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Synthesized nano ZnO and its comparative effects with ZnO and heptahydrate $ZnSO_4$ on sweet corn (*Zea mays* L. *saccharata*)

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Abstract
The field experiment was conducted at college farm, Navsari Agricultural university, Navsari (Gujarat) to evaluate the effect of precipitation synthesized of ZnO nanoparticles on qualitative attributes (protein and sugar content), nutrient content as well as fertility status of soil. The research was carried out in randomised block design with three replications. The seed treatment and foliar application of ZnO, $ZnSO_4.7H_2O$ and nanoscale synthesized of ZnO which precipitation synthesized nanoscale ZnO [0.5M of zinc nitrate $Zn(NO_3)_2$] and 1M of urea $[CO(NO_2)_2]$ (M_3) @ 500 mg kg^{-1}gave significantly responsive for increase the protein and sugar content as well as total nitrogen, phosphorus, iron and zinc while precipitation synthesized of novel ZnO nanoparticle [1M of zinc sulphate [$ZnSO_4$] and 2M of potassium hydroxides [KOH] (M_1) gave significantly higher total potassium and sulphur content in grain and straw of sweet corn.

Keywords: Nanoscale, ZnO, qualitative attributes, nutrient content

Introduction
World scenario, increasing the population has led to increasing the food production. The higher in the production of food to be necessary to use various kinds of technologies in the agricultural field. Nanotechnology is the one of the most immerging technology in smart agriculture. Nanotechnology is techniques which is the formation of nano dimension particles *i.e.* 100 nanometre or less [4, 22, 28]. In agricultural science the next noble frontier is nanotechnology [15] occupies a leading position in increasing the food production in the agriculture sector through efficient management along with the balance of soil nutrients [14]. Those nanoscale particles are having high reactivity surface area and catalytic surface, rapidly reaction and abundant adsorbed in water [26]. In globally Zn is the one of the most deficient of trace nutrient [23]. In the India, soil fertility which Zn is now evaluated the 4^{th} most important yield minimizing factor after (N), phosphorus (P), and potassium (K). Conventional fertilizer of Zn ($ZnSO_4.7H_2O$) reported to have very less fertilizer use efficiency of applied Zn (1-5%) [10]. Out of 17 essential micronutrient Zn is the one of most prior micronutrients for plant, human and animal. In the plant essentiality Zn in important trace element for growth and development of plant. In generally the plant system absorbed Zn as a divalent cation (Zn^{+2}) which act either as the metal constituent of functional structure and more than 300 number of enzymes [24]. The positive role for the synthesis of in indole acetic acid (IAA), protein, chlorophyll synthesis and formation of carbohydrate in plant [32]. Zinc has prominent role in the physiological function in all living system that is maintenance of functional and structural integrity of cell membranes as well as co-factor more than 300 enzyme [26]. Zinc is the structural constituents of phosphorus (P) mobilizing phosphatase and phytase enzyme, it can be hypothesized that the nanoscale ZnO application may help in increase secretion of P mobilizing enzyme, which is involved for mobilization of unavailable P for plant [29]. ZnO nanomaterial were also effect on soil microbiological indicators i.e. dehydrogenase activity (DHA), acid (ACP) and alkaline phosphatase (AKP) activities and FDA [13]. The biosynthesis of nanoscale Zn play a significant role in synthesis of carbohydrate, lipid, nucleic acid and protein as well as their degradation [30]. ZnO and bulk ZnO also found promising in vegetable crops such as lettuce. Nanoscale ZnO and non- nanomaterial ZnO increase the lettuce biomass and the rate of net photosynthetic as well as content of Zn in plant tissue was improved by nanomaterial application.

Nanoscale Zn formulation (nanoparticles of ZnO and nanoclay polymer composites of Zn) have been recently reported mostly on experiment of laboratory and greenhouse [19, 20]. Chitosan grafted zinc containing nanoclay polymer bio-composites (CZNCPBCs) were synthesized and to evaluated the release study of Zn^{+2} in Zn deficient soil. CZNCPBCs in deficient of Zn soils show smart release and increase the equilibrium water absorbency as well as moisture content at a particular tension [21]. Recent report on ZnO and bulk ZnO were found to be promising even in vegetable crop like lettuce (*Lactuca sativa* L.) [35]. ZnO NPs and bulk ZnO enhances the lettuce biomass and the net photosynthetic rate as well as the Zn content in plant tissue was improved in NPs treatment. Nanoscale synthesized of ZnNCPC was found to be most efficient of the carrier of Zn as compared to conventional source of $ZnSO_4$ and other nanoscale source of Zn [2]. In the present study an attempt has been made to study the Synthesized Nano Zn and its Comparative Effects on Sweet Corn (*Zea mays* L. *saccharata*).

Materials and method

The research was carried out during 2017-18 at the college farm, Navsari Navsari Agricultural University, Navsari. The research field is situated at $20^0 92'$ N and $72^0 89'$ E at an altitude of about 12 meter above mean sea level (MSL). The place is located 12 km away in the east from great historical place "Dandi" on the Arabian seashore. As per the 7th Approximation, the soils of the experimental sites are the member of fine, montmorillonitic *isohyperthermic* family of *VerticUstrochrepts* and Jalapore series. The experimental soil was previously cultivated crop and before planting soil sample was taken at a depth of 0-15 cm (shallow depth) and after analysis of Physio-chemical properties of soil. The analyzed of experimental soil was clay in texture having clay = 66.73%, silt 19.62 % and sand = 13.65 %. The bulk density (g/cm^3) = 1.42 and particle density (g/cm3) =2.61 as well as porosity is 46.03 % and the chemical properties of soil were $pH_{1:2.5}$ = 7.78, $EC_{1:2.5}$ = 0.43 dSm^{-1} and the easily oxidizable carbon content = 0.79% and experimental soil contain medium in available N =180 kg ha^{-1}, available P_2O_5 = 33 kg ha^{-1}, high in available K_2O = 354 kg ha^{-1} and the DTPA-TEA extractable of Fe = 13.86 mg kg^{-1}, Mn = 14.92 mg kg^{-1}, Cu = 3.85 mg kg^{-1} and Zn= 0.48 mg kg^{-1}.

Synthesis of nano zinc oxide (ZnO) formulation

The nano dimension formulation of ZnO were synthesized by precipitation process to numerous sources of the Zn at Central instrumental Laboratory, NAU, Navsari (Gujarat). The numerous chemical constituent used for nano ZnO synthesis *i.e.* 1 molar of zinc sulphate ($ZnSO_4$) with react the 2 molar of potassium hydroxides (KOH) (M_1); 0.2 molar of zinc nitrate ($Zn(NO_3)_2$) and 0.4M of potassium hydroxide (KOH) (M_2) [9] and by 0.5 molar of zinc nitrate ($Zn(NO_3)_2$) and 1M of Urea ($CO(NO_2)_2$) (M_3) [27].

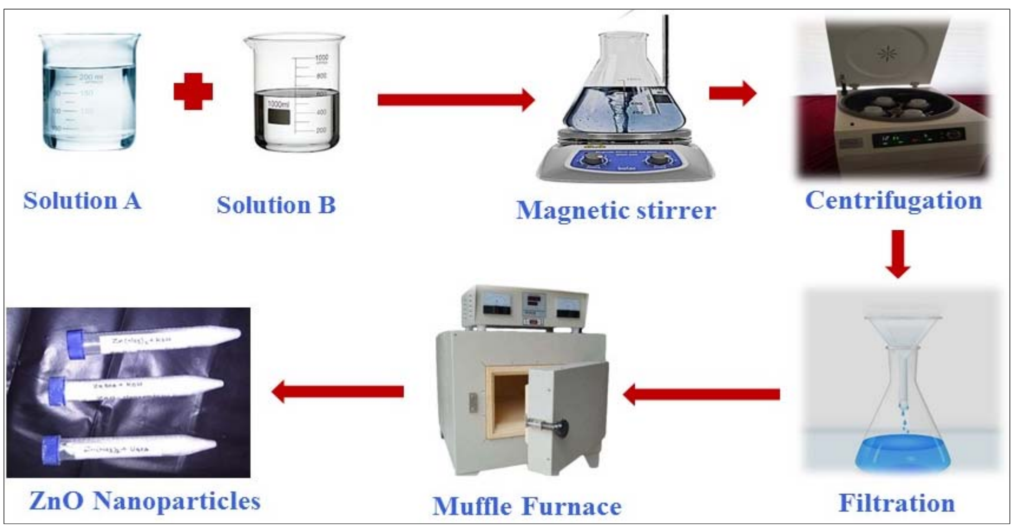

Fig 1: Synthesized of nanoscale ZnO nanoparticles through precipitation method

Treatment details

The randomized blocks design (RBD) arranged in twelve treatments with three replicates. The twelve treatments of bulk and nanoscale ZnO as well as $ZnSO_4$ were used as seed treatment and foliar application viz Control (T_1), ZnO seed treatment @ 3000 ppm (T_2), ZnO-NPs (M_1) seed treatment @ 1000 ppm (T_3), ZnO-NPs (M_2) seed treatment @ 1000 ppm (T_4), ZnO-NPs (M_3) seed treatment @ 1000 ppm (T_5), $ZnSO_4$ foliar application @ 5000 ppm (T_6), ZnO-NPs (M_1) foliar application @ 250 ppm (T_7), ZnO-NPs (M_1) foliar application @ 500 ppm (T_8), ZnO-NPs (M2) foliar application @ 250 ppm (T_9), ZnO-NPs (M_2) foliar application @ 500 ppm (T_{10}),ZnO-NPs (M3) foliar application @ 250 ppm (T_{11}), ZnO-NPs (M_3) foliar application @ 500ppm (T_{12}). The application of Zn was applied as seed treatment at the sowing time and foliar does applied at two various growth stage *viz.*45 DAS and 60 DAS. The plots size 3.6 m x 4.0 m which consisted of six lines with 60 cm x 20 cm spacing in the plant and row. The recommendation dose of fertilizer were applied at sowing and split application using 120:60:00 $N:P_2O_5:K_2O$ kg ha^{-1}. Among these the half dose of N (60 kg ha^{-1}) and full dose of P_2O_5 (60 kg ha^{-1}) were applied at the time of sowing and remaining half dose of nitrogen (60 kg ha^{-1}) was applied 30 DAS as top dressing. At the experimental field selected tag plant were collected and seeds and straw where seeds were dried in an oven with forced air circulation at 65°C and after seeds and straw were ground in a milling machine to analysis of macro and micronutrient content and uptake in sweet corn. The data were statistical analysis at Duncan's new multiple range test at the 5% probability level.

Results and Discussion

Effect on protein content in grain

The protein content in the grain of the sweet corn was significantly influence with the nano ZnO application as well as bulk source of Zn (Table 1). The protein content was significantly higher in grain (13.52%) was recorded in the application of nano ZnO (M_3) @ 500 mg kg^{-1} (T_{12}) while the lowest protein content (10.76%) and (10.65) were noted under the control (T_1) condition *i.e.*, not application of any source of Zn and the application of $ZnSO_4$ @ 5000 ppm, respectively. The nano source of ZnO where application in all treatment was significantly higher content of protein with respect of the control as well as foliar application of $ZnSO_4$. The foliar application of nano ZnO @ 500mg kg^{-1} increase approximately 20 % more protein with respect to the control and the foliar application of $ZnSO_4$ (Fig. 2). Zinc enhances cation-exchange capacity of the roots, which in turn enhances absorption of essential nutrients, especially nitrogen which is responsible for higher protein content. Zinc plays vital role in carbohydrate and proteins metabolism as well as plant growth hormone i.e. IAA. Zn is also an essential component of dehydrogenase, proteinase, and peptides enzymes as well as promotes starch formation, seed maturation and production. Sprayed of ZnO-NPs, treated plant showed higher value of protein content in spinach [11]. [16,17,25]. The role of zinc for protein synthesis when the rapid decrement in concentration of amino acid and amide and corresponding protein concentration increases after re supply of the Zn deficient plants [3]. In the meristematic tissue's protein content was severely depressed by zinc deficient plants [12]. The biosynthesis of nanoscale Zn significantly role of synthesis of protein [30]. Similar investigated found in the plant system Zn deficiency condition impaired the various metabolic process that is RNA metabolism and protein synthesis [12].

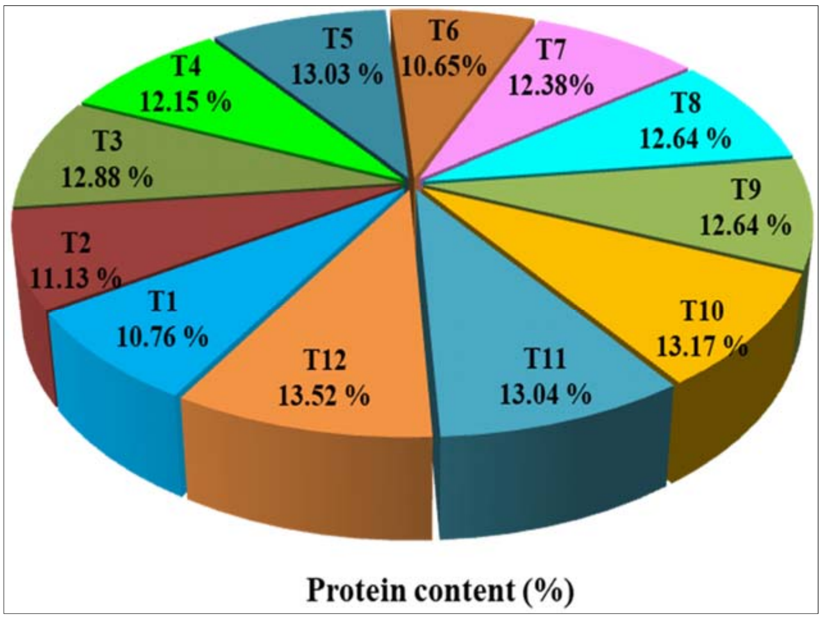

Fig 2: Effect of ZnO-NPs on protein content in grain of sweet corn

Sweet corn total sugar content

Numerous nano zinc oxide, bulk ZnO and $ZnSO_4$ were applied as foliar application and seed treatment on sweet corn were drastically influence the total sugar content in the grain. The foliar application of nano zinc *i.e.* ZnO-NPs (M_3) foliar application @ 500 mg kg^{-1} and nano ZnO (M_2) foliar application @ 500 mg kg^{-1} were found statistically higher total sugar content (19.57 %) followed by the foliar application of nano ZnO (M_1)@ 500 mg kg^{-1} (T_8), ZnO-NPs (M_2) @ 250 mg kg^{-1} (T_9). The foliar application of (T_{12}) nano ZnO (M_3) statistically increase the total sugar content (6.69 %) and (4.91%) with respect to control and foliar spray of $ZnSO_4$. (Fig. 3) Singh *et al.* (2013) found that application of zinc oxide NPs invariably increase pigments, protein and sugar contents and nitrate reductase activities in cabbage due to ZnO NPs induced activities of antioxidant enzymes viz. SOD, CAT, APX and POD [16].

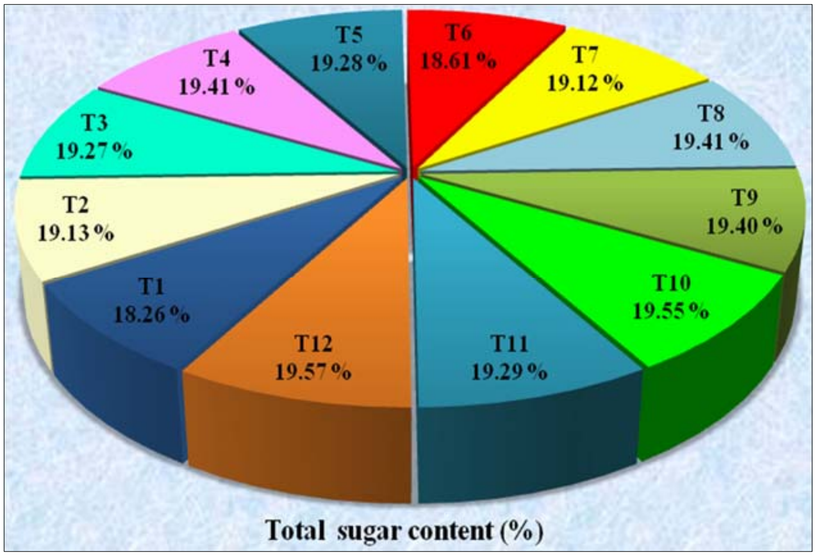

Fig 3: Effect of ZnO-NPs on total sugar content in grain of sweet corn

Table 1: Comparative effect of nano ZnO on protein and sugar content

Treatments	Protein (%)	Total sugar content (%)
1	10.76 h	18.25 e
2	11.13 g	19.12c
3	12.88 bcd	19.26bc
4	12.15 f	19.41 ab
5	13.03 bc	19.28 bc
6	10.65 h	18.60d
7	12.38 ef	19.12c
8	12.64 de	19.40 ab
9	12.64 de	19.40ab
10	13.17 ab	19.55a
11	13.04 bc	19.29bc
12	13.52 a	19.57 a
S.Em.±	0.13	0.06
C.D. at 5 %	0.37	0.18
C.V. %	1.77	0.57

Nutrient content of sweet corn

Effect of nano ZnO on total N, P_2O_5, K_2O, Sulphur and ironcontent

The foliar application of nano zinc oxide (M_3) @ 500 mg kg^{-1} (T_{12}) was recorded significantly higher nitrogen content in grain (2.16 %) and straw (1.28%) followed by the treatments seed treatment of nano ZnO (M_1) (T_3) (2.06%) and (M_2) @ 1000 mg kg^{-1}(T_5)(2.08%), foliar spray of ZnO-NPs @ 500 mg $kg^{-1}$$T_{10}$ (2.11 %) and T_{11} (2.08 %) in case N content in grain while T_9 (1.23%) and T_{10} (1.23%)in case of N content in straw of sweet corn. However, statistically noticed that the lowest nitrogen content in grain (1.72%) and straw (0.95%) was found in the control (T_1) treated plots. The foliar application of nano ZnO, approximately 20 to 21 % increase the nitrogen content in sweet corn grain.

Total P_2O_5 content in the grain and straw of sweet corn statistically influence show results in Table 2.The foliar spray of novel nanoscale ZnO (M_3) @ 500 mg kg^{-1} recorded significantly higher content of P_2O_5 (0.90%) in the seed and straw (0.60%) followed by the foliar application of nano dimension ZnO (M_1) @ 500 mg kg^{-1}, nano ZnO (M_2) @ 250 mg kg^{-1} and 500 mg kg^{-1} and ZnOnanoparticles @ 250 mg kg^{-1}. In the case of grain and T_4 (0.55%), T_7 (0.57%), T_8 (0.58%), T_9 (0.58%), T_{10} (0.58%) and T_{11} (0.57%) in straw of sweet corn. The lowest total P_2O_5 content was noted in the control treatment (T_1)

The precipitate synthesized nanoscale ZnO gave positive response for increasing K_2O content in grain and straw of *Zea mays* L. *saccharate*. The application of ZnO nanofertilizer (M_1) @ 500mg kg^{-1} (T_8) recorded statistically highest K_2O content (0.46%) in the grain followed by treatment of seed with nano ZnO (M_2) @ 1000 mg kg^{-1}(T_4), foliar application of ZnO-NPs (M_1)@ 250 mg kg-1 (T_7) and (M_2) @ 250 mg kg^{-1}(T_9) and (M_3) @ 500 ppm (T_{12}) while total K_2O content in straw (0.85%) significantly recorded into the foliar supply of nano ZnO (M_2) @ 500 ppm and followed by the T_3 (0.82%), T_4 (0.84%), T_7 (0.84%), T_8 (0.82%), T_9 (0.84%), T_{11} (0.80%) and T_{12} (0.82%). The statistically lowest K_2O content in grain (0.32 %) and straw (0.62%) was noted with the treatment T_1 (Control).

The ZnO-NPs (M_1) as a foliar application @ 500 mg kg^{-1} (T_8) recorded significantly higher content of sulphur in grain (0.43%) and and straw (0.32%) and remain followed by the foliar application of nanoscale ZnO(M_1) @ 250 mg kg^{-1}(T_7),(M_3) @ 250 mg kg^{-1}(T_{11}) and (M_3) @ 500 mg kg^{-1} (T_{12}) in the S content in grain while only seed treatment through the nano ZnO (M1) @ 1000 mg kg^{-1} in case of straw of sweet corn. The significantly lowest S content in grain (0.31%) and straw (0.18%) was observed under treatment T_1 (control).

Nano ZnO foliar spray (M_3) @500 mg kg^{-1} (T_{12}) recoded significantly higher Fe content in grain (22.73 mg kg^{-1}) and straw (20.86 mg kg^{-1}) of sweet corn and was followed by seed treatment of nano ZnO @ 1000 mg kg^{-1} (T_3) (22.20 $mgkg^{-1}$) and foliar application of nano ZnO (M1) @ 500 mg kg^{-1} (T_{10}) (22.27 $mgkg^{-1}$) and (M_3) @ 250 mg kg^{-1} (T_{11}) (21.67 $mgkg^{-1}$) in the case of Fe content in grain while T_3 (19.98 mg/kg) and T_{10} (20.40 mg/kg) in case of Fe content in straw of sweet corn. However, significantly the lowest Fe content in grain (16.33 mg/kg) and straw (15.03 mg/kg) was observed with the treatment T_1 (Control).

Similarly result found [7,31,34] effectiveness of chitosan nanoparticles in enhancing the uptake of nutrients, thus increasing the nutrients concentration such as nitrogen, phosphorous, potassium, calcium and magnesium in the robusta coffee plants significantly compared with that of control. Zinc enhances cation-exchange capacity of the roots, which in turn enhances surface absorption of essential nutrients, especially nitrogen which is responsible for higher protein content. [29] Reported that Zn is the structural constituent of P- mobilizing phosphatase and phytase enzyme, it can be hypothesized that the nano scale ZnO application may help in secretion of more P mobilizing enzymes, which is associated in fixed P mobilization for plant nutrient ion from the unavailable organic materials. Morphological change such as release of various kinds of protein, organic acid anions or phenolic substances, phosphorus mobilizing phytase and enzyme of phosphatase increase the availability of P in the rhizosphere [8]. The foliar application of ZnO-NPs (M_1) @ 500 ppm as well as foliar application of ZnO-NPs (M_2) found more K_2O content due to ZnO-NPs (M_1) were synthesized by ZnSO4+KOH and ZnO-NPs were synthesized by $Zn(NO_3)_2$+KOH so some amount of K content are present in M_1 and M_2 synthesized ZnO-NPs, [31]. Similar reported that the foliar application of nano scale ZnO was also increase the fe content in grain and straw rice crop [1].

Periodical Zn Content

The periodical Zn content in leaf as well as in grain at harvesting stage significantly influence with the application of nanoscale ZnO (Table 3). The seed treated with the nano dimension ZnO (M_1) @ 1000 ppm (T_3) noted significantly higher Zn content (19.73 $mgkg^{-1}$) at 30 days after sowing (DAS) and with statistically at par with T_2 *i.e.* bulk source of ZnO seed treatment @ 1000 mg kg^{-1} and ZnO(M_1) and (M_2) with seed treatment @ 1000 mg kg^{-1}. The periodical Zn content at 75 days after sowing in the leaf of sweet corn were significantly higher recorded in the foliar application of ZnO-NPs (M_3) @ 500 ppm (T_{12}) and was found at par with the foliar application of nano ZnO @ 250 mg kg^{-1} (T_9), 500 mg kg_{-1} (T_{10}) as well as ZnO nanoparticles (M_3) @ 250 mg kg^{-1}. After harvesting of sweet corn, the Zn content in grain and straw were positively influence with the application (seed treatment and foliar spray) nano scale ZnO. The foliar applied nano ZnO (M_3) @ 500 ppm (T_{12}) recorded significantly higher Zn content in grain (26.80 mg kg^{-1}) and straw (21.60 mg kg^{-1}) of sweet corn and followed by the foliar application of treatment T_8 and T_{10}. The significantly lowest Zn content in grain (14.80 mg/kg) and straw (13.53 mg/kg) were noted with the treatment T_1 (Control). [35] Results found that Zn uptake in corn exposed to ZnO-NPs during germination was much higher than that in corn exposed to Zn^{2+}, whereas Zn uptake in cucumber was significantly correlated with soluble Zn in suspension. ZnO NPs at foliar application was significantly effective for increasing the concentration of Zn content in grain and straw of rice (*Oryza sativa*) [1]. Reported that the application of ZNCPC significantly maintain DTPA Zn content at two different critical stage and increase the Zn content in rice acquisition as compared to $ZnSO_4.7H_2O$ [18]. The application of ZNCPC was recorded increasing the Zn use efficiency in rice rhizosphere [6].

Effect on fertility status of soil

To determine the effect of seed treatment and foliar application of ZnO-NPs on soil fertility status, treatment wise soil samples were collected and analysed for soil chemical properties viz. soil reaction ($pH_{1:2.5}$) and electrical conductivity ($EC_{1:2.5}$), fertility status viz. available N, P_2O_5, K_2O, S and DTPA extractable Fe and Zn after harvest of sweet corn. The results of the experiment suggested that non significant change observed in soil chemical properties amongst treatment with ZnO-NPs, after harvest of the crop. [33] Reported that ZnO-NPs and bulk particles have higher solubility in soil environment. Similar findings were reported by [5] on the effect of ZnO-NPs wheat growth and suggested that ZnO-NPs were no longer retained in the soil for longer period of time and dissolved in the soil, leaving no significant change in soil chemical properties.

Table 2: Effect of noval nanosacle ZnO-NPs on macro and micro nutrient content by grain and straw of sweet corn

Treatment	Grain					Straw				
	N	P_2O_5	K_2O	S	Fe	N	P_2O_5	K_2O	S	Fe
1	1.72d	0.66e	0.32f	0.33d	16.33e	0.95g	0.42d	0.62d	0.19f	15.03f
2	1.78d	0.73d	0.35e	0.31e	16.87e	1.01f	0.43cd	0.70c	0.25de	15.18f
3	2.06abc	0.75d	0.41bc	0.35cd	22.20abc	1.16d	0.48b	0.82a	0.31a	19.98bc
4	1.94c	0.81c	0.42b	0.39b	21.13bc	1.11e	0.55a	0.84a	0.28bc	17.63d
5	2.08ab	0.74d	0.39d	0.36c	21.07c	1.17cd	0.47bc	0.76b	0.26d	18.96c
6	1.70d	0.69e	0.33f	0.36c	18.53d	0.95g	0.43cd	0.66cd	0.19f	16.68e
7	1.98bc	0.85bc	0.43bc	0.41ab	19.53d	1.18cd	0.57a	0.84a	0.28c	17.58d
8	2.03bc	0.86b	0.46a	0.43a	21.33bc	1.17cd	0.58a	0.82a	0.32a	19.20bc
9	2.02bc	0.88ab	0.43bc	0.40b	19.40d	1.23ab	0.58a	0.84a	0.24e	17.46de
10	2.11ab	0.87ab	0.43bc	0.40b	22.27ab	1.23bc	0.58a	0.85a	0.26d	20.04bc
11	2.08 ab	0.88ab	0.41bc	0.42ab	21.67abc	1.16de	0.57a	0.80ab	0.24e	19.50bc
12	2.16 a	0.90a	0.42bc	0.41ab	22.73a	1.28a	0.60a	0.81ab	0.29b	20.86a
S.Em.±	0.04	0.01	0.01	0.01	0.37	0.02	0.02	0.02	0.004	0.30
C.D. at 5 %	0.12	0.04	0.04	0.02	1.09	0.05	0.05	0.05	0.011	0.88
C.V. %	3.57	3.11	5.31	3.64	3.19	2.77	5.14	3.96	2.46	2.85

Table 3: Effect of noval nanosacle ZnO-NPs on Zn content in grain and periodical leaf content of sweet corn

Treatments	Zn content in grain (mg kg^{-1})	Zn content in Leaf (mg kg^{-1})		
		30 DAS	75 DAS	At harvest
T_1	14.80g	15.33f	15.40h	13.53f
T_2	18.60f	17.67cd	17.53g	16.00e
T_3	19.80e	19.73a	20.00de	19.53b
T_4	22.07c	19.07bc	19.60ef	18.73bc
T_5	23.20b	19.67a	19.67ef	18.67bc
T_6	18.80f	16.80d	18.80f	16.33e
T_7	20.73d	16.80d	21.60bc	18.33c
T_8	23.33b	16.40de	20.73cd	20.73a
T_9	21.93c	15.67ef	22.53ab	18.33c
T_{10}	23.20b	16.33de	22.53ab	20.87a
T_{11}	23.33b	15.60ef	22.53ab	19.60b
T_{12}	26.80a	16.27de	23.40a	21.60a
S.Em.±	0.32	0.90	0.34	0.32
C.D. at 5 %	0.95	2.65	0.99	0.93
C.V. %	2.63	9.14	2.87	2.97

Conclusion

It was concluded that the foliar application @ 500 ppm of ZnO NPs (M_3) synthesized through mixing 0.5M zinc nitrate and 1M of urea by precipitation method with size 63.00 nm, gave significantly higher quality and nutrient composition in sweet corn grown under South Gujarat conditions, however, different treatments does not show any significant effect on soil fertility status after harvest of crop.

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