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Effect of Nanoscale Zinc Oxide Particles on Macronutrient Concentration of Groundnut (*Arachis hypogaea* L.)

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

In the present investigation, size dependent effects of nanoscale zinc oxide particulates (n-ZnO) on the macronutrient concentration of groundnut leaf, stem and kernel have been analysed. ZnO-nanoparticulates that were used in the study were prepared by modified oxalate decomposition method and the ZnO-nanoparticulates (mean size of 20, 25 and 30 nm) were characterized using

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techniques such as transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Dynamic light scattering (DLS) and X-ray diffraction analysis (XRD). Different concentrations (150, 200 and 400 ppm) of ZnO-nanoparticulates were applied (foliar spray) to reveal their effects on groundnut crop in comparison to bulk $ZnSO_4$ Statistically significant high kernel N content (0.49 %) was observed in n-ZnO of size 30 nm @ 400 ppm and highest P content in kernel (0.16 %) was observed in n- ZnO of size 30 nm @ 150 ppm. Whereas, highest kernel K content (0.7 %) was observed in both n-ZnO of size 25 nm and 30 nm @ 200 ppm. These results indicate that zinc nanoparticles significantly influenced the macronutrient (N, P, K) concentration of groundnut depending on their size and concentration.

Keywords: n-ZnO; size; concentration; groundnut.

1. INTRODUCTION

Nanoscale materials (100 nm) exhibits unique and novel properties compared to their bulk counter parts (Prasad et al., 2012). However, the application of nanoscale materials in agriculture as nutrients is relatively new and the record of consequent effects on crops is scant. Furthermore, it is clear from the theory that nanoscale materials possess size dependent characteristics and reactivity and also are distinct to each other (Subbaiah et al., 2016). 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.

The present study examines the interactions between Zn and other nutrients in soil, behaviour in plant growth. It stresses the need for identification of the factor responsible for any Zn response to the addition of another nutrient compound. Of the many interactions of Zn with other nutrients, the most widespread and important to crop production are those with N and P fertilizers on soils with limiting supplies of both Zn and N or P. Similar interactions of Zn with other essential nutrients will also be important in soils with low fertility. 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” [1]. Zinc nanoparticles are being used in various agricultural experiments by the researchers to understand its effect on growth, germination, and various other properties and reported encouraging results [2-5].

2. MATERIALS AND METHODS

ZnO nanoparticles of mean size of 20, 25, 30 nm diameter were used in the study. Nanocrystalline zinc oxide has been prepared 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 500°C. The characterization of the samples was done by Dynamic Light Scattering analysis, Transmission Electron Microscopy. The TEM samples were prepared by drop casting the suspensions on carbon coated Cu grids.

The morphological characterization of n-ZnO particulates was carried out using a high-resolution transmission electron microscope (HRTEM, JEOL 3010; Jeol Ltd., Peabody, MA, USA) to study the surface morphology by drop casting the nanoparticles suspension on the carbon-coated Cu grids. DLS technique was employed to determine the hydrodynamic diameter (size) (Nanopartica SZ-100, HORIBA), and FT-IR (Bruker, TENSOR 27) to identify the functional groups present in the hydrosol.

The experiment was conducted at College farm, Sri Venkateswara Agricultural College, Acharya N.G. Ranga Agricultural University, Tirupati during *Kharif,* 2018-19. The experiment was laid out in sandy clay loam textured soil in a randomized block design (RBD) with three replications and with the plot size of 4m× 4m. The initial soil parameters were pH 6.42; EC = 0.132 dSm^{-1};organic carbon = 0.50% (low);available nitrogen = 188.16 kg ha^{-1} (low); available P_2O_5 = 14.66 kg ha^{-1}; available K_2O= 564.4 kg ha^{-1} (high); available zinc = 16.6 ppm; and total zinc content of 21.3 ppm. Laboratory analysis is done by following standard procedures given by Jackson, [6] and piper, [7].

Field experiment was carried out in *kharif* 2018 with twelve treatments and three replications. 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}).

3. RESULTS AND DISCUSSION

The data on post-harvest concentration of macronutrients (N, P and K) in leaf, stem and kernel at harvest as influenced by the application of nano ZnO and bulk $ZnSO_4$ are presented in the Table 1.

3.1 Concentration of Macronutrients in Leaf, Stem and Kernel at Harvest

3.1.1 Nitrogen content

At harvest, the concentration of nitrogen in groundnut leaves and in stem was numerically higher, when compared to control and bulk $ZnSO_4$ @ 2000 ppm but, the differences were not statistically significantly ($p>0.05$). Highest leaf N content (0.84 %) was observed in treatment of 100 % RDF (T_2). Whereas, highest stem N content (0.70 %) was observed in treatment (T_7) n-ZnO of size 25nm @ 400 ppm over other treatments. Statistically significant ($p<0.05$) high kernel N content (0.49 %) was observed in T_{10} n-ZnO of size 30 nm @ 400 ppm which is 45 % more than control and 49 % more than bulk $ZnSO_4$ @ 2000 ppm.

3.1.2 Phosphorous content

Phosphorous content in groundnut leaves, stem and kernel was significantly ($p<0.05$) higher when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf P content (0.23 %) was observed 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 @ 200 ppm. The next best treatments were T_9 (0.17%) and T_{12} (0.14%).

Highest stem P content (0.27 %) 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. Highest P content in kernel (0.16 %) was observed in 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.

3.1.3 Potassium content

The concentration of potassium in groundnut at harvest was significantly higher ($p<0.05$) in when compared to control and bulk $ZnSO_4$ @ 2000 ppm. Highest leaf K content (1.08 %) 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. Highest stem K content (1.12 %) 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. Highest kernel K content (0.7 %) was observed in both T_8 and T_{11} 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 Afshar et al [8], Singh et al. [9], El-Metwally et al. [10].

Optimal levels of zinc improve the uptake of phosphorus and potassium. Zinc plays a key role 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. [11], Morshedi and Farahbakhsh [12]. 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. 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. These results were in good agreement with the reports of Yuvakkumar et al. [13], Afshar et al. [8], Prasad et al. [2].

Table 1. Size dependent effects of nanoscaleZnO particles on the 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**
T_1: control	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}
$T_{2:}$ RDF	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}
$T_{3:}$ RDF + $ZnSO_4$ @ 2000 ppm	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}
$T_{4:}$RDF + Nano ZnO (20nm)@ 400 ppm	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}
$T_{5:}$ RDF + Nano ZnO (20 nm)@ 200 ppm	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}
$T_{6:}$ RDF + Nano ZnO (20 nm)@ 150 ppm	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}
$T_{7:}$ RDF + Nano ZnO (25 nm)@ 400 ppm	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}
$T_{8:}$ RDF + Nano ZnO (25 nm)@ 200 ppm	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}
$T_{9:}$ RDF + Nano ZnO (25 nm)@ 150 ppm	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}
$T_{10:}$ RDF + Nano ZnO (30 nm) @ 400 ppm	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}
$T_{11:}$ RDF + Nano ZnO (30 nm) @ 200 ppm	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}
$T_{12:}$ RDF + Nano ZnO (30 nm) @ 150 ppm	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

**The mean values were separated by Duncan's Multiple Range Test (DMRT)*

4. CONCLUSIONS

While Zn interacts with other nutrients in many ways, few, other than those involving correction of deficiencies of both Zn and another nutrient, appear to be important in crop production. Where interactions do occur, they sometimes result, not from the nutrient to which they are attributed, but from other factors associated with the addition of the nutrient compound. The results of *kharif* season shows that, N, P and K concentrations in leaves, shoot and kernels varied significantly with the foliar application of different sizes and concentrations nanoscale ZnO particles.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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