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Efficacy of ZnO Nanoparticles as a Remedial Zinc fertilizer for Soya Bean and Wheat Corps

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ABSTRACT

The main objective of nano-fertilizers applications in agriculture is to minimize mineral fertilizers losses and increase yields to support agricultural production. Thus, this investigation was conducted in Gemmayze Station, El-Gharbia Governorate, Egypt, during the two growing seasons of 2017 and 2018 to investigate the efficacy of zinc nano particles on yield, quality and as a remedial zinc nano-fertilizer for soya bean and wheat corps. To confirm the size, shape, surface structure, crystalline composition, and analysis of elemental proportion, synthesized zinc nanoparticles have been characterized. ZnO nanoparticles were either applied foliar spray or soil addition at different concentrations (0, 5 and50 mg L^{-1}). In this experiment, three amounts of phosphorus were used (0, 50 and 100% of the prescribed dose). The obtained results showed that the foliar application of ZnO nanoparticles was effective for enhancing crop production compared to soil application one. In addition, foliar spray led to improve the quality of crop, and the highest increase of yield was noticed by using 50 ppm ZnO nanoparticles under maximum recommended dose of phosphorus fertilizer (100%P). This increase reached to 1.4- folds than control treatment under maximum P application (100%). However, the increment reached 1.9-folds than zero zinc with zero P application. ZnO nanoparticles improved crop yields quality in terms of protein, carbohydrate, crude lipid and N, P, K and Zn of soybean and wheat. The results showed slight decrease in nitrogen and potassium concentration in the soil with increasing ZnO nanoparticles concentration in both type's application (foliar spray and soil addition).

Keywords: ZnO nanoparticles, phosphorus fertilizer, soybean, wheat.

INTRODUCTION

Agriculture is the backbone of third-world economies, but it is currently facing a number of global difficulties; the world's population is extensively increasing, and food consumption is rapidly increasing; by 2050, the world's population is anticipated to increase from 6 billion to 9 billion people (Chen and Yada, 2011). As a result, effective technologies are needed to make agriculture more sustainable. Nanotechnology is a novel approach to achieving long-term agricultural improvement. Because of its significance in enhancing plant productivity, environmental security, biological supportability, and biological stability, nanotechnology has become critical in current agricultural operations (Yaseen et al., 2020). Nano-fertilizer production is regarded as the most essential option for reducing fertilization nutrient losses through increased nutrient management and micronutrient use efficiency (Gogos et al., 2012; Hafeez, 2013). Micronutrients is defined as the nutrients that plants need in lesser amounts, however, it has major role for enhancing crop production and quality. Soil nutrients status and management not only determine crop productivity but also nutrients concentration in plant parts consumed as food and feed as well. Cakmak et al., (2008) found that roughly one-third of arable soils worldwide are low in micronutrients, notably zinc, which has an impact on human nutrition. Zinc deficiency is common in dry zone soils, with available zinc ranging between 0.1 and 2.0 mg kg^{-1} (Gupta, 2005). Excessive use of phosphate fertilizers in soils deficient in micronutrients causes micronutrient insufficiency in the growing plants. Several researches on the interaction between zinc and phosphorus have been performed, and all of them have proven that their levels in plant tissues are imbalanced as a result of excessive phosphorus load, which causes zinc deficiency (Khorgamy and Farnis, 2009). Huamn zinc deficiency is dominant in the areas where people mainly depend upon cereals such as wheat as their major staple food (Cakmak, 2008). Zinc is an essential trace element for plant growth and development. It is one of the most important elements for the natural growth of wheat and other crops. This is due to the fact that zinc is an essential cofactor for over 300 enzymes involved in several physiological processes (Auld, 2001). Wheat (*Triticum aestivum* L.) is a key nutrient source for humans and animals, and it is used in the manufacture of food combinations all over the world. The quality and production of wheat plant may be affected by the management of macronutrients and micronutrients (Wiatrak, *et al.*, 2005). In addition, Soybean (*Glycine max* L.) is the most widely grown oilseed in the world. It is an important source of protein and oil which are derived from its seeds. It's worth noting that soybean is sensitive to zinc deficiency (Thenua et al., 2014). Mineral fertilizers are added to either soil or plants through several ways and forms in order to maximize its use efficiency. It has been noticed that foliar application of micronutrient is more beneficial than soil application, since application rates are lesser as

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compared to soil application. Through foliar application method, same amount of nutrients are applied and could be supplied easily to plant (Hanwate et al., 2018). In case of crop roots are unable to absorb some important nutrients such as Zn, because of soil properties, such as high pH, lime or heavy texture, and in this situation, foliar spraying is better as compared to soil application. Micronutrient foliar application has been found to be on par with, if not more important than, soil application (Kinaci and Gulmezoglu, 2007; Voogt et al., 2013). Antagonistic effects of P on soil applied Zn can also be mitigated by zinc foliar applications, so that P can be applied at desired level to achieve better yield (Zhang et al., 2012). In the first 6 to 12 hours after foliar treatment, zinc is known to be rapidly absorbed and translocated (Doolette et al., 2018). Nanotechnology is now being employed in agriculture for a variety of objectives and under a variety of conditions. The utilization of nanoparticles (NPs) as a source of critical plant nutrients is also possible (Munir et al., 2018). ZnO-NPs, with an estimated global annual production between 550 and 33,400 tons, are the third most commonly used metal-containing nanomaterials (Bondarenko et al., 2013; Connolly et al., 2016; Peng et al., 2017). Zn nanoparticles are thought to be absorbed 15–20 times more than their bulk particles (Srivastav et al., 2016). Because zinc-oxide nanoparticles are employed in a variety of commercial applications, they are likely to end up in the soil ecosystem. Recent study has revealed that foliar spraying of small amount of nutrients, notably Zn, significantly increases crop production (Sarkar et al. 2007). The aims of this study are to investigate the efficacy of nano zinc particle on yield, quality and as a remedial Zn nano fertilizer for soyabean and wheat crops.

MATERIALS AND METHODS

Materials

All reagents used in this study are of analytical grade (purity higher than 98%) and were used without further purification. Zinc nitrate $[Zn(NO_3)]_2$, starch, sodium hydroxide were purchased from Merck Company, Germany country.

Methods

Synthesis of zinc oxide nanoparticles

Zinc Oxide nanoparticles were prepared by wet chemical method (Yadav et al., (2006). Firstly, starch solution was prepared by dissolving 10 g of starch in one liter of distilled water. Thereafter, 0.1 mol of $[Zn(NO_3)]_2$ was added. The resulting solution was maintained under constant stirring using a magnetic stirrer until $[Zn(NO_3)]_2$ was completely dissolved. After complete dissolution of zinc nitrate, a 0.2 mol of sodium hydroxide solution was carefully added under continuously stirring. The reaction was allowed to proceed for 2 hr after complete addition of sodium hydroxide, and then remained overnight. Finally, the attained nanoparticles were then washed three times using distilled water. Washing was carried out to remove the by-products and any starch bound to the nanoparticles. The washed nanoparticles were dried overnight at 80 ˚C. Drying causes the complete conversion of Zn (OH) to ZnO.

Field Experiments

Two field experiments were conducted on a clay loam soil at Agricultural Research Station in Gemmayze, Gharbia, Egypt during the growing seasons of 2017and 2018 to evaluate the effect of phosphorus fertilizers and synthesized nano zinc on the quantitative and qualitative characteristics of the growing plants (soybean and wheat). The initial analysis of soil samples is shown in Tables 1 and 2. The studied soil has a silty clay loam texture with a majority of fine soil fractions of silt and clay. In addition, the pH of soil was of alkaline nature with an average pH value of 7.85, and EC value of 2.15 dS m^{-1}.

First experiment

Soybean (Giza 111) was planted on April 2017. A split- split design in a completely randomized block with three replications was done. Examined factors includes, factor A (main plot) was zinc application type (ground and foliar); factor B (sub plot) was three levels of phosphorus zero, 50 and 100% of the recommended dose of triple superphosphate and factor C (sub subplot) was three levels of nano zinc of 0, 5, 50 mg L^{-1}. 54 plots were used for this experiment; each plot sized (3 × 4) m consisted of 5 rows. The width between rows was 0.7 m and plots were separated with a distance of 1 m. Phosphorus and nano zinc concentrations were calculated and added to each plot. Soil application and foliar spray of Zn treatments were applied three times (15, 30 and 45 days) after emergence of plant. Soybean seeds were inoculated with rhizobium and then were placed in each plot, plants were allowed to grow for a period of 120 days. For all treatments, irrigation, weeding and all other agronomic activities, except those under research, were kept regular and uniform. At 120 days, plant samples from one square meter were taken randomly from each plot. Thereafter, seeds were separated from pod, to determine hundred grain weights (g). Grain, straw and biological yield (Kg $fed.^{-1}$) was determined from the whole plot area. Plant sample was then placed in an oven for 72 hours at 60 ^{0}C, after the dryness of the sample, it was completely grinded by using the stainless mill and stored in polyethylene bags for analysis. Grain crude protein percentage was calculated by multiplying the nitrogen concentration by 5.70 (AOAC 1990).

Second experiment

Second experiment was conducted in the successive winter season November 2017; using wheat (*Triticum aestivum L.*). A spilt split plot design in a randomized complete blocks arrangement with three replications was used. The plot size was 1m x 1m, each plot consisted of four rows, one meter long with 20 cm between rows (plot area 1 m^2). Two applications of Zn nanoparticles (soil addition and foliar spray) were for main plots. The phosphorus concentrations (0, 50,100% of recommended dose) were randomly arranged for sub plots. The three concentration of zinc (0, 5,50 mg L^{-1}) were randomly assigned for sub sub plots and foliar spray treatments were applied during tillering, booting and heading stages. The crops were then harvested in March, 2018 at full maturity. Plants of 1 m^2 area from each plot were selected, ten plants from each plot were sampled randomly for measuring different plant characters and yield attributes. Data on yield, grain yield (Kg $fed.^{-1}$) and dry weight were recorded. Protein percentage of grains = nitrogen percentage of grains multiplied by 5.70. Carbohydrate was extracted according to (Smith, *et al*., 1964) and determined using spectrophotometer according to (Murphy, 1958). Some physico-chemical properties and nutrient contents of soil in experimental site were determined.

Methods of analysis

Characterization of ZnO-nanoparticles

An X-ray diffractometer (Bruker, model D8 Advance) with nickel filtered Cu Kfa (λ = 0.1542 nm) radiation was used for drawing the X-ray diffraction pattern (XRD). Diffracted intensities were reported from 10 ° to 70 ° at 2 ° angles. In addition, surface area was determined by performing BET analysis of the produced nanoparticles by using Quantachrome analyzer (Nova 2000 series, USA) using N2 vapor adsorption experiments. The morphologies of the as-prepared products were studied using a field emission scanning electron microscope (FE-SEM) equipped with a microscope (JEOL JSM-6390) and a high-resolution transmission electron microscope (HR-TEM) (JEM-2100) at 200 kV accelerating voltage.

Table 1. Some chemical characteristics of the used soil

Season	pH (1:2.5)	EC (dSm^{-1})	Soluble ions in soil paste extract ($mmolL^{-1}$) Cations				Anions				Available, nutrients($mgkg^{-1}$)			
			Na^{+}	K^{+}	Ca^{++}	Mg^{++}	CO_3^{-}	HCO_3^{-}	Cl^{-}	SO_4^{-}	N	P	K	Zn
1st	7.9	2.2	7.19	2.53	6.24	6.04	--	8.6	9.6	3.80	89	9.0	439	6.9
2nd	7.8	2.1	9.56	1.44	5.2	4.8	--	9.3	7.50	4.20	134	9.6	419	7.85

Table 2. The physical properties of the used soil

Seasons	$CaCO_3$ ($g\ kg^{-1}$)	organic matter ($g\ kg^{-1}$)	Particle size distribution % Course sand	Fine sand	Silt	Clay	Textural class
1st	18.5	21.1	2.0	13.3	44.9	39.8	Silty Clay Loam
2nd	19.2	20.1	2.11	13.99	46.1	37.8	Silty Clay Loam

Soil analysis

Surface soil samples (0-30 cm) were collected from study sites, and some physico-chemical properties and nutrient contents of soil in experimental site were determined as follows: particle size distribution was measured by the hydrometer method; $CaCO_3$ content was measured according to the description of Scheibler calcimeter; soil reaction, pH and electrical conductivity were measured in soil-water suspension (1:2.5) and filtrate, respectively as mentioned by Jackson (1973) ; organic carbon content was measured by Walkley-Black method (Walkley and Black, 1934) ; total nitrogen was determined by the Kjeldahl method; available phosphorus and potassium were measured following the descriptions of Olsen *et al.*,1954 and Page *et al*., 1982. Available Zn was extracted by AB-DTPA and then measured by ICP (conductively coupled plasma), Lindsay and Norvell, 1978.

Plant analysis

The oil content in the seed of soybean was measured by Soxhlet"s apparatus as described in AOAC (2000). Dried plant materials were digested by using a mixture of concentrated sulphuric- perchloric acids according to the procedure of Chapman and Pratt (1961). Nitrogen concentration in seeds was determined by Kjeldahl method as described in AOAC (2000). Phosphorus concentration in seeds was determined by spectro- photometer according to Olsen *et al.*, 1954 and Zn followed the methods described by Jackson, 1973 and determined using ICP (conductively coupled plasma).

Statistical Analysis

Data obtained were exposed to the proper statistical analysis of complete randomized design (Snedecor and Cochran, 1967). Experiments were carried out in three replicates. Means obtained were differentiated using Duncan's new multiple ranges test (Duncan, 1955).

RESULTS AND DISCUSSION

X-ray diffraction (XRD) and BET analysis

As shown in Figure 1a. the XRD of all the prepared nano-n material having 2θ values with reflection planes at 26.72°, 33.58° and 52.17°; so the diffraction peak fit well with hexagonal structure of ZnO, which correspond to ZnO wurtzitc structure, and proves that ZnO was successfully synthesized. The appeared beak emphasis that the structure of the produced nanoparticles has a single phase with no impurity peaks. The obtained results of BET analysis showed that the produced nanomaterial has an specific surface area of 12.35 $m^2\ g^{-1}$, indicating that the average particle size of the produced nanomaterial within the nanoscale. Figure 1b&c represent the high-resolution images TEM of the prepared nanostructure zinc oxide. The high magnification image reveal that the uniform size of the prepared oxide with a range of 2.4 to 3.7 nm. Furthermore, the morphology of the prepared nanosize ZnO was investigated using SEM as seen in Figure 1d&e. The SEM Image at high magnification Figure 1d reveals an agglomeration. Moreover, the SEM images of the nanoparticles ZnO at high magnification Figure 1e shows that the morphology was undefined spherical shape with rough surface.

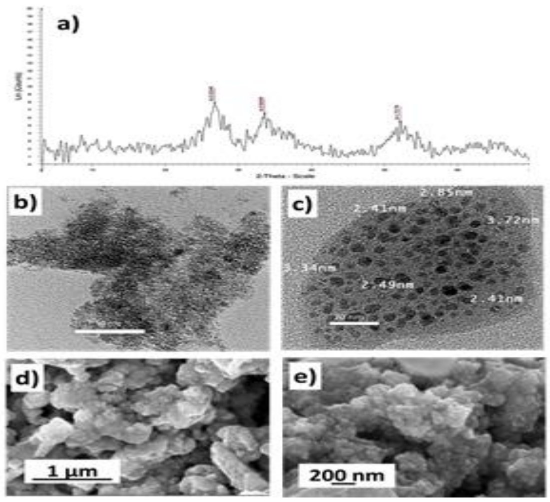

Fig. 1. X-ray diffraction pattern (a), HRTEM (b, c) and FESEM (d, e) of the as prepared nanostructure ZnO.

Effect of nano zinc and phosphorus fertilizer on crop productivity

The data observed in Tables 3 and 4 showed that there were substantial variations between all treatments relative to the control (zero zinc and phosphorus) treatments. The values of soya bean and wheat yields under foliar spray were recorded in the following descending order: 2369.4 > 2215.8 > 1945.9 kg fed.$^{-1}$ for soya bean and 6171 > 5654 > 4899 kg fed.$^{-1}$ for wheat at 50 mg L^{-1} of Zn with 100 P; 5 Zn with 100 % P then 50 mg L^{1-} Zn and 50 % phosphorus, respectively. It worth mentioning that there was a significant values of soya bean and wheat yields (kg fed.$^{-1}$) with using nano zinc (0, 5 and 50 mgL^{-1}) as the following order:1562 > 1533 > 1473 kg fed.$^{-1}$ for soya bean and 4970 > 4402 > 3282 kg fed.$^{-1}$ for wheat, respectively. Statistical analysis showed the same trend for phosphors application (0, 50 and 100 %) for soya bean and wheat yield (kg fed.$^{-1}$), yield values reached to 1359< 1740 < 2093 kg fed.$^{-1}$ for soyabean and 2995 < 4123 < 5538 kg fed.$^{-1}$ for wheat, respectively. The highest increase of yield was noticed by using 50 ppm of nano zinc in combination with 100% of phosphorus fertilizer dose. This increment reached to 1.4 folds compared to zero zinc with 100% P; while reached to 1.9 folds compared to the control treatment (zero zinc and zero P).

Similar trend was observed for straw yields of wheat and soyabean, application of nano-Zn in combination with highest P dose achieved maximum yields of straw (Figures 2 and 3). These results might be attributed to the beneficial role of nano-Zn for enhancing nutrient uptake by the growing plants; consequently, enhanced pigments formation, photosynthesis rate, translocation to the economic parts of the plant and dry material production (Hediat and salama, 2012). Zheng *et al.* (2005) showed that nano- fertilizers significantly improved the seed germination and total growth of the plant, dry matter production, chlorophyll production, rate of the photosynthesis and crop yield over the unlamented treatment. Our findings are in line with those of Singh et al. (2017), who concluded that foliar application of nano particles as fertilizer significantly increases crop yield. According to El-Ghamry *et al.* (2009), foliar Zn application leads to an increase in wheat yield and Zn contents in grain. However, the applications of micronutrient in agricultural practice rate not always increase its content in the plant (Wojtkowiak and Stepien, 2015). The beneficial effect of Zn is the stimulation of plant metabolism, resulting in high nutrient uptake by the root system of the growing plants (Cakmak, 2008). Nano fertilizer is easily absorbed by the epidermis of leaves, translocated to stems which promoting the absorption of active molecules and enhanced growth and productivity of wheat (Abdel-Aziz *et al*., 2016). From this research, it is evident that the foliar application of zinc influences soybean growth, resulting in beneficial changes in seed yield and yield growth characteristics. The prospective cause of such positive role might be due to the active role of these trace elements in metabolic process of plants and photosynthesis which reflected in increasing yield characteristics (Quary *et al*., 2006). Nano fertilizer enhances soybean seed germination, growth parameters (plant hight, leaf area index, no. of leaf per plant), dry matter, chlorophyll, rate of photosynthesis which results in more production (Braun and Roy, 1983). The previous investigation by Sadana *et al*., (2002) showed an increase of straw yield with foliar application of Zn. Similarly, Soleimani, (2006) reported increase in biological yield with foliar application of zinc. The results also agreed with Grewal *et al*., (1997) and Torun *et al*., (2001)) who reported increased dry matter production for application of micronutrients over control treatment. This could be explained due to the provision of micronutrients at latter stages which may enhance accumulation of assimilate in the grains and thus resulting in heavier grains of wheat. The results are in line with Guenis *et al*., (2003) and Soylu *et al*., (2005) who reported significant increase in thousand grains weight with foliar application of micronutrients.

Table 3. Effect of zinc nanoparticles on grain yields of soybean.This included the standard deviation (±SD) and calculation by Fisher's least significant difference (LSD) test.

Zn (ppm)	P %	Yield kg fed^{-1} Soil addition	Yield kg fed^{-1} Foliar spray
0	0	1225 ^{n}	1225 ^{n}
	50	1400 ^{j}	1400 ^{j}
	100	1633^{g}	1633^{g}
5	0	1270^{m}	1310 ^{l}
	50	1442 ^{i}	1755 ^{d}
	100	1675 ^{f}	2135 ^{b}
50	0	1335 ^{k}	1394 ^{j}
	50	1470 ^{h}	1875 ^{c}
	100	1710 ^{e}	2283 ^{a}
LSD at 0.05%		12.35	
Standard deviation for different treatment	±179.7		±366.0

Means with the same letter within column are not significantly different

Table 4. Effect of zinc nanoparticles on grain yields of wheat. This included the standard deviation (±SD) and calculation by Fisher's least significant difference (LSD) test.

Zn (ppm)	P %	Yield kg fed^{-1} Soil addition	Yield kg fed^{-1} Foliar spray
0	0	2390 n	2390 n
	50	2915 l	2915 l
	100	4182 f	4182 f
5	0	2622 m	2969 k
	50	3135 j	4103 f
	100	4371 e	5654 b
50	0	2996 k	3297 i
	50	3555 h	4899 c
	100	4516 d	6171 a
LSD at 0.05%		4.529	
Standard deviation for different treatment		±767.1 ±1275.3	

Means with the same letter within column are not significantly different

Effect of nano zinc and phosphorus fertilizer on quality characteristic of soybean

Quality characteristic of soybean was shown in (Fig. 4). For oil content, nano zinc and phosphorus fertilizer enhanced oil content in grains of soybean. Clearly, oil contents gradually increased by increasing the rates of applied nano-Zn and P fertilizer compared to control treatment (zero zinc and phosphors). Application of 5 and 50 mg/L foliar nano zinc with 100% P led to increase in oil and protein content reached to 22.83 and 23.09% for Oil and 39.29 and 39.48% for Protein respectively. The increase in oil content with P application could be due to the fact that P contributed to the synthesis and esterification of fatty acids by accelerating biochemical reactions in glyoxalate cycles (Dwivedi and Bapat, 1998). This result has conformity with Payday's study (Pandey *et al.* 2006); who declared that Zinc had positive effect on protein content of soybean. It is well known that ribosome composed mainly of Zn; consequently, Zn deficiency may lead to slow down amino acid accumulation and protein synthesis in plant tissues. Also, the positive effects of nano zinc on protein content of soybean have been reported by (Hemantarajan and Trivedi, 1997).

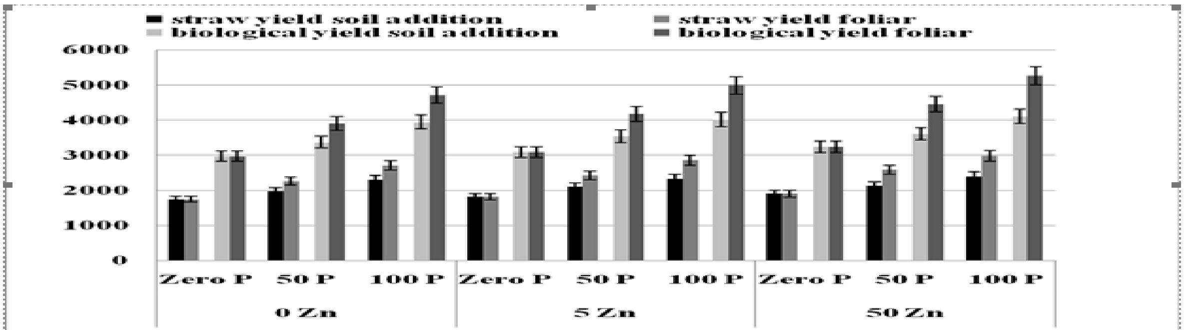

Fig. 2 Effect of nano zinc and phosphorus on straw and biological yield (kg/fed.) of soya bean

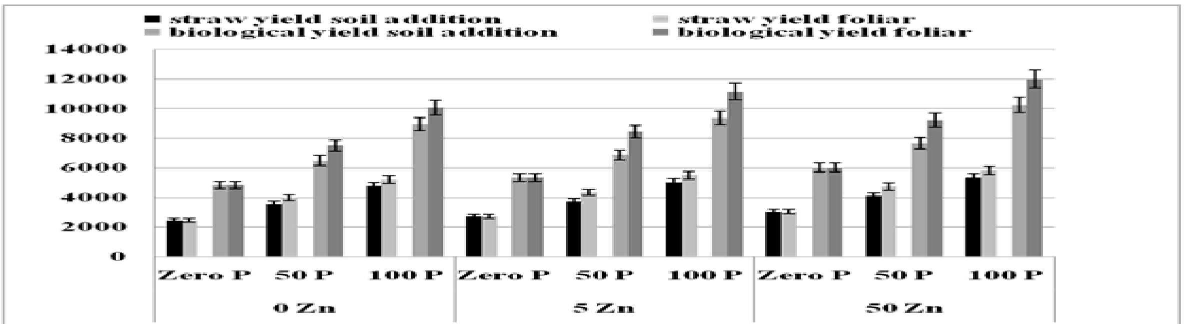

Fig. 3 Effect of nano zinc and phosphorus on straw and biological yield (kg/fed.) of wheat

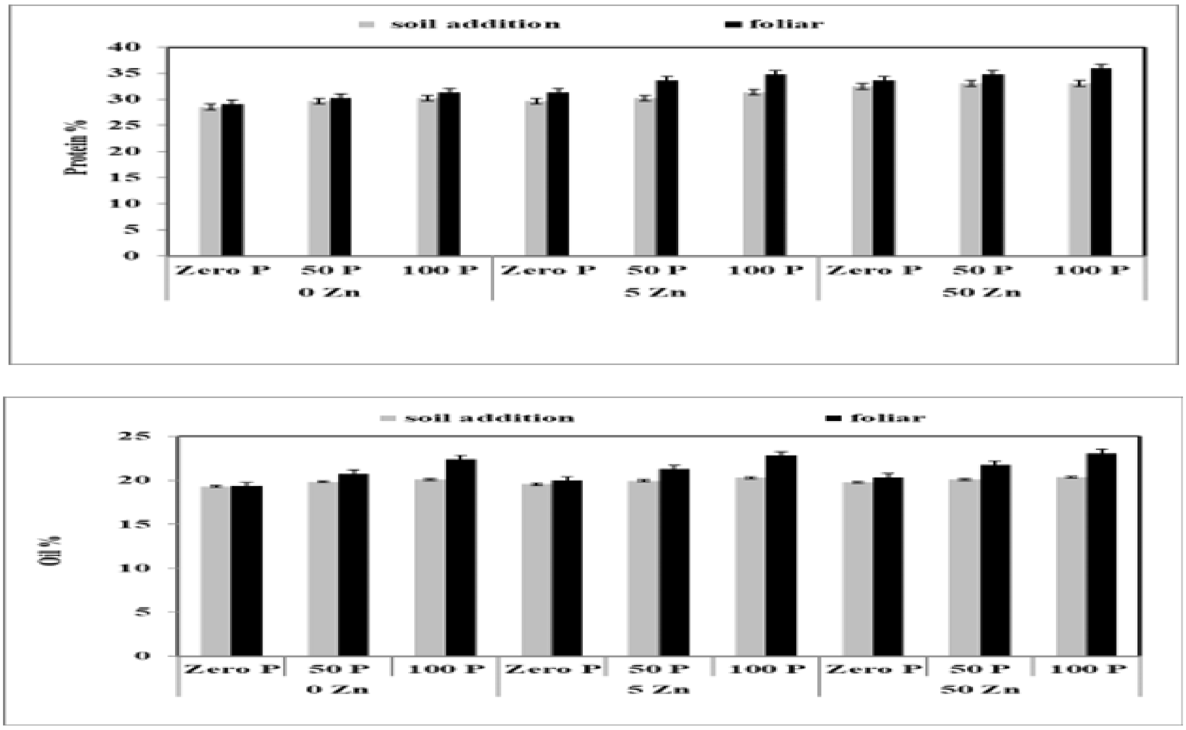

Figure 4. Effect of nano zinc and phosphorus fertilizer on yield quality of soybean plant

Effect of nano zinc and phosphorus fertilizer on Quality characteristic of wheat

Quality characteristic of wheat as affected by nano zinc and phosphorus fertilizer are shown in (Fig.5). Protein percent of wheat was increased with increasing levels of nano Zn and P levels. The increment was more beneficial by using Zn foliar spray compared to soil addition. There was an obvious difference between all treatments compared to control treatment (zero zinc and phosphors). The highest values of carbohydrates and protein were recorded with applying nano Zn (50 mgL^{-1}) foliar spray with 100% P followed with 5 mgL^{-1} nano Zn with 50% P. These values reached to 74.96 and 74.68% for carbohydrates and 13.42 and 13.29% for protein. The increment in protein contents might be attributed to the improvement in the growth and grain yield (Masoud et al., 2012; Havlin *et al.,* 2014 and Khanday *et al.,* 2017). Also, the positive effects of nano zinc on protein content have been reported by (Baybordi and Mamedov, 2010) in wheat. Nano fertilizers provide more surface area and more availability of nutrients to the growing crops which help to increase these quality parameters of plants (such as protein, oil content, total carbohydrate and sugar content) by enhancing the rate of reaction or synthesis process in the plant system (Mahajan *et al.,* 2013).

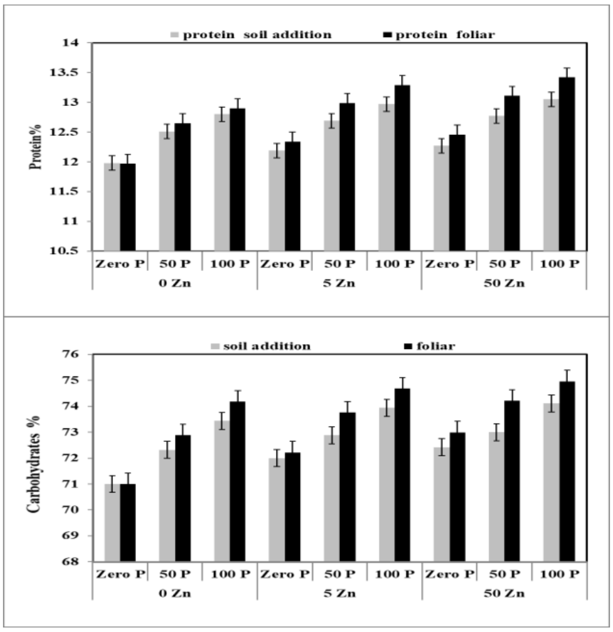

Fig. 5. Effect of phosphorus fertilizer and nano zinc on yield quality of wheat plant

Effect of nano zinc and phosphorus fertilizer on some nutrients contents in plants

Data presented in Table 5 shows the major nutrients contents of N, P and K in either soya beans or wheat plants. There were significant differences in nutrient contents of both plants. There was an increase in nitrogen content by using nano zinc under phosphors fertilizers while slightly increase was observed in potassium content compared to control (zero zinc and zero phosphorus). Regarding the zinc nutrient, it was found that soil application of nano-Zn negatively affected by P application; by increasing the rate of P fertilizer, the uptake of Zn was decreased. However, foliar spray of nano-Zn showed different trend; increasing the rate of P soil application led to increase Zn contents in the growing plants. Clearly, soil application of nano-Zn in combination with P fertilizer led to antagonism interaction between these two metal ions in soil. The same trend was observed in relation to the content of phosphorous in the plant under the use of nano zinc and phosphate fertilization. It worth mentioning that phosphorus content in plant was decrease by nano zinc application while phosphorus content of grain and straw significantly increased with phosphorus fertilization. The results are agreement with Oprica *et al.* (2014) who reported that the application of micronutrients in the foliar fertilizer formulation may have stimulated the uptake efficiency of the soil applied NPK. Further, the foliar application of zinc eliminates antagonistic effect of zinc and phosphorus and may thus jointly boost the yield of the crop and maintain a favorable balance between P and Zn in plant and may also increase the phosphorus utilization by its effect on phosphate metabolism (Rossel and Ulrich, 1964).

Table 5. Effects of nano zinc and phosphorus fertilizer on some nutrient contents in plants. This included the standard deviation (±SD) and calculation by Fisher's least significant difference (LSD) test.

			Soybean						
			Soil addition				**Foliar spray**		
Zn (ppm)	**P%**	**N %**	**P %**	**K %**	**Zn mg/Kg**	**N %**	**P %**	**K %**	**Zn mg/Kg**
	0	5	0.150	0.90	6.12	5.1	0.150	0.91	6.13
0	50	5.2	0.193	0.92	6.07	5.3	0.193	0.93	6.12
	100	5.3	0.263	0.99	6.02	5.5	0.263	1.02	6.12
	0	5.2	0.148	0.92	6.23	5.5	0.149	0.94	6.52
5	50	5.3	0.192	0.69	6.17	5.9	0.193	0.99	6.53
	100	5.5	0.250	1.04	6.11	6.1	0.266	1.01	6.53
	0	5.7	0.146	0.91	6.48	5.9	0.149	0.95	7.41
50	50	5.8	0.188	0.98	6.25	6.1	0.193	1.01	7.38
	100	5.8	0.135	1.06	6.14	6.3	0.265	1.05	7.40
LSD		0.5408	0.0533	0.0754	0.0754	0.5408	0.0533	0.0754	0.0754
Standarddeviation for different treatment		±0.1	±0.02	±0.04	±0.04	±0.14	±0.02	±0.02	±0.19
			Wheat						
	0	1.72	0.170	0.210	21.50	1.73	0.170	0.171	21.57
0	50	1.86	0.197	0.220	21.02	1.88	0.198	0.198	21.56
	100	1.93	0.210	0.220	20.65	1.90	0.221	0.221	21.55
	0	1.84	0.168	0.168	22.82	1.85	0.170	0.170	23.45
5	50	1.90	0.192	0.192	21.48	1.91	0.197	0.197	23.45
	100	1.96	0.214	0.214	21.11	1.97	0.220	0.220	23.46
	0	1.87	0.166	0.166	24.78	1.89	0.169	0.169	25.63
50	50	1.90	0.188	0.188	22.18	1.93	0.191	0.191	25.64
	100	1.87	0.210	0.210	22.08	1.98	0.216	0.216	25.64
LSD		0.3535	0.0533	0.0533	0.2500	0.3535	0.0533	0.0533	0.2500
Standarddeviation for different treatment		±0.02	±0.01	±0.01	±0.42	±0.02	±0.01	±0.01	±0.59

Also, some studies proved the significance of nano fertilizers, for increasing nutrient use efficiency (Naderi and Danesh-Sharaki, 2013). Root growth and vegetative in wheat was improved by foliar feeding of micronutrients which led to increase the uptake of macro and micronutrients (Bameri *et al.,* 2012). Nano fertilizer has large surface area and particle size less than the pore size of leaves which can increase penetration into the plant tissues and improve uptake and nutrient use efficiency (Dimkpa *et al.,* 2015 and Qureshi *et al.,* 2018). The imbalanced use of fertilizers, especially phosphorus fertilizers has caused the imbalance of nutrients, especially micronutrients in the soil, reduced the absorption of iron, zinc, copper and manganese by plant (Swiader and Ware, 2002). Foliar use of Zn increased the concentration of

Zn in the grain according to Pahlavan-Rad and Pessarakli (2009).

Effect of nano zinc and phosphorus fertilizer on some nutrients content in soil

After harvesting of soybean and wheat crops, for soil addition application of nano Zn at three doses and three levels of phosphorus fertilizers, the results showed increases of Zn and P concentration in soil by increasing both types of applied fertilizer (Table 6). On the contrary, the data showed that slight differences in concentration of Zn and phosphorus in the soil with increase concentrations when using the foliar spray of nano zinc, also, nitrogen concentration in the soil was slightly decreased with increase concentrations of fertilizers added in both types application (soil addition and foliar spray). Reduction of N content in soil, could be possibly due to increasing the amount of N in the harvested portions of the plants because the synergistic interaction between N and P in cereals. This data had conformity with Milkh *et al*., (2005).

As for the K, the results showed slight changes in potassium concentration in the soil with increasing nano-Zn concentration, while increasing the concentration of phosphate fertilizer led to reduce the concentration of potassium in soil. The results are in agreement with Malakouti and Tehrani, (2006); who's reported that the use of phosphorus fertilizers in the soil and a small amount of the zinc will result in Zn deficiency on plants and soil. The phosphorus and zinc can form a poorly soluble compound that decreases the available zinc absorption in plants. Also, high soil P reduces the growth of plant roots and mycorhizal volume, which will reduce the absorption of zinc by plants, while the increase of nitrogen contents is possibly due to the symbiotic nitrogen because nodulation and N2 fixation are strongly influenced by P availability. Nitrogen fixing plants have an increased requirement for P over that receiving direct nitrogen fertilization, probability due to need for nodule development and signal transduction (Saxena and Rewari, 1991).

Table 6. Effects of nano zinc and phosphorus fertilizer on some nutrients in soil after harvest. This included the standard deviation (±SD) and calculation by Fisher's least significant difference (LSD) test.

Zn (ppm)	P%	Soil addition N	P	K	Zn	Foliar spray N	P	K	Zn
					mg/Kg				
Soybean									
0	0	132.4	9.08	439.0	6.05	131.6	9.05	438.3	6.08
	50	130.2	9.42	436.7	6.07	130.4	9.51	437.3	6.1
	100	128.4	9.87	437.7	6.12	130.8	9.99	437.2	6.13
5	0	131.3	9.05	438.3	6.08	131.4	9.01	438	6.1
	50	129.7	9.47	436.3	6.51	130.2	9.57	437.5	6.2
	100	126.7	9.89	436.2	7.03	129.2	9.98	437.1	6.3
50	0	131.6	9.06	437.7	5.23	131.8	9.1	437.7	6.14
	50	128.8	9.71	436.2	6.95	130.4	9.76	436.8	6.21
	100	126.3	9.93	435.8	7.11	129.1	9.99	437.4	6.29
LSD		2.243	0.8082	1.655	0.315	2.243	0.8082	1.655	0.315
Standard deviation for different treatment		±0.65	±0.12	±0.30	±0.21	±0.32	±0.13	±0.12	±0.03
Wheat									
0	0	73.46	7.11	327.21	7.080	73.55	7.14	328.33	7.06
	50	72.8	7.19	326.92	7.070	73.61	7.16	327.88	7.10
	100	72.22	7.11	326.79	7.090	73.41	7.13	327.52	7.12
5	0	72.06	7.66	327.18	7.110	72.62	7.68	328.34	7.09
	50	71.27	7.74	326.89	7.530	72.65	7.71	327.65	7.21
	100	71.11	7.88	326.74	7.910	72.57	7.73	327.48	7.28
50	0	71.52	8.21	327.16	7.310	71.54	7.24	328.29	7.12
	50	71	8.41	326.84	7.710	71.34	8.28	327.60	7.35
	100	70.45	8.67	326.7	8.120	71.2	8.31	327.45	7.31
LSD		0.2664	0.1410	4.351	2820	0.2664	0.1410	4.351	2820
Standard deviation fordifferent treatment		±0.25	±0.18	±0.06	±0.13	±0.31	±0.16	±0.12	±0.03

In the soil addition treatment, the highest increase of soil content of P (50 and 100%) reached to 1.1 and 1.1 times than control for soya bean and 1.02 and 1.06 time than control for wheat, respectively. While the highest increase of soil content of Zn (5 and 50 Zn ppm) reached to 1.08 and 1.11 times than control for soyabean and 1.24 and 1.27 time than control for wheat, respectively.

In general, zinc nanoparticles foliar application treatments significantly increased grain yield and its components of wheat and soybean cultivars.

Several studies have reported positive effects of nanoparticles on plant germination, growth and performance. For example, increased seed germination and growth of seedling, improved photosynthetic efficiency, biomass, and total protein, sugar, nitrogen, and micronutrients were observed in several crop plants; e.g., soybean (Dimkpa et al., 2017) and wheat (Zhang et al., 2018). About the interaction of zinc and phosphorus numerous studies have been done and all confirms this point that zinc and phosphorus imbalance in the plant, As a result excessive accumulation of phosphorus, causing zinc imposed deficiency. (Salimpour et al., 2010).

CONCLUSION

Nano-zinc showed 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.

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تاثير استخدام جزيئات اكسيد الزنك النانويه كسماد على محصولى فول الصويا والقمح

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الهدف الرئيسي من تطبيقات الأسمدة النانوية في الزراعة هو تقليل خسائر الأسمدة المعدنية وزيادة الغلة لدعم الإنتاج الزراعي. لذلك تم إجراء هذا البحث في محطة الجميزة بمحافظة الغربية بمصر خلال موسمي النمو 2017 و 2018 لدراسة فاعلية جزيئات الزنك النانوية على محصول وجودة نبات فول الصويا و القمح. ، تم تمييز جزيئات الزنك النانوية المركبة لتأكيد الحجم والشكل وبنية السطح والتركيب البلوري. تم استخدام جزيئات ZnO النانوية إما بالرش الورقي أو إضافة ارضية بتركيزات مختلفة (0 ، 5 و 50 مجم لتر $^{-1}$). في هذه التجربة تم استخدام ثلاث مقادير من الفسفور (0 و 50 و 100٪ من الجرعة الموصى بها). أظهرت النتائج المتحصل عليها أن الرش الورقي لجسيمات ZnO النانوية كان فعالاً في زيادة إنتاج المحاصيل مقارنةً بالاضافة الارضية. بالإضافة إلى ذلك ، أدى الرش الورقي إلى تحسين جودة الثمار ، ولوحظت أعلى زيادة في المحصول باستخدام 50 جزء في المليون من جزيئات ZnO النانوية تحت الجرعة القصوى الموصى بها من السماد الفسفوري (100٪ P). وصلت هذه الزيادة إلى 1.4 ضعف مقارنة بمعاملة الكونترول (100٪ P). ومع ذلك ، وصلت الزيادة إلى 1.9 ضعف من صفر زنك مع تطبيق صفر P. تعمل جزيئات ZnO النانوية على تحسين جودة المحاصيل من حيث البروتين والكربوهيدرات والدهون الخام و N و P و K و Zn لفول الصويا و القمح. أظهرت النتائج انخفاضًا طفيفًا في تركيز النيتروجين والبوتاسيوم في التربة مع زيادة تركيز الجسيمات النانوية ZnO في كلا النوعين (الرش الورقي والإضافة الارضية).