, under end season drought stress. *International Research Journal of Applied and Basic sciences*. 3(8): 1709-1717.

Afshar, I., Akbar, R. and Minoo, S. 2014. Comparison of the effects of spraying different amounts of nano ZnO and bulk ZnO on wheat. *International Journal of Plant, Animal and Environmental Sciences*. 4: 688-693.

Anandaraj, K., Ilakkiya, R. and Natarajan, N. 2018. Synthesis of zinc oxide (ZnO), silver (Ag), copper oxide (CuO) and titanium oxide (TiO_2) nanoparticles. *International Journal of Current Microbiology and Applied Sciences.* 7(11): 1514-1521.

Aneesh, P. M., Vanaja, K. A and Jayaraj, M. K. 2007. Synthesis of ZnO nanoparticles by hydrothermal method. *Nanophotonic Materials*, 6639(5): 277-278.

Armin, M., Akbari, S and Mashhadi S. 2014. Effect of time and concentration of nano-Fe foliar application on yield and yield components of wheat. *International Journal of Biosciences*. 4: 69-75.

Ashoka., Mudalagiriyappa, P and Desai, B. K. 2008. Effect of micronutrients with or without organic manures on yield of baby corn-chickpea sequence. *Karnataka Journal of Agricultural Sciences*. 21(4): 485-487.

Bakhtiari, M., Moaveni, P. and Sani, B. 2015. The effect of iron nanoparticles spraying time and concentration on wheat. *Biological forum*. 7(1): 679-683.

Banfield, J and Zhang, H. 2001. Nanoparticles in the environment. *Reviews in Mineralogy and Geochemistry*, **44** (1): 1-58.

*** As per the thesis format guidelines (2019) prescribed by Acharya N.G. Ranga Agricultural University, Guntur, 522034 for thesis presentation.**

Benzon, H. R. L., Rubenecia, M. R. U., Ultra, V. U and Lee, S. C. 2015. Nano-fertilizer affects the growth, development, and chemical properties of rice. *International Journal of Agronomy and Agricultural Research*. 7(1): 105-117.

Cakmak, I. 2000. Identification and correction of widespread zinc deficiency in Turkey – A success story (A NATO-Science for Stability Project). *Proceedings of the International Fertilizer Society* 552: 1– 26.

Devlin, R. M., and Withan, F. H. 1983. *Plant Physiology*. Wadsworth publishing company: California.

Dhoke, S. K., Mahajan, P., Kamble, R. and Khanna, A. 2013. Effect of nanoparticles suspension on the growth of mung (*Vigna radiata*) seedlings by foliar spray method. *Nanotechnology Development*. 3(1): 1. doi:10.4081/nd.2013.e1

Du, W., Sun, Y., Ji, R., Zhu, J., Wu, J. and Guo, H. 2011. TiO_2 and ZnO nanoparticles negatively affect the wheat growth and soil enzyme activities in agricultural soil. *Journal of Environment Monitoring*, 13: 822-828.

El-Metwally I. M., Doaa M. R., Abo-Basha, M. E and El-Aziz, A. 2018. Response of peanut plants to different foliar applications of nano- iron, manganese and zinc under sandy soil conditions, *Middle East Journal of Applied Sciences*.8(2): 474-482.

Ewais, E. A., Ismail, M. A and Badawy, A. A. (2017). vegetative growth, photosynthetic pigments and yield of *phaseolus vulgaris* (L.) plants in response to the application of biologically synthesized zinc oxide nanoparticles and zinc sulfate. *Al Azhar Bulletin of Science*. 9 : 33-46.

Farnia, A. and Omidi, M. M. 2015. Effect of nano-zinc chelate and nano-biofertilizer on yield and yield components of maize (*Zea mays* L.) under water stress condition. *Indian journal of Natural Sciences*. 5(29): 4614- 4624.

Gopala Gowda, N., B. Shivaraj, and A. Gowda. 1994. Effect of zinc and molybdenum application on yield and uptake of zinc by groundnut. *Journal of Research, Andhra Pradesh Agricultural University* 22: 40–42.

Harish, M. S and Gowda, R. (2017). Effect of nanoscale zinc oxide on plant growyh, seed yield and quality in groundnut. *Mysore journal of agricultural sciences*, 51(3): 637-643.

Hasnidawani, J. N., Azlina, H. N., Norita, H., Bonnia, N. N., Ratim, S. and Ali, E. S. 2016. Synthesis of ZnO nanostructures using sol-gel method. *Procedia Chemistry*, 19**:** 211-216.

Jackson, M.L. 1973. Soil chemical analysis. *Prentice Hall of India Pvt. Ltd*. New Delhi. 134-204.

Janmohammadi, M., Amanzadeh, T., Sabaghnia, N., & Dashti, S. 2016. Impact of foliar application of nano micronutrient fertilizers and titanium dioxide nanoparticles on the growth and yield components of barley under supplemental irrigation. *Acta Agriculturae Slovenica*, *107(2), 265.* doi:10.14720/aas.2016.107.2.01

Javed, R., M. Usman, S. Tabassum, and M. Zia. 2016. Effect of capping agents: Structural, optical and biological properties of ZnO nanoparticles. *Applied Surface Science*. 386: 319–326.

Jayarambabu, N, Kumari, B.S, Rao, K.V. and Prabhu, Y.T. 2015: Beneficial role of zinc oxide nanoparticles on green crop production. *International journal of multidisciplinary advanced research trends*. 2(1): 273-282.

Jezek, M., Christoph-Martin, G., Bayer, A and Karl-Hermann, M. 2015. Photosynthetic capacity, nutrient status and growth of maize (*Zea mays* L.) upon $MgSO_4$ leaf-application. *Frontiers in Plant Science*. 5: 1-10.

Jhanzab, H. M, Razzaq, A., Jilani, G., Rehman, A., Hafeez, A and Yasmeen, F. 2015. Silver nano-particles enhance the growth, yield and nutrient use efficiency of wheat. *International Journal of Agronomy and Agricultural Research.* 7(1): 15-22.

Jyothi, T. V and Hebsur, N. S. 2017. Effect of nanofertilizers on growth and yield of selected cereals - A review. *Agricultural Reviews*, 38(2): 112-120.

Kim, S., Kim, J. and Lee, I. 2011. Effects of Zn and ZnO nanoparticles and Zn^{2+} on soil enzyme activity and bioaccumulation of Zn in *Cucumis sativus*. *Journal of Chemical Ecology*, 27: 49-55.

Kisan, B., Shruthi, H., Sharanagouda, H., Revanappa, S. B. and Pramod, N. K. 2015. Effect of nano-zinc oxide on the leaf physical and nutritional quality of spinach. *Agrotechnology,* 5: 132-134.

Kobayashi, Y., and Mizutani, S. (1970). Studies on the wilting treatment of corn plant: The influence of the artificial auxin control in nodes on the behavior of rooting. *Proceedings of the Crop Science Society of Japan*

39: 213–220.

Kumar, K, M., Mandal, B. K., Naidu, E, A., Sinha, M., Kumar, K, S., and Reddy, P. S. 2013. Synthesis and characterisation of flower shaped Zinc Oxide nanostructures and its antimicrobial activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 104(2013) 171–174.*

Laware, S. L. and Raskar, S. (2014). Influence of zinc oxide nanoparticles on growth, flowering, and seed productivity in onion. *International Journal of Current Microbiology and Applied Sciences*, **3**(7): 874-881

Lindsay, W. L and Norvell, W. A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Science Society America J.* 42: 421-428.

Liu, X., Chen, X., Ren, J., Chang, M., He, B and Zhang, C. 2019. Effects of nano-ZnO and nano-SiO_2 particles on properties of PVA/xylan composite films. International journal of biological macromolecules. 132: 978-986

Liu, Y., Zhou J. and Larbot, A. 2007. Preparation and characterization of nano ZnO. *Journal of Material Process Technology*, 189: 379-385.

Luther, W. (2004). Industrial Application of Nanomaterials —Chances and risks, VDI Technologiezentrum GmbH, Dusseldorf, Germany.

Mazaherinia, S., Astaraei, A.R., Fotovat, A and Monshi, A. 2010. Nano iron oxide particles efficiency on Fe, Mn, Zn and Cu concentrations in wheat plants. *World Applied Sciences Journal*. 7(1): 36-40.

Moezzi, A., McDonagh, A. M. and Cortie, M. B. 2012. Zinc oxide particles: Synthesis, properties and applications. *Chemical Engineering Journal*, 185- 186: 1-22.

Moghaddam, M. N., Sabzevar, A. H and Mortazaei, Z. 2017. Impact of ZnO and silver nanoparticles on legume-Sinorhizobium symbiosis. *Advanced Studies in Biology, 9, 83–90.* doi:10.12988/asb.2017.712

Moll, J., Okupnik, A., Gogos, A., Knauer, K., Bucheli, T. D., van der Heijden, M. G. A., & Widmer, F. 2016. Effects of titanium dioxide nanoparticles on red clover and its rhizobial symbiont. *PLOS ONE, 11(5), e0155111*.doi:10.1371/journal.pone.0155111

Moreno, M.L.L., Rosa, G.I., Viezcas, J.A.H., Michel, H.C., Botez, C.E., Videa, J.R.P and Torresdey, J.L.G. 2010. Evidence of the differential biotransformation and genotoxicity of ZnO and CeO_2 nanoparticles on soybean (*Glycine max*) plants. *Environmental Science & Technology*. 44(19): 7315-7320.

Morshedi, A and Farahbakhsh, H. 2010. Effects of potassium and zinc on grain protein contents and yield of two wheat genotypes under soil and water salinity and alkalinity stresses. *Plant Ecophysiology* . 2: 67-72.

Narendhran, S., Rajiv, P., and Sivaraj, R. 2016. Influence of zinc oxide nanoparticles on growth of S*esamum indicum* L. in zinc deficient soil. *International Journal of Pharmacy and Pharmaceutical Sciences,* 8(3): 365-371.

Ni, Y., Wei, X., Hong, J. and Ye, Y. (2005). Hydrothermal preparation and optical properties of ZnO nanorods. *Materials Science and Engineering B,* 121: 42-47.

Olsen, S.R., Cole, C.V., Watanabe, F.S and Dean, L.A. 1954. Estimation of available phosphorus in soil by extraction with sodium bicarbonate. United States Department of Agriculture, circular number: 939.

Pandey, A. C., Sanjay, S. S. and Yadav, R. S. (2010). Application of ZnO nanoparticles in influencing the growth rate of *Cicer arietinum*. *Journal of Experimental Nanoscience,* **5(6):** 488-497.

Panse, V. G and Sukhatme, P. V. (1985). Statistical methods for agricultural research, New delhi.

Peralta-Videa, J. R., Zhao, L., Diaz, B. C., Ge, Y. and Priester, J. H. (2014) Cerium dioxide and zinc oxide nanoparticles alter the nutritional value of soil cultivated soybean plants. *Plant physiology and biochemistry*, 80: 128-135.

Piper, C.S. 1950. *Soil and plant analysis.* Hans publishers, Bombay. India

Potarzycki, J and Grzebisz, W. 2009. Effect of zinc foliar application on grain yield of maize and its yielding components. *Plant Soil Environment*. 55 (12): 519-527.

Powers, K.W., Brown, S. C., Krishna, V. B., Wasdo, S. C., Moudgil, B. M. and Roberts, S. M. (2006). Research strategies for safety evaluation of nanomaterials. Part VI. Characterization of nanoscale particles for toxicological evaluation. *Toxicological Sciences,* **90**: 296-303.

Prasad, T. N. V. K. V., Sudhakar, P., Sreenivasulu, Y., Latha, P., Munaswamy, V., Raja Reddy, K., Sreeprasad, T. S., Sajanlal, P. R and Pradeep, T. 2012. Effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut. *Journal of Plant Nutrition*. 35: 905-927.

Priester, J. H., Ge, Y., Meilke, R.E., Horst, A. M. and Mortiz, S. C. 2012. Soybean susceptibility to manufactured nanoparticles with evidence for food qulity and soil fertility interruption. *PNAS*, 109: E2451- E2456.

Ramapuram, N., Sumathi, V., Prasad, T.N.V.K.V., Sudhakar, P., Chandrika, V and Reddy, B. R. 2018. Unprecedented synergistic effects of nanoscale nutrients on growth, productivity of sweet sorghum [*Sorghum bicolor* (L.) Moench] and nutrient biofortification. *Journal of Agricultural and Food Chemistry*. DOI: 10.1021/acs.jafc.7b04467.

Rameshraddy, Pavithra, G.J., Mahesh, S., Geetha, K.N. and Shankar, A.G. 2017. Seed priming and foliar spray with nano zinc improves stress adaptability and seed zinc content without compromising seed yield in ragi (Finger millet), *International journal of Pure and Applied Bioscience*. 5(3): 251-258

Raut, S., Thorat, P. V and Thakre, R. 2013. Synthesis of zinc oxide (ZnO) nanoparticles using *Ocimum Tenuiflorum* leaves. *International Journal of Science and Research*, ISSN : 2319-7064.

Saleem, M., Fang, L., Wakeel, A., Rashad, M. and Kong, C. Y. 2012. Simple preparation and characterization of nano-crystalline zinc oxide thin films bysol-gel method on glass substrate. *World Journal of Condensed Matter Physics*, 2: 10-15.

Saraswathi, Y., Sheety, M. V., Kumar, D and Gurumurthy, K.T. 2017. Effect of nano ZnO on growth and yield of finger millet (*Eleusine coracana* (L.) Garten.). *Agriculture Update*. 12(8): 2333-2337.

Schmid, G. (2001). Metals, In: Nanoscale Materials in Chemistry, Ed: Kenneth J. Klabunde, Wiley-Interscience, New York. p. 15-59.

Shen, L., Bao, N., Yanagisawa, K., Domen, K., Gupta, A. and Grimes, C.A. 2006. Direct synthesis of ZnO nanoparticles by a solution-free mechanochemical reaction. *Nanotechnology*. 17(20):5117-5123.

Shukla, A. K., Behera, S. K., Lenka, N. K., Tiwari, P. K., Chandra Prakash, Malik, R. S., Sinha, N. K., Singh, V. K., Patra, A. K. and Chaudhary, S. K. 2016. Spatial variability of soil micronutrients in the intensively cultivated Trans-Gangetic Plains of India. *Soil & Tillage Research.* 163: 282-289.

Shyla, K. K. and Natrajan, N. 2014. Customizing zinc oxide, silver and titanium dioxide nanoparticles for enhancing groundnut seed quality. *Indian Journal of Science and Technology*. 7: 1376–1381.

Singh, A. L., Basu, M. S. and Singh, N. B. (2004). *Mineral Disorders of Groundnut*. New Delhi, India: *ICAR Publications.*

Singh, M. D., Jayadeva, H. M., Chirag, G and Mohan, M. H. 2017. Effects of nano zinc oxide particles on seedling growth of maize (*Zea mays* L.) in germinating paper test. *International Journal of Microbiology Research*. 9(5): 897-898.

Singh, N. B., Amist, N., Yadav, K., Singh, D., Pandey, J. K. and Singh, S. C. (2013). Zinc oxide nanoparticles as fertilizer for the germination, growth and metabolism of vegetable crops. *Journal of Nanoengineering and Nanomanufacturing*, 3: 353-364.

Sridevi, D. and Rajendran, K. V. (2009). Preparation of ZnO Nanoparticles and nanorods by using CTAB assisted hydrothermal method. *International journal of Nanotechnology and applications.* **3:**43-48.

Subbaiah, B.V and Asija, G.L. 1956. A rapid procedure for determination of available nitrogen in soils. *Current Science.* 25: 259-260.

Subbaiah, L.V.,Prasad, T.N.V.K.V., Krishna, T. G., Sudhakar, P., Reddy, B. R and Pradeep, T. 2016. Novel effects of nanoparticulate delivery of zinc on growth, productivity, and zinc biofortification in maize (*Zea mays* L.). *Journal of Agricultural and Food Chemistry*. DOI:10.1021/acs.jafc.6b00838J.

Tang, E., Tian, B., Zheng, E., Fu, C. and Cheng, G. (2008). Preparation of ZnO nanoparticles via uniform precipitation method. *Chemical Engineering Communication*, **195**: 479-491.

Tarafdar, J. C., Raliya, R., Mahawar, H., Rathore, I. 2014 . Development of zinc nano fertilizer to enhance crop production in pearl millet *(Pennisetum americanum). Journal of Agricultural Research.* DOI 10.1007/s40003-014-0113-y.

Upadhyaya, H., Shome, S., Sarma, R., Tewari, S., Bhattacharya, M.K. and Panda, S.K. 2018. green synthesis, characterization and antibacterial activity of ZnO nanoparticles. *American Journal of Plant Sciences*. 9, 1279-1291.

Wang, M. and Thanou, M. (2010). Targeting nanoparticles to cancer. *Pharmacogical research*. 62(2): 90-99.

Watson, D.J. 1952. The physiological basis for variation in yield. *Advances in Agronomy*. 6: 103-109.

Wigginton, N. S., Haus, K. L. and Hochella Jr. M. F. 2007. Aquatic environmental nanoparticles. *Journal of Environmental Monitoring*. 9: 1306 -1316.

Yong-hong, Ni., Xian-Wen, Wei. and Jiam-ming, hong. (2008). Hydrothermal preparation of ZnO nanoparticles. *Materials Science*, 16(4):523-536.

Yuvaraj, M. and Subramanian, K.S. 2014a. Fabrication of zinc nano fertilizer on growth parameter of rice. *Trends in Biosciences.* 7(17): 2561-2563.

Yuvaraj, M and Subramanian, K.S. 2014b.Controlled-release fertilizer of zinc encapsulated by a manganese hollow core shell. *Soil Science and Plant Nutrition*. 1–8.

Zak, A. K., Razali, R., Majid, W. and Darroundi, M. (2011). Synthesis and characterization of a narrow size distribution of ZnO nanoparticles. *International Journal of Nanomedicine*, 6: 1399-1403.

Zhi, J., Sun, L. D., Yin J. L. and Yan C. H. (2006). Synthesis and control of ZnO morphology via simple solution route. *Journal* of Materials Chemistry, 14: 4172-4177.

Plate 1. Experimental field with the Groundnut crop at vegetative stage.