

# Original Research Article

## **Effect of zinc nanoparticles on plant growth and soil characters**

### **Abstract**

A field experiment with three replications was conducted on sprinkler irrigated sandy soil during two successive summer and winter seasons (summer 2021 and winter 2021/2022), which cultivated with corn (*Zea mays*) and faba bean (*Vicia faba L.*) at Agricultural Research Station farm in Ismailia Governorate, Egypt. Faba bean (*Vicia faba L.*) was cultivated as an indicator crop to evaluate the residual effect of different rates of zinc nutrient in nanoparticles form Vis. Mineral [ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (22.75% Zn)] on corn and bean growth and yield along with some soil chemical properties. The zinc nutrient forms were applied by fertigation through sprinkler irrigation system. The obtained results revealed that the corn and bean parts dry matter, yield and some soil chemical properties including available soil nutrients content, EC, pH and SOM were greatly improved in general with additions of these nutrients forms. During nanoparticle treatments, the most effective treatment was with the rate of half dose from minerals at recommended dose (ZnNPs at 50 % MNRD). Mineral forms in normal recommended dose (MNRD) gave nearly equal effect with ZnNPs at 50 % MNRD.

**Keywords:** Zinc nanoparticles, corn, faba bean, soil properties.

### **1. Introduction**

Zinc (Zn) represents the second most plentiful transition metal in organisms after iron (Auld, 2001). Zn is a fundamental micronutrient for plants, animals and humans. Generally, Zn absorbed as cation ( $\text{Zn}^{2+}$ ) in plants, which works as the metal component or as a functional structure or a regulatory co-factor of many enzymes (Prasad *et al.*, 2012). Zinc is now an integral part of fertilizer recommendation for most crops in several countries. It is generally applied along with NPK as basal fertilizer at seeding (transplanting in case of rice) although its foliar application is also recommended (Prasad, 2006). The essentiality of Zn as a plant nutrient was established first in corn by (Maze, 1915) and later in rice by (Nene 1966). Zinc deficiency in corn results in stunted growth and the top leaves are shorter and turn white, giving the name 'white bud' to the Zn deficiency in maize (Comberato and Maloney, 2012). Zinc is a prosthetic group in a large number of proteins and is involved in the activation of all the six groups of enzymes, namely, oxidoreductases, transferases, hydrolases, lysases isomerases and ligases (Barak and Helmke, 1993). Zinc deficiency leads to inhibition of protein synthesis in plants, which is marked by a decline in RNA (Price *et al.*, 1972), either due to reduced activity of Zn- RNAPM (Soloiman and Wu, 1985) or reduced structural integrity of ribosomes (Obata and Umehayashi, 1988), or by their enhanced degradation (Cakmak *et al.*, 1996). Zinc deficiency therefore leads to accumulation of amino acids and amides in leaves and shoot tips. Zinc deficiency also leads to loss in membrane integrity (Sparrow and Graham, 1988). One of the important site of protein synthesis in plants is pollen

tubes, which could have a fairly high concentration of Zn ( $150 \text{ mg kg}^{-1}$ ) (Miyazawa et al., 2002) and adequate Zn is essential for pollen tube formation in lentils (Pandey et al., 2006). Nanotechnology is an evolutionary science and has introduced many novel applications in the many fields of sciences as biotechnology and agricultural industries. Nanoparticles (NPs) are molecular aggregates or atomic with size between 1 and 100 nm (Ball 2002; Roco 2003), that can sharply change their physical-chemical advantages compared to macro-molecules (Nel et al., 2006; Hediat, 2012). They have powerful advantages as a result of unique physical and chemical characteristics and huge surface area relative to the size, which give them the possibility to improve the life quality and contribute competitiveness in industry field (Homa and Aghili, 2014). However, as a result of their unique advantages, some researches have been done on the toxicological effect of NPs on plants, yet research focusing on the investigation of the beneficial effects of NPs on plants still incomplete. NPs can prospect to improve the nano-pesticide fertilizers, herbicides and genes, which target specific cellular organelles to release their content in plants (Siddiqui et al., 2015). Despite the much information available on the toxic effect of NPs in plant system, few studies have been conducted on mechanisms, by which NPs exert their effect on plant growth and development. In many studies, increasing evidence suggests that ZnONPs increase plant growth and development Siddiqui et al., 2015, peanut (Prasad et al., 2012), soybean (Sedghi et al., 2013), wheat (Ramesh et al., 2014) and onion (Raskar and Laware, 2014). Seeds germination and seedling roots are sensitive stages in the plant growth circle and it is the critical stage of plants to the alteration in surrounding environment (Liu et al., 2011; Sfaxi-Bousbih et al., 2010). Thus, this stage is a best trend to study the toxicological mechanisms in plants by environmental contaminants (Sujing et al., 2012). There are controversial reports about the effect of NPs on the growth and germination of plants (Mahajan et al., 2011). The influence of ZnONPs on Cd toxicity on germination parameters of Faba bean (*Vicia faba* L.) have been studied by Salah and Naif 2015. Their results indicated that the levels of ZnONPs decreased Cd level in the seedling of Faba bean, as well as germination parameters whereas increased some growth parameters. Uzu et al. (2009) explained the route of nanoparticles when it used as foliar application. When nanoparticles were applied on leaf surfaces, it entered through the stomatal openings or through the bases of trichomes and then translocated to various tissues. Lopez et al., (2010) showed that soybean root elongation was promoted at  $500 \text{ mg ZnONPs.L}^{-1}$  but reduced at higher concentration, this could be attributed to an excess of Zn ions released by NPs or an interaction between the NPs and root surface. The interaction of ZnONPs with plant could be influenced by the species of plants. Cakmak (2008) reported that zinc deficiency is problem in food crops, causing decreased crop yields and nutritional quality. In most parts of cereal growing areas, soils have variety of chemical and physical problems that significantly reduce availability of Zn to plant roots; therefore, application of Zn is essential to improve zinc concentration in cereal grains. Zinc application for grains is also a great important for crop productivity which resulted better seedling vigor, denser stands and higher stress tolerance on potentially Zn-deficient soils. Zinc derived from foliar

applications is a greater bioavailability for grains than soil application and useful in solving Zn deficiency. **Korezeniowska (2008)** showed that the foliar application of zinc at reproductive growth stages increase grain and straw yield significantly in wheat. **Remya et al. (2010)** reported that nanoparticles provided an efficient means to distribute pesticides and fertilizers, because its route in plant will be through vascular system, thus these nanoparticles can be successfully used to unload agrochemicals (fungicides, insecticides, etc.), or other substances (plant hormones, elicitors, nucleic acids) and finally leading to enhancing growth. **Park et al., (2019)** investigated interaction of ZnO-NP and plant during germination and early growth under greenhouse conditions. They found that ZnO-NP influence plant temperature and temperature variations which are useful indicators of stress response, plant transpiration and energy balance. The applied of ZnO-NP had an important effect on plant production and physiological parameters. **Mervat and Bakry (2020)** reported that the treatment of flax plant with nano ZnO improved the studied growth parameters, biochemical aspects, and consequent yield in the absence and presence of compost. **Christian et al., (2020)** studied urea coated with ZnO-NPs and evaluated its effects on wheat (*Triticum aestivum* L.). The results indicated that the grain yield and nutrients uptake (N, P, K and Zn) were improved in comparison with urea not coated with ZnO-NPs. **Kolenc'ik et al., (2020)** showed that ZnO-NP agricultural application provides great benefits for plant physiology and consequent production. The physiological value is reflected in improved crop water stress index (CWSI), and in stomatal conductance (Ig), which is a function of plant water stress and leaf water potential level. **Pérez et al., (2020)** reported both ZnS and ZnO nanoparticles are promising novel fertilizer nutrients for crops. **Haipeng et al., (2021)** demonstrates that ZnO NPs improve the rice yield, rice quality, and Zn content of the grain. ZnO NPs application exhibited favorable benefits in rice processing, appearance, and nutritional value. **Gehan et al., (2021)** showed that the nano-zinc had a positive effect in increasing wheat and soybean yields compared to control (without zinc). The use of nano-zinc spray had more effect on yield of wheat and soybean than soil addition application, yield of soybeans and wheat increased by 37% and 33%, respectively, compared to the soil addition of nano-zinc. **Marek et al., (2022)** indicated that zinc oxide nanoparticles provide promising nano fertilizer dispersion in sustainable agriculture. ZnO-NP exposure positively affected yield, thousand-seed weight, and the number of pods per plant, significant changes in stomatal conductance, crop water stress index, and plant temperature.

## 2. Materials and methods

### 2.1. Materials:

To achieve the aforementioned target, a field experiment was carried out on sprinkler irrigated sandy soil during two successive summer and winter seasons (summer 2021 and winter 2021/2022), which cultivated with corn (*Zea mays*) and faba bean (*Vicia faba* L.) at Agricultural Research Station farm in Ismailia Governorate, Egypt, to study the potential benefits of applied different forms of zinc nutrient (mineral and

nanoparticles) on corn and bean growth and yield along with some soil chemical properties including available soil nutrients content, EC, pH and SOM.

## 2.2. Treatments:

The applied treatments of the studied zinc nutrient included mineral form as zinc sulfate  $ZnSO_4 \cdot 7H_2O$  (22.75% Zn) and zinc nanoparticles (ZnNPs) which supplied by *Sigma Aldrich Int. Co* as zinc oxide (ZnO), spherical shape with size (<100 nm) were added by fertigation through sprinkler irrigation system, with special reference to the control treatment (untreated plants) and normal recommended dose of mineral form (MNRD). The recommended dose in spraying solution was  $2g.l^{-1}$  with the rate of 600 liter.fed<sup>-1</sup>. Zinc sulfate was added in the recommended dose (RD) from mineral sulfate salts, while zinc nanoparticles (ZnNPs) was added as a fraction of mineral salts rate in normal recommended dose as [ZnNPs at 10% MNRD, 25% MNRD, 50% MNRD, 75% MNRD and 100% MNRD]. Observations were recorded for many parameters such as; dry weights of plant parts, yield, available soil nutrients content, soil EC, soil pH and SOM. The experiment was designed in randomized complete block design with three replicates was used, with an area of 20 m<sup>2</sup> having the dimensions (4x5 m). The plot area was divided into 5 bands in case of corn and 8 bands in case of bean, each band extended 5 m. The distance between each two successive bands was 75 cm in case of corn and 25 cm in case of bean. Corn plants were transplanted at the distance of 25 cm apart, while bean at 15 cm. Soil fertilizers were applied according the recommendation of agricultural research center (**ARC 2003**) for corn and bean plant production. The dry weight of shoots and roots and yields were evaluated. Some soil characters (EC, pH and soil organic matter SOM) as well as available soil macro and micro nutrients content were evaluated also. The different treatments illustrated in table (1).

**Table (1): Applied treatments in the experiment.**

Ser.	Treatments No.	Treatments Symbol		Rate of applied zinc nanoparticles (ZnNPs)	
1	T0	Control		Control (without foliar fertilization treatments)	
2	T1	MNRD		Mineral fertilizers in Normal Recommended Dose.	
3	T2	ZnNPs	A	10 % MNRD	10% RD of Zn as Zn nanoparticles
4	T3		B	25 % MNRD	25%RD of Zn as Zn nanoparticle
5	T4		C	50 % MNRD	50% RD of Zn as Zn nanoparticles.
6	T5		D	75 % MNRD	75% RD of Zn as Zn nanoparticles.
7	T6		E	100 % MNRD	100% RD of Zn as Zn nanoparticles

**Table (2): Characters of zinc nanoparticles (ZnNPs) used in the studied experiment**

Characteristics	Qualitative values
Chemical formula	ZnO
Form	Nano Powder
Image(TEM)	Sphere
Size	<100 nm
MP (melting point)	1975 ° C
Assay	99% metal base
Surface Area	(15 – 25) m.g <sup>-1</sup>
Density	5.505 g.cm <sup>-3</sup>

**Table (3): Some physical and chemical characters of experimental soil.**

Characteristics	Values
pH (1 :2.5 soil – water suspension)	7.90
Calcium Carbonate %	0.40
Organic matter %	035
ECe dS/m ( soil saturation paste extract)	2.69
Soluble Cations (me. L <sup>-1</sup> )	
Ca <sup>++</sup>	9.69
Mg <sup>++</sup>	4.76
Na <sup>+</sup>	12.73
K <sup>+</sup>	0.83
Soluble Anions (me.L <sup>-1</sup> )	
CO <sub>3</sub> <sup>-</sup>	0.00
HCO <sub>3</sub> <sup>-</sup>	3.73
Cl <sup>-</sup>	14.45
SO <sub>4</sub> <sup>-</sup>	9.89
Available macronutrients (mg. Kg <sup>-1</sup> )	
N	15.20
P	6.06
K	78.80
Available micronutrients (mg. Kg <sup>-1</sup> )	
Fe	4.02
Zn	1.01
Mn	2.95
Some physical properties	
Coarse Sand %	78.00
Fine sand %	14.70
Silt %	4.80
Clay %	2.50
Textural class	Sand

### 2.3. Methods of analysis:

Soluble cations and anions in soil and water were measured according to **Page et al. (1982)** while soil organic matter and calcium carbonate content according **Black (1982)**. Soil samples were extracted by DTPA according to **Lindsay and Norvell (1978)** and micronutrients in water and soil were analyzed by inductively coupled argon plasma

spectroscopy (ICP) (perking elmer-400) according to **Cottenie et al. (1982)**. Nanoparticles manufactured by (**Sigma Aldrich Methods of Nanomaterials 2009**). The obtained results were subjected to analysis of variance according to **Snedecor and Cochran, (1982)** and the treatments were compared by using LSD at 0.05 level of probability.

### **3. Results and Discussions**

#### **3.1. Effect of different treatments on growth and yield cultivated plants:**

##### **3.1.1. Effect on growth of plants:**

Data of plant growth parameters are presented in tables (4) and (5) revealed that the treatment of (ZnNPs at 50 %) was the best treatment of nanoparticles fertilization with respect to dry weights (DWs) of shoots, roots and whole plants. There were significant differences in the values of shoots, roots and whole plants dry weights for corn and bean between the treatment (ZnNPs at 50 % RD) and control. While these differences were non-significant for the same treatment when compared to the treatment MNRD. The treatment consisted of zinc nanoparticles in the rate of 50% RD gave the highest value of roots and whole plant (DWs) in the case of corn and bean, followed with the treatment MNRD. Considering the treatments of nanoparticles fertilization, we can notice that the dose in the half dose of MNRD nearly equal with the fully dose of recommended mineral fertilization. While when the rate of nanoparticles reduced or increased over the rate of half mineral recommended dose, the values of plant parts dry weight will be reduced. Referring to the rate of increase (relative increase) in plant growth parameters as resulted to control, it is clear that these increases ranged from about 24, 7.50 and 11.74 % over the control, in case of treatment ZnNPs at the rate of 10% (which received zinc nanoparticles in the rate of 10% mineral fertilization from recommended dose), for root, shoot and whole plant dry weights of corn, respectively. While the increase rates for bean parts were 6.74, 9.34 and 8.83 %, respectively. While the increase rates were 55.54, 43.35, 46.48, 42.69, 45.87 and 45.25% for the treatment of (ZnNPs at the rate of 50 % RD), with respect to the dry weights of plants' roots, shoots and whole plant for corn and bean, respectively. In general, the results may suggest that nanoparticles fertilization in the half rate of recommended mineral fertilization gave the positive effect on growth of plants, while the higher or lower than this rate gave the negative effects. Also the mineral fertilization in the recommended dose nearly gave equal results with nanoparticles in the rate of half mineral fertilization at recommended dose. The improving in the growth and dry matter yield of cultivated plants related strongly with the balance amount of nutrients, while the deficiency or excess in nutrients requirement affected negatively on growth status of plants. Also improvement in the growth may be due to the involvement of zinc as a micronutrient in different physiological process like enzyme activation, electron transport and stomata regulation which ultimately resulted in greater dry matter.

**Table (4): Effect of different treatments on dry matter of corn roots, shoots and whole plant.**

Parameters (Kg.plot <sup>-1</sup> )		Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>
				10%	25%	50%	75%	100%	
Root DW*	Value	6.50	9.89	8.06	8.59	10.11	9.01	8.27	1.92
	R.I	---	52.15	24.00	32.15	55.54	38.62	27.23	---
Shoot DW*	Value	18.80	27.06	20.21	22.05	29.95	24.25	22.03	4.28
	R.I	---	43.94	7.50	17.29	43.35	28.99	17.18	---
Whole plant DW*	Value	25.30	36.95	28.27	30.01	37.06	33.26	30.30	4.16
	R.I	---	46.05	11.74	20.98	46.48	20.98	19.76	---

DW\*: Dry weight evaluated per one plant. RI: Relative Increase. NPs: Nanoparticles.

**Table (5): Effect of different treatments on dry matter of bean roots, shoots and whole plant.**

Parameters (Kg.plot <sup>-1</sup> )		Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>
				10%	25%	50%	75%	100%	
Root DW*	Value	0.89	1.28	0.95	1.01	1.27	0.95	0.89	0.23
	R.I	---	43.82	6.74	13.48	42.69	6.74	0.00	---
Shoot DW*	Value	3.64	5.20	3.98	4.51	5.31	4.77	4.35	1.10
	R.I	---	42.86	9.34	23.80	45.87	31.04	19.51	---
Whole plant DW*	Value	4.53	6.48	4.93	5.52	6.58	5.72	5.24	0.90
	R.I	---	43.05	8.83	21.85	45.25	26.27	16.77	---

DW\*: Dry weight evaluated per one plant. RI: Relative Increase. NPs: Nanoparticles.

### 3.1.2. Effect on yield of plants:

Results scheduled in table (6) indicated that there were significant differences in corn and bean yield between the control and the treatments 25 , 50 and 75 % ZnNPs. While there were non-significant differences between the same treatments (25 , 50 and 75 % ZnNPs) and MNRD treatment. The corn and bean yield responded to the studied treatments almost typically according to the descending orders: MNRD > ZnNPs at 50% RD > ZnNPs at 75% RD > ZnNPs at 25% RD > ZnNPs at 100% RD > ZnNPs at 10% RD > Control for the corn, while ZnNPs at 50% RD > MNRD > ZnNPs at 25% RD > ZnNPs at 75% RD > ZnNPs at 100% RD > ZnNPs at 10% RD > Control for the bean. Considering the rate of increase in plant yields as related to control, it is clear that this increase could be arranged as the following: The relative increase values of the tested nanoparticles treatments ranged from about 2.28 and 22.77 % up to 37.93 and 55.54 % for corn and bean yield, respectively. Such results of zinc nutrient effects on growth and yield of plants may be according to its role in physiological and biochemical process. Zinc increased the rate of photosynthesis and resulted to increase yield of plant. At the small amount of applied nutrients, the yield of plant had been declined due to micronutrient deficiency while high rate of used nutrients may cause toxicity and will gave negatively effects on yield and growth parameters.

**Table (6): Effect of different treatments on yield of corn and bean plants.**

Parameters (Kg.plot <sup>-1</sup> )		Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>
				10%	25%	50%	75%	100%	
Corn	yield*	14.50	20.00	15.34	16.74	19.85	17.81	16.41	2.38
	R.I	---	37.93	5.79	15.44	36.89	2.28	13.17	---

Bean	yield*	6.50	10.00	7.98	9.71	10.11	9.05	8.01	2.30
	R.I	---	53.85	22.77	49.38	55.54	39.23	23.23	---

Yield\*: was evaluated as kilogram per plot. R.I: Relative increase

### 3.2. Effects of different treatments on the content of soil available macronutrients:

Data in tables (7) and (8) showed that the soil available macronutrients contents were greatly affected by the different applied nanoparticles and mineral fertilization treatments. There were significant differences in soil available N, P and K after corn and bean harvest between the control and the treatments MNRD, 50 and 75 % Zn NPs treatments. While, there were a slight difference between the same treatments and MNRD treatment. The averages values of nutrients content under the control treatment for corn were about (13.85, 6.06 and 98.51) mg.kg<sup>-1</sup> for N, P and K, respectively. While these values under bean treatments were (10.69, 5.03 and 79.81) mg.kg<sup>-1</sup> for N, P and K, respectively. The values of nutrients contents were increased under the different treatments according to the following ranges:- **For nitrogen treatments**; the values were ranged (13.85-40.01) mg.kg<sup>-1</sup> for corn, meanwhile in case of bean these values were (10.69-49.71) mg.kg<sup>-1</sup>; **For phosphorous treatments**; the values were ranged (6.06-18.01) mg.kg<sup>-1</sup> for corn meanwhile in case of bean these values were (5.03-19.81) mg.kg<sup>-1</sup>; **For potassium treatments**; the values were ranged (98.51-210) mg.kg<sup>-1</sup> for corn meanwhile in case of bean these values were (79.81-201) mg.kg<sup>-1</sup>. The minimum increments values of nutrients were given for **nitrogen and potassium** under zinc nanoparticle treatments in the rate of 10%RD for corn and bean, respectively. While the **phosphorus** nutrient values were minimized with ZnNPs at 100%RD for corn and bean, respectively. Meanwhile, the maximum increments for **nitrogen and potassium** under zinc nanoparticle treatments at 50% for corn and bean, respectively. For **phosphorus**, the values were maximized under the treatment of mineral normal recommended dose MNRD for corn and bean, respectively. The phosphorus content values were decreased as the rate of zinc nanoparticles increased. These results were caused by antagonistic relationship between Zn and P as the result of competition at the adsorption sites of plant root. These observations were in agreements with these reported of **Rajaie et al. (2009)**.

**Table (7): Effects of different treatments on the content of soil available macronutrients after corn harvest.**

Parameters (mg.kg <sup>-1</sup> )		Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>
				10%	25%	50%	75%	100%	
N	content	13.85	38.21	14.31	18.45	40.01	26.10	21.11	12.04
	R.I	---	175.88	6.90	33.21	188.88	88.45	52.42	---
P	content	6.06	14.93	18.01	16.31	15.03	11.80	9.71	5.01
	R.I	---	146.37	197.19	149.14	148.02	94.72	50.23	---
K	content	98.51	210.00	115.00	120.00	198.78	126.00	139.00	35.82
	R.I	---	113.18	16.74	21.82	101.79	27.92	41.10	---

**Table (8): Effects of different treatments on the content of soil available macronutrients after bean harvest.**

Parameters (mg.kg <sup>-1</sup> )		Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>
				10%	25%	50%	75%	100%	
N	content	10.69	48.31	16.45	19.34	49.71	28.71	23.41	15.39
	R.I	---	351.92	55.12	80.92	365.01	168.57	118.99	---

<b>P</b>	<i>content</i>	5.03	17.63	19.81	17.13	18.31	13.01	11.91	3.28
	<i>R.I</i>	---	250.49	293.84	240.56	264.02	158.65	136.78	---
<b>K</b>	<i>content</i>	79.81	201.00	103.00	114.00	195.06	129.00	147.00	40.35
	<i>R.I</i>	---	151.85	29.06	42.86	144.41	61.63	84.19	---

### 3.3. Effects of different treatments on the content of soil available micronutrients:

Data in tables (9) and (10) showed the effects of studied treatments on soil available micronutrients content. There were significant differences in soil available iron and manganese content between the control and the treatments MNRD, 10, 25 and 75 % ZnNPs treatments. While, there were slight differences between the treatment MNRD and 10, 25 and 75 % ZnNPs treatments. While for zinc, the significant differences were between the control and the treatments MNRD, 25, 75 and 100 % ZnNPs treatments. While, there were slight differences between the treatment MNRD and 50, 75 and 100 % Zn NPs treatments. The observed effects could be summarized as follows; The increase in the nutrients content as compared to control treatment were subjected to the next scheme:-  
**For iron nutrient contents:** The values of nutrients content increased from (4.02 and 3.01 to 18.81 and 19.3) mg.kg<sup>-1</sup> for corn and bean, respectively; **For zinc nutrient contents:** The values of nutrients content increased from (0.75 and 0.51 to 8.34 and 9.31) mg.kg<sup>-1</sup> for corn and bean, respectively; Meanwhile, **For manganese nutrient contents:** The values of nutrients content increased from (3.34 and 2.91 to 15.41 and 13.51) mg.kg<sup>-1</sup> for corn and bean, respectively. The maximum increments values of iron content were given under the ZnNPs at the rate of 10% RD, while zinc content values were minimized under the same treatment for corn and bean, respectively. Meanwhile, the manganese increment values were maximized under the treatment of ZnNPs at 25% RD which gave the low values with zinc for corn and bean, respectively. Total concentrations of zinc nanoparticles treatments were in reversible relationship with iron and manganese concentration. These results coincided with **Ana et al. (2001)**. The competitive relationship between these elements may be due to the participation of these nutrients in the same biochemical systems. These results also agree with **Nand et al. (1990)**.

**Table (9): Effects of different treatments on the content of soil available micronutrients after corn harvest.**

Parameters (mg.kg <sup>-1</sup> )	Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>	
			10%	25%	50%	75%	100%		
<b>Fe</b>	<i>content</i>	4.02	11.35	18.81	15.31	11.78	6.81	5.61	6.31
	<i>R.I</i>	---	182.34	367.91	280.60	195.27	69.40	39.55	---
<b>Zn</b>	<i>content</i>	0.75	4.50	0.98	1.01	4.95	5.76	8.34	3.20
	<i>R.I</i>	---	500.00	30.66	34.66	560.00	668.00	1012.00	---
<b>Mn</b>	<i>content</i>	3.34	6.41	12.31	15.41	7.12	3.71	4.03	2.45
	<i>R.I</i>	---	91.92	268.56	361.38	64.06	11.08	20.66	---

**Table (10): Effects of different treatments on the content of soil available micronutrients after bean harvest.**

Parameters (mg.kg <sup>-1</sup> )	Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>	
			10%	25%	50%	75%	100%		
<b>Fe</b>	<i>content</i>	3.01	14.78	19.3	17.11	15.34	7.83	6.54	5.24
	<i>R.I</i>	---	391.03	541.53	468.44	409.63	160.13	172.76	---
<b>Zn</b>	<i>content</i>	0.51	6.06	0.97	1.51	6.81	7.21	9.31	4.38
	<i>R.I</i>	---	1088.24	90.20	196.11	1235.36	1313.73	1725.50	---
<b>Mn</b>	<i>content</i>	2.91	5.31	11.07	13.51	10.01	3.01	4.31	2.12

	<b>R.I</b>	---	82.50	280.41	364.26	343.99	3.44	48.11	---
--	------------	-----	-------	--------	--------	--------	------	-------	-----

### 3.4. Effects of different treatments on some soil chemical characters:

Data in tables (11) and (12) showed that there were significant differences in values of soil electrical conductivity (EC) and soil organic matter (SOM) content between the control and the treatments 50 and 75 % ZnNps. While there were slight differences between these treatments and MNRD treatment. The data indicated also that there was a slight decrease in soil pH values after corn and bean harvest.

#### 3.4.1 Effects on soil organic matter (SOM) content:

Data indicated that the investigated soil organic matter content degraded from (0.51 and 0.61) % in the case of soil before cultivation to (0.45 and 0.36) % at the treatment of control and mineral fertilization at normal recommended dose MNRD for corn and bean, respectively.

For the zinc nanoparticle treatments, the lowest values were existed under the treatments in the rate of half dose of mineral fertilization in recommended dose (50% RD), these values were 0.46 and 0.38% for the treatments of ZnNPs at 50% RD, respectively.

Meanwhile, the other nanoparticle treatments gave the values of organic matter higher than this rate but still lower than the value of soil organic matter (SOM) before cultivation in case of corn and nearly equal control in case of bean as the results of nature of bean roots.

The observations on soil organic matter (SOM) can be explained by referring to alteration processes of organic matter at rhizosphere. SOM may be subjected to degradation as the result of different treatments due to consumption during mineralization reactions and exhausted processes by soil microbes. The cultivation of soil without organic matter demands led to decrease the content of soil organic matter, therefore the lowest results for SOM were found under the treatments which presented the highest values of growth and yield of plant, these results mainly found under the treatments of MNRD and ZnNPs at 50% RD, respectively which possess the highest values of growth and yield. Other results will reflect higher values as relation to minimize the powerful of plant growth under these treatments. These results agree with **Da Rocha et al. (2014)**.

#### 3.4.2 Effects on soil pH:

Data indicated that the investigated soil pH slightly decreased gradually with applied treatments. These values were decreased from 7.68 and 7.90 in the case of soil before cultivating to 7.29 and 7.46 at the treatments of control and ZnNPs in the dose of 50% RD for corn and bean, respectively.

For all of the different treatments, the values of MNRD were nearly equal with ZnNPs at 50% RD and the other treatments were higher than these rates and still lower than the value of pH before cultivation for corn and bean, respectively.

According to these previous results and acidifying effect of soil application fertilizers on soil after plant removal, the values of pH were decreased in the locations of treated plants at root zones and consequently the lowest values were found under the same treatments which gave the highest value of plant growth (these treatments were MNRD and ZnNPs at 50% RD). These results were coincided with **Habashy et al. (2008)**.

### 3.4.3 Effects on EC (Soil Salinity):

Results indicated that EC values were increased with applied treatments. The values increased from (2.71 and 2.51)  $\text{dSm}^{-1}$  in the case of soil before cultivating up to (3.81 and 3.71)  $\text{dSm}^{-1}$  for the treatments of ZnNPs at 50% RD for corn and bean, respectively. EC values related positively with availability of soil nutrients. The treatments with high nutrients contents induced high EC values.

From aforementioned results of pH and nutrient soil contents, it can be concluded that the residual effects of cultivating plants under different treatments led to increase the available nutrients status in soil and consequently increase the values of soil electrical conductivity (EC) especially under the treatments which were accompanied with high values of nutrients. These results agree with **Seifi et al. (2010)**.

**Table (11): Effects of different treatments on some soil chemical characters after corn harvest.**

Parameters	Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>	
			10%	25%	50%	75%	100%		
EC ( $\text{dS.m}^{-1}$ )	Value	2.71	3.74	3.38	3.58	3.81	3.71	3.58	0.87
	R.I	---	38.01	24.72	32.10	40.60	36.90	32.10	---
pH (1:2.5)	Value	7.68	7.36	7.57	7.48	7.29	7.38	7.47	0.25
	R.I	---	-4.17	-1.43	-2.60	-5.11	-3.91	-2.86	---
OM (%)	Value	0.51	0.45	0.68	0.59	0.46	0.53	0.65	0.19
	R.I	---	-11.76	33.33	15.71	-9.80	3.92	-27.45	---

**Table (12): Effects of different treatments on some soil chemical characters after bean harvest.**

Parameters	Control	MNRD	Rates of Zn NPs					LSD <sub>0.05</sub>	
			10%	25%	50%	75%	100%		
EC ( $\text{dS.m}^{-1}$ )	Value	2.51	3.67	2.98	3.41	3.71	3.60	3.48	0.75
	R.I	---	46.22	18.73	25.86	47.81	43.43	38.65	---
pH (1:2.5)	Value	7.90	7.51	7.72	7.61	7.46	7.57	7.64	---
	R.I	---	-4.94	-2.28	-3.67	-5.57	-14.18	-3.30	---
OM (%)	Value	0.61	0.36	0.57	0.47	0.38	0.44	0.51	0.16
	R.I	---	-40.98	-6.56	-22.95	-37.70	-27.87	-16.40	---

### Conclusion

From aforementioned results, it can be concluded that, the foliar application of zinc nutrient in the form of nanoparticles induced equal effects with mineral forms in the rate of half concentration from recommended dose. By these results, nanoparticles application may save the amount of agrochemicals used in fertilizers. The higher or lower quantities of nanoparticles more than this rate were not effective, may be due to the excessive or shortage need, respectively for plant requirements.

### References

Ana Flor Lopez; Fermin Morales; Anunciacion Abadia and Javier Abadia, 2001. Iron deficiency associated changes in the composition of the leaf apoplasmic fluid from

- field grown pear (*Pyrus communis L.*) trees. *Journal of Experimental Botany*, 52(360): 1489-1498.
- ARC: Agriculture Research Center of Agriculture Ministry, Egypt, 2003. Recommendations for tomato cultivation and production. Bulletin 408; 2003. Published by ARC; Giza, Egypt.
- Auld, D. S., 2001. Zinc coordination sphere in biochemical zinc sites. *Biometals*, 14: 271-313.
- Ball, P., 2002. Natural strategies for the molecular engineer. *Nanotechnology*, 13: 15-28.
- Barak, P. and P.A. Helmke, 1993. The chemistry of zinc. In *Zinc in Soils and Plants* (A.D. Robson, Ed.). Kluwer Academic Publishers, Dordrecht, pp: 1-13.
- Black, C. A., 1982. *Methods of Soil Analysis*. Soil Sci. Soc. of America, Inc. Pub. Matison Wisconsin, U.S.A.
- Cakmak, I., 2008. Enrichment of cereal grains with zinc: Agronomic or genetic biofortification, *Plant Soil*, 302: 1-17.
- Cakmak, I., A. Yilmaz, M. Kalayri, H. Ekiz, B. Torun, B. Erenoglu and H.J. Brown, 1996. Zinc deficiency as a critical problem in wheat production in Central Anatolia. *Plant and Soil*, 180: 165-172.
- Christian O. Dimkpa; Joshua Andrews; Job Fugice1; Upendra Singh; Prem S. Bindraban; Wade H. Elmer; Jorge L. Gardea-Torresdey and Jason C. White, 2020. Facile Coating of Urea With Low-Dose ZnO Nanoparticles Promotes Wheat Performance and Enhances Zn Uptake Under Drought Stress. *Frontiers in Plant Science Journal*; Volume 11; Article 168.
- Comberato, J. and S. Maloney, 2012. Zinc deficiency in corn. *Soil Fertility Update*, Purdue University ([www.soilfertility.inf/zincdeficiencycorn.pdf](http://www.soilfertility.inf/zincdeficiencycorn.pdf)).
- Cottenie, A., M. Verloo, L. Kieken, G. Velghe and R. Comerlync, 1982. *Chemical analysis of plants and soils*. Fac. Agric., State Univ.,Gent, Belgium, 63.
- Da Rocha, J.P. R., G.K. Donagemma, F.V. Andrade, R.R. Passos, E.S. Balieiro and H.A. Ruiz, 2014. Can Soil Organic Carbon Pools Indicate the Degradation Levels of Pastures in the Atlantic Forest Biome? *Journal of Agricultural Science*, 6(1): 84-95.
- Gehan H. AbdElAziz; Lamyaa A. Abd El-Rahman; Shreen S. Ahmed and E. Samira, 2021. Mahrous Efficacy of ZnO Nanoparticles as a Remedial Zinc fertilizer for Soya Bean and Wheat Corps *J. of Soil Sciences and Agricultural Engineering*, Mansoura Univ., 12 (8): 573-582.
- Habashy, N.R., R.N. Zaki and A.M. Awatef, 2008. Maximizing Tomato Yield and its Quality under Salinity Stress in a Newly Reclaimed Soil. *Journal of Applied Sciences Research*, 4(12): 1867-1875.
- Haipeng Zhang, R. Wang, Z. Chen, P. Cui, H. Lu, Y. Yang and H. Zhang, 2021. The Effect of Zinc Oxide Nanoparticles for Enhancing Rice (*Oryza sativa L.*) Yield and Quality. *Agriculture Journal*, 11(12): 1247.
- Hediat, M. H. Salama, 2012. Effects of silver nanoparticles in some crop plants, Common bean (*Phaseolus vulgaris L.*) and corn (*Zea mays L.*). *International Research Journal of Biotechnology*, 3(10): 190-197.

- Homa, M. and R. Aghili, 2014. Effect on Germination and Early Growth Characteristics in Wheat Plants (*Triticum aestivum* L.) Seeds Exposed to TiO Nanoparticles. *Journal of Chemical Health Risks*, 4(1): 29-36.
- Kolenc'ík, M.; Ernst, D.; Urik, M.; D'urišová, L'; Bujdoš, M.; Šebesta, M.; Dobroc'ka, E.; Kšin'an, S.; Illa, R.; Qian, Y., 2020. Foliar application of low concentrations of titanium dioxide and zinc oxide nanoparticles to the common sunflower under field conditions. *Nanomaterials*, 10: 1619.
- Korzeniowska, J., 2008. Response of ten winter wheat cultivar to boron foliar application in a temperate vlimate (South West Poland). *Agron Res. J.* 6: 471-476.
- Lindsay, K.L. and W.A., Norvell, 1987. Development of DTPA soil test for zinc, iron, manganese and copper. *Soil. Am. J.*, 42: 421-428.
- Liu, T.T., P. Wu, L.H. Wang and Q. Zhou, 2011. Response of Soybean Seed Germination to Cadmium and Acid Rain. *Bio Trace Elem Res.*, 144(1-3): 1186- 1196.
- Lopez M.M.L, C.E., Botez, V.J.R., Peralta and T.J.L., Gardea, 2010. Evidence of the differential biotransformation and genotoxicity of ZnO and CeO<sub>2</sub> nanoparticles on soybean (*Glycine max*) plants. *Environ Sci Technol.*, 44:7315-7320.
- Mahajan, Pramod, S. K. Dhoke, and A. S. Khanna, 2011. Effect of Nano-ZnO Particle Suspension on Growth of Mung (*Vigna radiata*) and Gram (*Cicer arietinum*) Seedlings Using Plant Agar Method. *Journal of Nanotechnology*, 2011: pp.7.
- Kolenc'ík, M., D. Ernst, M. Komár, M. Urik, M. Šebesta, L. urišová, M. Bujdoš, I. Černý, J. Chlpík, M. Juriga, R. Illa, Y. Qian, H. Feng, G. Kratošová, K. Barabaszová, L. Ducsay and E. Aydın, 2022. Effects of Foliar Application of ZnO Nanoparticles on Lentil Production, Stress Level and Nutritional Seed Quality under Field Conditions. *Nanomaterials Journal*, 12: 310.
- Maze', P., 1915. Determination des mineraux necessaires au development du maize. *Compt. Rend. L'Acad. Sci. Paris*, 160: 211-214.
- Mervat Shamon Sadak and Bakry Ahmed Bakry, 2020. Zinc-oxide and nano ZnO oxide effects on growth, some biochemical aspects, yield quantity, and quality of flax (*Linum uitatissimum* L.) in absence and presence of compost under sandy soil. *Bulletin of the National Research Centre*, 44: 98.
- Miyazawa, M., S.M.N. Giminez, M.J.S. Yabe, E.L. Oliviera and M.Y. Kamogava, 2002. Absorption and toxicity of copper and zinc in bean plants cultivated in soil treated with chicken manure. *Water, Air and Soil Pollution*, 138: 211- 222.
- Nand, K.F.; V.C., Baligar and R.J., Wright, 1990. Iron nutrition of plants: An overview on the chemistry and physiology of its deficiency and toxicity. *Pesq. Agropec. Bras., Brasflia*, 25(4): 553-570.
- Nel, A., T. Xia, L. Madler and N. Li, 2006. Toxic potential of materials at the nanolevel. *Science*, 311: 622-627.
- Nene, Y.L., 1966. Symptoms, causes and control of khaira disease of paddy. *Bulletin of the Indian Phytopathology Society*, 3: 99-101.
- Obata, H. and M. Umebayashi, 1988. Effect of zinc deficiency on protein synthesis in cultured tobacco plant cells. *Soil Science and Plant Nutrition*, 34: 351-357.

- Page, A.L., 1982. "Methods of soil analysis" II chemical and Microbiological properties.(Ed.2) soil. Sci. Am. Inc., Madison, W.I.
- Pandey, N., G.C. Pathak and C.P. Sharma, 2006. Zinc is critically required for pollen function and fertilization in lentil. *Journal of Trace Elements in Medicine and Biology*, 20: 89-96.
- Park, S.J., G.S. Das, F. Schütt, R. Adelung, Y.K. Mishra, K.M. Tripathi and T. Kim, 2019. Visible-light photocatalysis by carbon-nanoonion- functionalized ZnO tetrapods: Degradation of 2,4-dinitrophenol and a plant-model-based ecological assessment. *NPG Asia Mater*, 11: 8.
- Pérez Velasco, E.A., R. Betancourt Galindo, L.A. Valdez Aguilar, J.A. González Fuentes, B.A. Puente Urbina, S.A. Lozano Morales, S. Sánchez Valdés, 2020. Effects of the morphology, surface modification and application methods of ZnO-NPs on the growth and biomass of tomato plants. *Molecules*, 25: 1282.
- Prasad, R., 2006. Zinc in soils and in plant, human and animal nutrition. *Indian Journal of Fertilizers*, 2(9): 103-119.
- Prasad, T. N., P. Sudhakar, Y. Sreenivasulu, P. Latha, V. Munaswamy, K. Raja Reddy, T. S. Sreepasad, P. R. Sajanlal and T. Pradeep, 2012. Effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut. *Journal of Plant Nutrition*, 35: 905-927.
- Price, C.A., H.E. Clark, and H.E. Funkhouser, 1972. Functions of micronutrients in plants. In *Micronutrients in Agriculture* (J.J. Mortvedt, P.M. Giordano and W.L. Lindsay, Eds.), pp 731-742. Soil Science Society of America, Madison, WI.
- Rajaie, M.; A.K. Ejraie; H.R. Owliaie and A.R. Tavakoli, 2009. Effect of zinc and boron interaction on growth and mineral composition of lemon seedlings in a calcareous soil. *International Journal of Plant Production* 3 (1): 1735-8043.
- Ramesh, M., K. Palanisamy, K. Babu and N.K. Sharma, 2014. Effects of bulk & nano-titanium dioxide and zinc oxide on physio-morphological changes in *Triticum aestivum* Linn. *J Glob Biosci.*, 3: 415-422.
- Raskar, S.V. and S.L. Laware, 2014. Effect of zinc oxide nanoparticles on cytology and seed germination in onion. *Int. J. Curr Microbiol. App. Sci.*, 3: 467-473.
- Remya N., H.V. Saino, G.N. Baiju, Y.T. Maekawa, Y. Yoshida and D.S. Kumar, 2010. Nanoparticulate material delivery to plants. *Plant Science*, 179: 154-163.
- Roco, M.C., 2003. Broader societal issue on nanotechnology. *Journal of Nanoparticle Research*, 5: 181-189.
- Salah M. H. Gowayed and Naif M. Kadasa, 2015. Influence of Zinc Oxide Nanoparticles on Cadmium Toxicity on Germination of Faba Bean (*Vicia faba L.*) *Journal of Plant Production Sciences; Suez Canal University*, 4: 21-26.
- Sedghi, M., M. Hadi and S.G. Toluie, 2013. Effect of nano zinc oxide on the germination of soybean seeds under drought stress. *Ann West Uni Timis, oara ser Biol.*, XVI (2): 73-78.

- Seifi M.R., R. Alimardani and A. Sharifi, 2010. How Can Soil Electrical Conductivity Measurements Control Soil Pollution?. *Research Journal of Environmental and Earth Sciences*, 2(4): 235-238.
- Sendecore, G.W. and W.G. Cochran, 1982. "Statistical methods". The Iowa state univ. press, Ames, Iowa, USA.
- Sfaxi-Bousbih, A., A. Chaoui and E.I. Ferjani, 2010. Cadmium impairs mineral and carbohydrate mobilization during the germination of bean seeds. *Ecotox Environ Safe*, 73(6): 1123-1129.
- Siddiqui, Manzer H., Mohamed H. Al-Wahaibi, Mohammad Firoz and Mutahhar Y. Al-Khaishany, 2015. *Nanotechnology and Plant Sciences Nanoparticles and Their Impact on Plants*. Springer International Publishing Switzerland. *Soil Science*, 168: 256-261.
- Sigma Aldrich, *Methods of Nanomaterials Material Matters*, 2009. Bulletin vol.4 No.1 (ISSN 1933-9631) is publication of Aldrich Chemical Co. Inc:Aldrich is a member of Sigma-Aldrich Group©2009Sigma-Aldrich Co.
- Soloiman and Wu, Soloiman, D. and Wu, F.Y.M., 1985. Preparation and characterization of various Escherichia coli RNA polymerases containing one or two intrinsic metal ions. *Biochemistry*, 24: 5079-5082.
- Sparrow, D.H. and R.D. Graham, 1988. Susceptibility of zinc deficient wheat plants to colonization by *Fusarium graminearum* Schwab Group I. *Plant and Soil*, 112: 261-266.
- Sujing, L., C. Yang, W. Xiea, C. Xiab and P. Fanc, 2012. The effects of cadmium on germination and seedling growth of *Suaeda salsa*. *Procedia Environmental Sciences*, 16: 293-298.
- Uzu, G., S., Sobanska, G. Sarret., M. Munoz and C. Dumat, 2009. Foliar lead uptake by lettuce exposed to atmospheric pollution. *Environ. Sci. Technol.*, 44: 1036-1042.