Efficiency of Some Nanoparticles Spray on Fruit Quality of "Zaghloul" Date Palm and Assessment of their Accumulation on Human Health

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Abstract

This investigation was conducted to estimate the impact of pre-harvest application of zinc, magnetite, selenium and silver nanoparticles at (30, 60 and 90 ppm) for each on yield and fruit quality as compared with untreated fruits of "Zaghloul" date palm during (2018 and 2019) seasons. All treatments were sprayed on bunches and performed three times at the beginning of growth, after fruit setting, and at one month later. The sprayed fruits were harvested at Khalal stage in September, yield and quality were evaluated at harvest day. Results showed that all treatments enhanced yield and fruit quality as the best treatment was zinc oxide nanoparticles at 90 ppm as increased yield, bunches weight, fruit weight, flesh weight and fruit firmness; also gave the highest total soluble solids, total sugars and total anthocyanin content. Moreover, gave the lowest decreased seeds weight as compared with the control. Furthermore, the metal concentrations in sprayed fruit with some nanoparticles were found within the permissible limits regulated for health standard. In addition, health risk index for zinc, magnetite, selenium and silver nanoparticles were less than 1, which indicated to "Zaghloul" date palm fruits supplied with ZnONPs, Fe3O4NPs, SeNPs and, AgNPs, were free of risks on human health and can be considered as appropriate strategy for improving yield, nutritional status and quality of "Zaghloul" date palm.

Keywords: Date palm, nanoparticles, zinc oxide, magnetite, selenium, silver, health risk index.

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Introduction

Date palm (*Phoenix dactylifera* L.) fruits are considered among the most storage products playing an important role in economic, nutrition and special life in the Arab countries (El-Sersawy *et al*., 2019). Dates are now available all over the world and can be an inseparable part of the daily diet due to the increased production and exports (Al-Yahyai and Manickavasagan, 2012). “Zaghloul” date palm is the most important of soft date and its produce fruits of high quality are very demanded in the Egyptian market (Khayyat *et al*., 2007). In general, it could be consumed at the Khalal stage due to the conversion of soluble tannins to insoluble form, which reduces their astringency and sweet taste (Farag, 2016). Nanoparticles have a wide range of applications in the agricultural field due to their unique properties, including high penetration ability, larger surface area and high chemical activity (Agrahari and Dubey, 2020). Fertilizers at the nanometer scale (1–100 nm) increase greatly the points of impact because of their reduced size, which in turn could improve the interaction and uptake of micronutrients in crop fertilization (Singh *et al*., 2017). Food safety issues and potential health risks is one of the most serious environmental concerns (Cui *et al*., 2005). The human health risk assessment requires identification, collection, and integration of information on the chemicals health hazards, exposure of human to the chemical and relationships between exposure, dose and adverse effects World Health Organization (WHO, 2010). In this regard, a human potential health risk assessment is the process to estimate the nature and possibility of adverse health effects in humans exposed to toxins and chemicals in polluted environmental media, now or in the future (Sobhanardakani, 2016). Kliewer and Casteel (2003) recorded that, spraying of ZnNPs and FeNPs on date palm cultivar Sakkoti at 0.005–0.04 % improved yield and fruit quality compared to conventional fertilizers. Spraying pre-harvest nanoparticles treatments of Zinc Oxide nanoparticles (ZnONPs), silver nanoparticles (AgNPs) had increased bunch weight, fruit weight and the total yield, Also improved quality parameters as increased total soluble solids, total sugars content and total anthocyanin content and reduced total acidity, total soluble tannins and total phenols content (Kamal *et al*., 2021). The advantages of ZnONP use in the agriculture have been reported including a safe chemical substance and source of zinc supplement and fortification (Suyatma *et al*., 2014). Apart from these many applications, ZnO, due to its low toxicity is listed as "Generally Recognized as Safe" (GRAS) by the US Food and Drug Administration (21, CFR 182, 8991) (Bhumi *et al*., 2014a). Zn is essential for human life, yet excessive intake of these metals may have safe and non-carcinogenic impacts on human health (Kamunda *et al*., 2016). Zinc and iron elements are playing fundamental role in building or activation of various enzymes involves to nutrients absorption, biosynthesis of metabolic compounds and phytohormone formation (Elanchezhian *et al*., 2017). Magnetic treatments may affect phytohormones production leading to improve cell activity and plant growth (Maheshwari, 2009). Selenium can be obtained as supplements from food or meat, and the best method of enrichment to satisfy human requirements is to enhance its level in agricultural crops by means of spraying selenium or addition as selenite or selenates in fertilizers (Carvalho *et al*., 2003). Malik *et al*. (2011) showed that, Selenium increased photosynthesis and stimulates cell division, this could be the reason that fruits increased the weight and fruits dimensions in the present experiment. World Health Organization (WHO, 1996) reported that, selenium (Se) is a trace element that is not considered an essential nutrient for plant growth; it is an important element for both animals and humans in trace amounts, based on the recommendations, a maximum daily intake of Se 200 µg Se/day. The health benefits of Se, which include cancer protection. It had been reported to be toxic, but recent research has shown that its toxicity depends on the concentration (Uttam and Abioye, 2017). Ma *et al*. (2010) noticed that, AgNPs has great influence on plant growth and development such as germination, growth and senescence inhibition. The smaller AgNPs have higher surface to volume ration, which means enhanced reactivity (Roduner, 2006). The adverse health effects depend on NPs dose, concentration and composition (Buzea *et al*., 2017). European Food Safety Authority have also evaluated a number of silver complexes intended for use in food contact materials latest in 2011 (EFSA, 2011) and classified silver in the SCF list 3 with a group of specific migration limit of 0.05 mg/kg food. Severity of the toxicity of the AgNPs is also influenced by the mode of administration and exposure duration (Yokel and MacPhail, 2011). This investigation is aim to comparing the effect of spray some nanoparticles pre harvest treatment (zinc oxide, magnetite, selenium and silver) on enhancing growth, increasing yield of "Zaghloul" date palm fruits and improving fruit quality with consider evaluating the potential risks of nanoparticles accumulating and the daily intake of metals on human health.

Materials and methods

"Zaghloul" date palms (soft cultivar), It is grown in clay loam soil at the experimental farm of the Central Laboratory for Date Palm Researches and Development, Agricultural Research Center (ARC), Giza, Egypt. The experiment was designed as a completely randomized block design each treatment was replicated three times, one palm per each. Therefore, thirty uniform in vigor "Zaghloul" date palms of 26 years old received normal cultural practices were selected for achieving of this study. The leaf/bunch ratio was adjusted at the value of 8:1 for all experimental palms. Bunches were sprayed three times at the beginning of the vegetative growth (last week of April), after fruit setting (last week of May) and one month later (last week of June). Control palms sprayed with water only. The non-ionic surfactant tween 20 at 0.05% (v/v) was added to all spraying solutions to reduce the surface tension and increase the contact angle of sprayed droplets and applied directly for the trees with a handheld sprayer until run off in the early morning during 2018 and 2019 seasons.

1. Chemical synthesis of the nanoparticles

1.1. Synthesis of Zinc oxide (ZnO) nanoparticles

Zinc oxide nanoparticles were created using a wet chemical method (ZnO-NPs) (Lee *et al.*, 2013). Under flow control and gentle magnetic stirring at 50°C, 20 mL of aqueous a solution of 1 M sodium hydroxide was added to 0.1 M $\{Zn(NO_3)_2 \cdot 6H_2O\}$ in 100 mL distilled water. The reaction mixture was kept at this temperature for one hour before being allowed to cool at room temperature. To remove ions, the white precipitate was rinsed with distilled water and centrifuged for 10 minutes at 4000 rpm. The resulting precipitate was dried for 6 hours in an 80°C hot air oven.

1.2. Synthesis of Magnetite (Fe_3O_4) nanoparticles

This strategy could be the most promising because of its simplicity and effectiveness. A 2:1 molar ratio of ferric chloride and ferrous chloride was used. The Fe^{2+} and Fe^{3+} solutions were made by dissolving the ions in distilled water and heating the solution containing both ions to 50°C for 10 minutes. The solution was precipitated by ammonia solution after heating at 50°C with continuous stirring on the magnetic stirrer. Iron oxide particles were precipitated, which were black in colour. These particles were then removed from the solution with a powerful magnet and rinsed several times with distilled water. The magnetite that has precipitated is black in hue. The powder was then dried overnight in a hot air oven at 100°C. The total reaction can be expressed as follows:

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O$$

The shape and size of the produced powder were investigated using scanning electron microscopy on the model (Peng *et al*., 2012).

1.3. Synthesis of selenium (Se) nanoparticles

SeNPs were synthesized by the (chemical reduction) of sodium selenite with glutathione reduced form and stabilizing it with bovine serum albumin (BSA). In a sterile cabinet, 3 mL of 25 mM Na_2SeO_3, 3 mL of 100 mM GSH, and 0.15 g BSA were combined with 9 mL of double-distilled water (dH_2O). All of the solutions were prepared in a sterile setting with double-distilled water in a sterile cabinet. 1M NaOH was added to the reactant solution after mixing to bring the pH of the solution to the alkaline media. SeNPs were produced as soon as NaOH was added, as evidenced by a colour change in the reactant solution from clear white to clear red. The SeNPs were then recovered by centrifuging the solution at 13,000 rpm for 30 minutes at 4°C temperature using a cooling centrifuge (Cooling centrifuge C-24 BL) (Tran and Webster, 2011).

1.4. Synthesis of silver (Ag) nanoparticles

Aqueous phase mixing of $AgNO_3$ to various concentration of $C_6H_5Na_3O_7 \bullet 2H_2O$ solution has been used to synthesize colloidal silver nanoparticles. (AgNPs) were made by heating a solution of $AgNO_3$ (1.0×10^{-3} M) until it started to boil in deionized water. As soon as the boiling started, drops of sodium citrate solution were added to the $AgNO_3$ solution. The hue of the solution gradually changed to a greyish yellow, suggesting that the Ag^{+} ions had been reduced. The solution was heated for an extra period of time before being cooled to room temperature and used for further experiments (Zhou and Wang, 2012).

2. Preparation of nanoparticles

ZnONPs, Fe_3O_4NPs, SeNPs, AgNPs and CsNPs, were prepared in deionized water to final concentrations of 30, 60 and 90 ppm (w/v), All bunches were sprayed with equal amounts of 1 liter/ bunch.

3. Characterization of the prepared nanoparticles

Zinc oxide nanoparticles (ZnONPs), Magnetite nanoparticles (Fe_3O_4NPs), Selenium nanoparticles (SeNPs), and Silver nanoparticles (AgNPs) were synthesized at the Naqaa Foundation for Scientific Research, Technology and Development, Giza, Egypt. Particle size measurements of ZnONPs, Fe_3O_4NPs, SeNPs and AgNPs, were carried out at Nanotechnology & Advanced Material Central Lab (NAMCL), Agricultural Research Center, with a Zetasizer (Nano-ZS90, Malvern, UK), the size of the ZnONPs were found to be <90 nm, Fe_3O_4NPs were found to be <40 nm, SeNPs were found to be <60 nm and AgNPs were found to be <50 nm.

4. Pre-harvest treatments were as following:

4.1. Spraying of zinc oxide nanoparticles at 30, 60 and 90 ppm.
4.2. Spraying of magnetite nanoparticles at 30, 60 and 90 ppm.
4.3. Spraying of selenium nanoparticles at 30, 60 and 90 ppm.
4.4. Spraying of silver nanoparticles at 30, 60 and 90 ppm.
4.5. Spraying with distilled water (control)

"Zaghloul" Date palm fruits were harvested at khalal stage in the first of September, when untreated fruit reached commercial maturity, indicated by fruits are crunchy, red and total soluble solids reached about 25 (ºBrix). Yield (kg/palm) for each treatment was estimated in both seasons. Fruits were transported directly to the laboratory without any signs of mechanical damage or deterioration and selected with homogeneous size, color and form. Samples of fruits were taken from each replicate of each treatment at the harvest date to evaluate their physical and chemical characteristics.

5. Quality assessments

5.1. Physical properties

Samples of 30 fruits per each treatment (10 fruits from each bunch (as a replicate) were randomly taken to determine:

5.1.1. Palm yield and bunch weight: To determine the total yield at harvest, each bunch was weighed separately using weighing balance and was expressed in kilogram (kg).

5.1.2. Fruit weight: Fruit weight was determined by a digital balance (A&D, Japan) with an accuracy of ±0.01 g.

5.1.3. Flesh weight:

Flesh weight = Fruit weight - Seed weight

5.1.4. Seed weight: For seed weight assessment, samples of 50 fruits from each treatment and control were obtained from each replicate (g).

5.2. Chemical properties

5.2.1. Total soluble solids (TSS)

Soluble solids were measured by using a digital refractometer (Atago, Japan) at room temperature and expressed in (Brix˚).

5.2.2. Total sugars content (TSC)

Total sugar content was measured in the methanol extract by using the phenol sulfuric acid method and the concentration was calculated as g /100 g fresh weight the method described by (Smith *et al*., 1956).

5.2.3. Total anthocyanin content (TAC)

Anthocyanin was extracted by one gram from fruit peel tissue was blended with 85 ml ethanol (95 %) and 1.5 N, HCL the color of clear was measured at 520 nm as reported by (Ranganna, 2007).

6. Determination of Zn, Fe, Se and Ag concentration in fruits

Concentrated H_2SO_4 (99.7 %) was used to digest dried samples (0.5 g). Zn, Fe, Se and Ag concentrations were determined using an atomic absorption spectrophotometer (Pye Unicam model SP-1900, US) as stated by (Allen *et al*., 1984).

7. Risk assessment of heavy metals accumulation in sprayed "Zaghloul" date palm fruits with some nanoparticles pre-harvest treatments on human health

The following formulas were used to compute the daily intake of metals (DIM) and the health risk index (HRI) according to (Farrag *et al*., 2016).

7.1. Daily intake of metals (DIM)

$$DIM = \frac{(C_{metal} \times C_{factor} \times D_{food\ intake})}{B_{Average\ weight}}$$

Where C_{metal} is concentration of the metal (mg/ kg) in "Zaghloul" fruits, C_{factor} is the conversion factor (0.085) for conversion of fresh to dry weight fruit, $D_{food\ intake}$ is the daily intake of fruits (0.345 and 0.232 kg person/day for adults and children, respectively). $B_{average\ weight}$ is the average body weight (70 and 32.7 kg for adults and children, respectively) according to (Wang *et al*., 2005).

7.2. Health risk index (HRI)

$$HRI = \frac{DIM}{RfD}$$

Where RfD is the reference oral dose (mg/kg-day) for each metal as 0.30 for Zn, 0.70 for Fe, 0.005 for Se and 0.005 for Ag. (IRIS, 2003) reported that, humans are considered to be safe if ($HRI < 1$).

8. Experimental design and statistical analysis

The experiment was laid out as a randomized complete block design (RCBD) with three-replicates, one palm for (each replicate). All data were subjected to analysis of variance using (SAS, 2012) and the means were compared by the least significant difference (LSD) test at p=0.05 and subjected to statistical analysis as described by (Snedecor and Cochran, 1990).

Results and discussion

9. Physical properties

Effect of zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe_3O_4NPs), selenium nanoparticles (SeNPs) and silver nanoparticles (AgNPs) treatments on physical properties of "Zaghloul" date palm cultivar.

9.1. Palm yield, bunch weight and fruit weight

Data in (Table 1) show that the use of some nanoparticles pre-harvest application played a significant influence on increasing bunch weight, fruit weight and the total yield (Kg) per palm on "Zaghloul" date palm cultivar during two growing seasons (2018 and 2019).

Table (1): Effect of zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe3O4NPs), selenium nanoparticles (SeNPs) and silver nanoparticles (AgNPs) treatments on total yield, bunch weight and fruit weight of "Zaghloul" date palm during 2018 and 2019 seasons

Pre-harvest treatments		Yield (kg/palm)		Bunch (kg)		Fruit weight (g)	
		2018	2019	2018	2019	2018	2019
ZnONPs	30ppm	211.66^{c}	214.26^{c}	21.16^{c}	21.42^{c}	32.16^{c}	32.36^{c}
	60ppm	217.26^{b}	220.76^{b}	21.72^{b}	22.07^{b}	32.55^{b}	32.75^{b}
	90ppm	221.56^{a}	223.70^{a}	22.15^{a}	22.37^{a}	33.97^{a}	34.22^{a}
Fe_3O_4NPs	30ppm	206.60^{f}	210.30^{f}	20.60^{f}	21.03^{f}	30.20^{f}	30.43^{f}
	60ppm	209.13^{e}	216.30^{e}	20.91^{e}	21.63^{e}	30.61^{e}	30.85^{e}
	90ppm	210.00^{d}	219.13^{d}	21.10^{d}	21.91^{d}	30.98^{d}	31.26^{d}
SeNPs	30ppm	193.26^{i}	197.26^{i}	19.32^{i}	19.73^{i}	28.11^{i}	28.26^{i}
	60ppm	198.33^{h}	199.53^{h}	19.83^{h}	19.95^{h}	28.41^{h}	28.63^{h}
	90ppm	199.76^{g}	203.73^{g}	19.97^{g}	20.37^{g}	28.74^{g}	29.91^{g}
AgNPS	30ppm	179.53^{l}	183.27^{l}	17.95^{l}	18.33^{l}	27.00^{l}	27.17^{l}
	60ppm	182.23^{k}	187.07^{k}	18.22^{k}	18.71^{k}	27.38^{k}	27.66^{k}
	90ppm	187.56^{j}	193.60^{j}	18.75^{j}	19.36^{j}	27.87^{j}	28.99^{j}
Control		110.30^{p}	111.80^{p}	11.03^{p}	11.18^{p}	14.13^{p}	15.29^{p}

Means having the same letter(s) within a column are insignificantly different at 5% level.

Moreover, the highest significant values of yield, bunch weight, and fruit weight were recorded of all zinc oxide nanoparticles (ZnONPs) treatments followed by all treatments of magnetite nanoparticles (Fe3O4NPs) followed by all treatments of selenium nanoparticles (SeNPs) treatments and then all treatments of silver nanoparticles (AgNPs). ZnONPs at 90 ppm recorded the highest total yield (221.56 and 223.70 kg/ palm) and bunch weight (22.15 and 22.37 kg) fruit weight (33.97 and 34.22 g) while the lowest total yield was in the control treatment (110.30 and 111.80 kg/ palm), bunch weight (11.03 and 11.18 kg) and fruit weight (14.13 and 15.29 g) in the two seasons, respectively. Kumar *et al*. (2017) pointed that, applications of zinc nanoparticles showed a promising yield of strawberry plants. Josue *et al*. (2019) revealed that, application of ZnONPs at a concentration of 1000 ppm on pepper plants positively increased fruit yield compared to control.

Table (2): Effect of zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe3O4NPs), selenium nanoparticles (SeNPs) and silver nanoparticles (AgNPs) treatments on flesh weight, seed weight and fruit firmness of "Zaghloul" date palm during 2018 and 2019 seasons

Pre-harvest treatments		**Flesh weight (g)**		**Seed weight (kg)**		**Fruit firmness (Lb/inch2)**	
		2018	**2019**	**2018**	**2019**	**2018**	**2019**
ZnONPs	**30ppm**	30.32^{c}	30.44^{c}	1.84^{f}	1.92^{g}	17.50^{c}	17.55^{b}
	60ppm	30.69^{b}	30.80^{b}	1.86^{d}	1.95^{e}	17.51^{b}	17.56^{a}
	90ppm	32.13^{a}	32.25^{a}	1.83^{g}	1.97^{c}	17.52^{a}	17.56^{a}
Fe_3O_4NPs	**30ppm**	28.39^{f}	28.51^{f}	1.81^{h}	1.92^{g}	17.49^{e}	17.53^{d}
	60ppm	28.79^{e}	28.91^{e}	1.81^{h}	1.94^{f}	17.50^{d}	17.54^{c}
	90ppm	29.15^{d}	29.30^{d}	1.83^{g}	1.96^{d}	17.50^{d}	17.54^{c}
SeNPs	**30ppm**	26.28^{i}	26.32^{i}	1.83^{g}	1.94^{f}	17.48^{f}	17.51^{f}
	60ppm	26.56^{h}	26.67^{h}	1.85^{e}	1.96^{d}	17.49^{e}	17.52^{e}
	90ppm	26.88^{g}	27.94^{g}	1.86^{d}	1.97^{c}	17.49^{e}	17.52^{e}
AgNPS	**30ppm**	25.16^{l}	25.33^{l}	1.84^{f}	1.85^{j}	17.48^{f}	17.49^{g}
	60ppm	25.50^{k}	25.75^{k}	1.88^{c}	1.90^{i}	17.48^{f}	17.49^{g}
	90ppm	25.98^{j}	27.07^{j}	1.89^{b}	1.92^{g}	17.48^{f}	17.49^{g}
Control		11.67^{p}	12.76^{p}	2.46^{a}	2.53^{a}	16.46^{i}	16.51^{j}

Means having the same letter(s) within a column are insignificantly different at 5% level.

9.2. Flesh weight, seed weight and fruit firmness

All nanoparticles treatments increased significantly fruit dimension and volume as compared with control in the two studied seasons (Table 2). The best results concerning fruit length were obtained by spraying all zinc oxide nanoparticles (ZnONPs) treatments followed by all treatments of magnetite nanoparticles (Fe3O4NPs) followed by all treatments of selenium nanoparticles (SeNPs) treatments and then all treatments of silver nanoparticles (AgNPs). Zinc oxide nanoparticles (ZnONPs) especially at 90 ppm gave the highest flesh weight (32.13 and 32.25 g) and fruit firmness (17.52 and 17.56 Lb/inch2) and the lowest flesh weight (11.67 and 12.76 g) and fruit firmness (16.46 and 16.51 Lb/inch2) were recorded in control fruits in both seasons, respectively. The seed weight was not significantly affected by spraying all preharvest treatments in both seasons. From the mentioned results, control treatment gave the highest value of seed weight. These results are in agreement with those (Bybordi and Shabanov, 2010) reported that Zinc (Zn) is one of the essential elements for plants. Zn is required for the synthesis of auxins, chlorophyll, starch and metabolism of carbohydrates that's led to improve quality of fruits. The involvement of Zn in the synthesis and translocation of carbohydrates and proteins (Yogeratnam and Greenham, 1982) as well as preserving the structural stability of cell membranes (Welch *et al*., 1982) could be linked to the increased soluble solids and firmness and decreased phenolic content of fruits during ZnONPs fertilization in our study.

10. Chemical Properties

Effect of zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe3O4NPs), selenium nanoparticles (SeNPs) and silver nanoparticles (AgNPs) treatments on chemical properties of "Zaghloul" date palm cultivar.

10.1. Total soluble solids (TSS), total sugars content (TSC) and total anthocyanin content (TAC)

The present results (Table 3) indicated that all conductive nanoparticles treatments more effective statistically in increasing total soluble solids in (ºBrix) and total sugars content and total anthocyanin content as compared with untreated fruits. Dates sprayed with ZnONPs at 90 ppm gave the highest significant total soluble solids content (41.34 and 42.12 ºBrix), total sugar content (31.27 and 32.11 g/100 g FW) and total anthocyanin content (28.52 and 29.34 mg/100 g FW) in the first and second seasons, respectively). In contrast, the lowest total soluble solids in (ºBrix) were observed at control fruit which recorded (23.33 and 24.23 ºBrix), total sugar content (19.13 and 20.21 g/ 100 g FW) and total anthocyanin content (17.14 and 17.51 mg/100 g FW) in the first and second seasons, respectively. Our findings are consistent with those of (Davarpanah *et al*., 2016), who found that application of zinc oxide nanoparticles (ZnONPs) resulted in considerable improvements in pomegranate fruit quality, including more soluble solids, lower titratable acidity, lower soluble tannins, lower phenolic content, higher maturity index, and higher juice pH.

Table (3): Effect of zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe3O4NPs), selenium nanoparticles (SeNPs) and silver nanoparticles (AgNPs) treatments on total soluble solids (TSS), total sugar content (TSC) and total anthocyanin content (TAC) of "Zaghloul" date palm during 2018 and 2019 seasons

Pre-harvest treatments		**Total soluble solids (ºBrix)**		**Total sugar (g/ 100g FW)**		**Total anthocyanin content (mg/100g FW)**	
		2018	**2019**	**2018**	**2019**	**2018**	**2019**
ZnONPs	**30ppm**	40.68[c]	41.71[c]	30.21[c]	31.19[c]	27.74[c]	28.53[c]
	60ppm	40.97[b]	41.99[b]	31.02[b]	32.08[b]	28.16[b]	29.00[b]
	90ppm	41.34[a]	42.12[a]	31.27[a]	32.21[a]	28.52[a]	29.34[a]
Fe_3O_4NPs	**30ppm**	38.15[f]	39.54[f]	28.78[f]	29.74[f]	24.34[f]	25.42[f]
	60ppm	39.34[e]	40.13[e]	29.03[e]	30.03[e]	25.09[e]	26.00[e]
	90ppm	39.56[d]	40.51[d]	29.14[d]	30.21[d]	25.33[d]	26.22[d]
SeNPs	**30ppm**	36.25[i]	37.21[i]	26.63[i]	27.16[i]	22.85[i]	23.68[i]
	60ppm	37.02[h]	38.03[h]	27.02[h]	28.01[h]	23.03[h]	24.15[h]
	90ppm	37.23[g]	38.25[g]	27.15[g]	28.21[g]	23.19[g]	24.28[g]
AgNPS	**30ppm**	34.94[l]	35.25[l]	24.63[l]	25.42[l]	20.16[l]	21.32[l]
	60ppm	35.37[k]	36.16[k]	25.08[k]	26.15[k]	21.34[k]	22.04[k]
	90ppm	35.66[j]	36.74[j]	25.31[j]	26.39[j]	21.71[j]	22.74[j]
Control		23.33[p]	24.23[p]	19.13[p]	20.21[p]	17.14[p]	17.51[p]

Means having the same letter(s) within a column are insignificantly different at 5% level.

11. Risk assessment of heavy metals accumulation in sprayed "Zaghloul" date palm fruits with some nanoparticles pre-harvest treatments on human health

Nanomaterials may be having potential hazards to human health Just like any other chemical substance, some nanomaterials are hazardous and others not. The nanoscale of the particles does not in itself imply a hazard. Instead, the potential effects are based on the adverse effects a nanomaterial may cause and the amount taken up by an organism (human) from Zaghloul" date palm fruits. The risk associated with heavy metal accumulation in "Zaghloul" fruits to human is performed throughout determination of the daily intake of metals (DIM) and the health risk index (HRI). The metals mean in sprayed "Zaghloul" date palm fruits with some nanoparticles, DIM and HRI for adults and children Table (4). The metals mean in the fruits sprayed with some nanoparticles (ZnO, Fe_3O_4, Se and Ag) were estimated to estimate the daily consumption of minerals (Zn, Fe, Se, Ag), The highest concentration of Fe measured when sprayed fruits with Fe_3O_4NPs at 90 ppm (0.92 mg/kg^{-1}), In contrast, The lowest concentration of Se measured when sprayed fruits with SeNPs at 30 ppm (0.12 mg/kg^{-1}). Therefore, the highest DIM in both adults and children measured for Fe when sprayed fruits with Fe_3O_4NPs at 90 ppm was (4.496E-04 and 5.548E-04, respectively). The value of DIM in adults of Fe for treated "Zaghloul" date palm fruits with Fe_3O_4NPs at 30, 60 and 90 ppm were (3.861E-04, 4.105E-04 and 4.496E-04 respectively), and in children were (4.764E-04, 5.065E-04 and 5.548E-04, respectively). In contrast, The lowest DIM in both adults and children measured for Se when sprayed fruits with SeNPs at 90 ppm was (1.710E-04 and 2.110E-04, respectively). The value of DIM in adults of Se for treated "Zaghloul" date palm fruits with SeNPs at 30, 60 and 90 ppm were (5.865E-05, 9.286E-05 and 1.710E-04, respectively), and in children were (7.236E-05, 1.145E-04 and 2.110E-04). Moreover, Children posed to higher health risks than adults since the DIM via consumption of fruits found to be significantly higher for children as compared to adults. Furthermore, the analysis indicated that the HRI values were <1 in all treatments (ZnONPs, Fe_3O_4NPs, SeNPs and AgNPs) which shows that all concentrations used are safe for adults and children. Hence, in the present investigation, the risk associated with heavy metals contamination through consumption of "Zaghloul" date palm fruits treated with ZnONPs, Fe_3O_4NPs, SeNPs and AgNPs by adults and children in the study area assumed to be relatively safe in general. These results are in agreement with the finding demonstrated in Refs. United States Environmental protection Agency (US EPA, 2005). However, Long-term human exposure to hazardous levels of heavy metals in food may result in a variety of chronic disorders. Human exposures to “nano” form iron oxides are now under investigation in a variety of biomedical applications, although administration is not usually via the lung (Long *et al*., 2014). Furthermore, human epidemiological evidence from a number of studies suggests that iron oxide is not a human carcinogen, and therefore, based upon the complete weight of evidence, we conclude that “bulk” iron oxides are not human carcinogens (Camilla *et al*., 2016). Selenium is a naturally occurring mineral required for good health. It is obtained from food, the amount of selenium available in a diverse diet with meat, grains, vegetables, fruits and nuts is typically sufficient to negate the necessity for supplementation (Levander, 1991). Selenium toxicity can occur with acute or chronic ingestion of excess selenium. Symptoms of selenium toxicity include nausea; vomiting; nail discoloration, brittleness, and loss; hair loss; fatigue; irritability; and foul breath odor (often described as “garlic breath”) (Yang *et al*., 1983). Acute Zn poisoning can result in tachycardia, vascular shock, dyspeptic nausea, vomiting, pancreatitis, diarrhea and hepatic parenchyma damage (Salgueiro, 2000). Acute symptoms of overexposure to silver salts are decreased blood pressure, diarrhea, stomach irritation and decreased respiration. Chronic symptoms from prolonged intake of low doses of silver salts are fatty degeneration of the liver and kidneys and changes in blood cells (Venugopal and Luckey, 1978). Regular monitoring of these metals in agricultural crops in the research area is critical in this regard to avoid excessive metal buildup in the food chain. Where, health risk index for Zn, Fe, Se and Ag in fruits did not across the allowable limit set by World Health Organization and Food and Agriculture Organization (WHO and FAO) (less than 1). This indicated that all treated fruits with ZnONPs and Fe_3O_4NPs, SeNPs and AgNPs were fit for consumption. Therefore, all consumers including adults and children have no potential health risk through consuming treated “Zaghloul” date palm fruits by some nanoparticles from the study area.

Conclusions

The results indicate that pre-harvest treatments with zinc oxide nanoparticles (ZnONPs), magnetite nanoparticles (Fe_3O_4NPs), selenium nanoparticles (SeNPs), and silver nanoparticles (AgNPs), each at 90 ppm, effectively enhanced fruit weight, yield, and quality parameters of "Zaghloul" date palms. These treatments are safe, with metal concentrations in the treated fruit remaining within acceptable health standards.

Recommendations:

- Perform safety assessments of nanomaterials before applying them to fruits.

- Label the fruits to indicate that nanomaterials have been used, ensuring they are within acceptable limits.

Table (4): Metal mean in sprayed "Zaghloul" date palm fruits with some nanoparticles, DIM and HRI for adults and children.

Pre-harvest treatments		Metal mean (mg kg^{-1})	Metal RfD (mg kg^{-1} day^{-1})	DIM		HRI		Remarks
				Adults	Children	Adults	Children	
ZnONPs	**30ppm**	0.49^{f}	Zn 0.3	$2.394E\text{-}04^{f}$	$2.954E\text{-}04^{f}$	0.0007^{g}	0.0009^{h}	Safe
	60ppm	0.54^{e}	Zn 0.3	$2.639E\text{-}04^{e}$	$3.256E\text{-}04^{e}$	0.0008^{g}	0.0010^{g}	Safe
	90ppm	0.67^{d}	Zn 0.3	$3.274E\text{-}04^{d}$	$4.040E\text{-}04^{d}$	0.0010^{f}	0.0013^{f}	Safe
Fe_3O_4NPs	**30ppm**	0.79^{c}	Fe 0.7	$3.861E\text{-}04^{c}$	$4.764E\text{-}04^{c}$	0.0005^{i}	0.0006^{j}	Safe
	60ppm	0.84^{b}	Fe 0.7	$4.105E\text{-}04^{b}$	$5.065E\text{-}04^{b}$	0.0005^{i}	0.0007^{i}	Safe
	90ppm	0.92^{a}	Fe 0.7	$4.496E\text{-}04^{a}$	$5.548E\text{-}04^{a}$	0.0006^{h}	0.0007^{i}	Safe
SeNPs	**30ppm**	0.12^{k}	Se 0.005	$5.865E\text{-}05^{k}$	$7.236E\text{-}05^{k}$	0.0117^{e}	0.0144^{e}	Safe
	60ppm	0.19^{j}	Se 0.005	$9.286E\text{-}05^{j}$	$1.145E\text{-}04^{j}$	0.0185^{d}	0.0229^{d}	Safe
	90ppm	0.35^{g}	Se 0.005	$1.710E\text{-}04^{g}$	$2.110E\text{-}04^{g}$	0.0342^{a}	0.0422^{a}	Safe
AgNPs	**30ppm**	0.20^{i}	Ag 0.005	$9.775E\text{-}05^{i}$	$1.206E\text{-}04^{i}$	0.0195^{c}	0.0241^{c}	Safe
	60ppm	0.29^{h}	Ag 0.005	$1.417E\text{-}04^{h}$	$1.748E\text{-}04^{h}$	0.0283^{b}	0.0349^{b}	Safe
	90ppm	0.35^{g}	Ag 0.005	$1.710E\text{-}04^{g}$	$2.110E\text{-}04^{g}$	0.0342^{a}	0.0422^{a}	Safe

Reference oral dose mg kg^{-1} day^{-1} for each metal based on Ref. US EPA (2005) RfD: reference oral dose; DIM: Daily intake of metals; HRI: Health risk index.

References

Agrahari, S. and Dubey A. (2020). Nanoparticles in Plant Growth and Development. In Biogenic Nano-Particles and their Use in Agro-ecosystems. Springer, Singapore, 9-37.

Allen, S.F.; Grimshaw, H.F. and Rowl, A.B. (1984). Chemical Analysis. Methods in plant ecology. Blackwell, Oxford, pp. 185-344.

Al-Yahyai, R. and Manickavasagan, A. (2012). An overview of date palm production. Dates: production, processing, food, and medicinal values. CRC Press, Boca Raton, 3–12.

Bhumi, G., Raju, Y. R. and Savithramma, N. (2014a). Screening of Zinc oxide nanoparticles for cell prolifertaion synthesized through Adhatodavasicanees. Int. J. Drug Dev. Res., 6: 97-104.

Buzea, C. and Pacheco, I. (2017). Nanomaterial and nanoparticle: origin and activity. Nanoscience and plant-soil systems. Switzerland: Springer International Publishing, 71-112.

Bybordi, A. and Shabanov, A. (2010). Effects of the Foliar Application of Magnesium and Zinc on the Yield and Quality of Three Grape Cultivars Grown in the Calcareous Soils of Iran. Sci. Biol., 2: 81-86.

Camilla, P.; Thomas, R. C., and Thomas, B. (2016). Review of the Evidence from Epidemiology, Toxicology, and Lung Bioavailability on the Carcinogenicity of Inhaled Iron Oxide Particulates. Chemical Research in Toxicology, 29: 237−254.

Carvalho, K.M.; Gallardo-Williams, M.T.; Benson, R.F.; Martin, D.F. (2003). Effects of selenium supplementation on four agricultural crops. J. Agric. Food Chem., 51: 704-709.

Cui, Y.J.; Zhu, Y.G.; Zhai, R.; Huang, Y.; Qiu, Y. and Liang, J. (2005). Exposure to Metal Mixtures and Human Health Impacts in a Contaminated Area in Nanning, China, Environ. Int. 31: 784–790.

Davarpanah, S.; Tehranifara, A.; Davarynejad, G.; Abadia, J. and Khorasani, R. (2016). Effects of foliar applications of zinc and boron nanofertilizers onpomegranate (Punica granatum cv. Ardestani) fruit yield and quality. Scientia Horticulturae, 210: 1-8.

EFSA Scientific Committee, (2011). Scientific Opinion on Guidance on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain. EFSA Journal; 9: 1-36.

ELanchezhian, R.; Kumar, D.; Ramesh, K.; Biswas, A.; Guhey, A. and Patra, A. K., (2017). Morpho-physiological and biochemical response of maize (*Zea mays* L.) plants fertilized with nano-iron (Fe_3O_4) micronutrient. In Journal of Plant Nutrition, 40: 1969–1977.

El-Sersawy R.Y., M.A.S. Ali, M.R.A. Tohamy and M.M. Atia (2019). Efficiency of some essential plant oils on sewee date palm fruit spoilage caused by *Botrytis cinerea* under cold storage conditions. Zagazig J. Agric. Res., Vol. 46 No. (5) 2019.

Farag, K.M. (2016). Date palm, A Wealth of Healthy Food. Encyclopedia of Food and Health (FOHE). Chapter, 00215. Elsever, MRW Production Department at: MRW – FOHE @ ebevier. com.

Farrag, K.; Elbastamy, E.; Ramadan, A. (2016). Health risk assessment of heavy metals in irrigated agricultural crops, El-Saff wastewater canal, Egypt. *Clean- Soil, Air, Water*. 44: 1174-1183.

Josué, I.G.; Guillermo, N.M.; Emilio, O.S.; Ricardo, H.L.; Enrique, D.B., Rigoberto, V.A., Pablo, A.R. and Francisco, Z.G. (2019). Foliar Application of Zinc Oxide Nanoparticles and Zinc Sulfate Boosts the Content of Bioactive Compounds in Habanero Peppers. Journal of plants, 8: 1-20.

Kamal, H.M.; Abd Elwahab,S.M.; Gadalla, E.G. and Zainhoum, A.A. (2021). Efficiency of Zinc, Silver and Chitosan Nanoparticles Spray on Yield and Fruit Quality of Zaghloul Date Palm. Plant Cell Biotechnology and Molecular Biology 22(35&36):23-33.

Kamunda, C.; Mathuthu, M. and Madhuku, M. (2016). Health Risk Assessment of Heavy Metals in Soils from Witwatersrand Gold Mining Basin, South Africa. Int. J. Environ. Res. Publ. Health. 13: 663 – 674.

Khayyat, M.; Tafazoli, E.; Eshghi, S. and Rajaee, S. (2007). Effect of nitrogen, boron, potassium and zinc on yield and fruit quality of date palm Am-Euras. J. Agric. Environ. Sci., 2: 289- 296.

Kliewer, W.M. and Casteel T. (2003). Canopy management. In: Hellman, E. (Ed.), Corvallis, Oregon State University Press, *Oregon Viticulture*. 177– 184.

Kumar, U. J.; Bahadur, V.; Prasad, V. M.; Mishra, S. and Shukla, P. K. (2017). Effect of different concentrations of iron oxide and zinc oxide nanoparticles on growth and yield of strawberry (*Fragaria x ananassa* Duch) cv. Chandler. International Journal of Current Microbiology and Applied Sciences. 6: 2440–5.

Lee, B.W.; Koo, J.H.; Lee, T.S.; Kim, Y.H. and Hwang, J.S. (2013). Synthesis of ZnO nanoparticles via simple wetchemical routes. Advan. Mater. Res. 699: 133-137.

Levander, O. A. (1991). Scientific rationale for the 1989 recommended dietary allowance for selenium. *J Am Diet Assoc.* 91: 1572–1576.

Long, N.V.; Thi, C.M.; Yong, Y.; Cao, Y.; Wu, H. and Nogami, M. (2014). Synthesis and characterization of Fe-based metal and oxide based nanoparticles: discoveries and research highlights of potential applications in biology and medicine. Recent Pat. Nanotechnol. 8: 52-61.

Ma, Y.; Kuang, L.; He, X.; Bai, W.; Ding, Y.; Zhang, Z.; Zhao, Y. and Chai, Z. (2010). Effect of rare earth oxide nanoparticles on root elongation of plants. Chemosphere,78: 273-279.

Maheshwari, L.B. (2009). Magnetic treatment of irrigation water: evaluation of its effects on vegetable crop yield and water productivity. Ph.D. Thesis. University of Western Sydney, School of Environ And Agriculture.

Malik, J.A.; Kumar, S.; Thakur, P.; Sharma, S.; Kaur, R.; Kaur, R.; Pathania, D.; Bhandhari, K.; Kaushal, N.; Singh, K.; Srivastav, A. and Nayyar, H. (2011). Promotion of growth in mungbean (*Phaseolus aureus* Roxb.) by selenium is associated with stimulation of carbohydrate metabolism. Biology of Trace Elements Research 143: 530–539.

Peng, L.; Qin, P.; Lei, M.; Zeng, Q.; Song, H.; Yang, J.; Shao, J.; Liaoa, B. and Gu, J. (2012). Modifying Fe_3O_4 nanoparticles with humic acid for removal of Rhodamine B in water. Journal of Hazardous Materials, 210: 193-198.

Ranganna, S. (2007). Handbook of analysis and quality control for fruit and vegetables product. 2nd ED. New Delhi, India.

Roduner, E. (2006). Size matters: why nanomaterials are different. Chem Soc Rev 35: 583-592.

Salgueiro, M.; Zubillaga, J.; Lysionek, M.; Sarabia, A.; Caro, M.I. and Paoli, R. (2000). Zink as an Essential Micronutrients: A Review, Nutr. Res. 20: 737–755.

Singh, A.; Singh, N.B.; Afzal, S.; Singh, T. and Hussain, I. (2017). Zinc oxide nanoparticles: A review of their biological synthesis, antimicrobial activity, uptake, translocation and biotransformation in plants. J. Mater. Sci. 53, 185-201.

Smith, F.A., Gilles, M., Hanihun, K.J. and Gedees, A.P. (1956). Clorometric methods for determination of sugar and related substances. Analysis Chem., 28: 350.

Snedecor, G.W. and Cochran, W.G. (1980). Statistical Methods. 7th Edn.Iowa State Univ. Press Ames. Low USA.

Sobhanardakani, S and Jamshidi, K. (2015). Assessment of metals (Co, Ni, and Zn) content in the sediments of Mighan Wetland using geo-accumulation index. *Iran J Toxicol*, 9: 1386–1390.

Suyatma, N.E.; Ishitakawa, Y. and Kitazawa, H. (2014). Nanoreinforcement of pectin flm to enhance its functional packaging properties by incorporating ZnO nanoparticles. Advanced Materials Research, 845: 451-456.

Tran, P.A.; Webster, T.J. (2011). Selenium nanoparticles inhibit Staphylococcus aureus growth. Int J Nanomed, 6: 1553-1558.

US EPA (2005). (United State Environmental Protection Agency), Toxicological review of zinc and compounds, EPA/635/R-05/002, CAS NO. 7440-66-6, Washington.

Uttam, S. and Abioye, F.L.S. (2017). Selenium in the Soil-Plant Environment: A Review. Int. J. Appl. Agric. Sci. 3: 1–18.

Venugopal, B. and Luckey, T.D. (1978). Metal toxicity in mammals. In Chemical toxicology of metals and metalloids. New York: Acedemic Press., 32–36.

Wang, X.; Sato, T.; Xing, B.; Tao, S. (2005). Health Risks of Heavy Metals to the General Public in Tianjin, China via Consumption of Vegetables and Fish, *Sci. Total Environ*. 350: 28- 37.

Welch, R.M.; Webb, M.J.; Loneragan, J.F. (1982). Zinc in membrane function and its role in phosphorus toxicity. In Proceedings of the 9th Plant Nutrition Colloquium, Coventry, UK, 22: 710–715.

(WHO) World Health Organization (1996). Trace elements in human nutrition and health. Geneva; p. 160. ISBN: 92 4156173 4.

(WHO) World Health Organization (2010). WHO Human Health Risk Assessment Toolkit: Chemical Hazards. International Programme on Chemical Safety.

Yang, G.Q.; Wang, S.Z.; Zhou, R.H.; Sun, S.Z. (1983). Endemic selenium intoxication of humans in China. *Am J Clin Nutr.* 37: 872–881.

Yogeratnam, N. and Greenham, D.W.P. (1982). The application of foliar sprayscontaining N, Mg, Zn and B to apple trees. I. Effect on fruit set and cropping. J. Hortic. Sci. 57: 151–154.

Yokel, R.A. and MacPhail R.C. (2011). Engineered nanomaterials: exposures, hazards, and risk prevention. J Occup Med Toxicol, 6: 7.

Zhou, G. and Wang W. (2012). Synthesis of Silver Nanoparticles and their Antiproliferation against Human Lung Cancer Cells In vitro. Orient. J. Chem., 28: 651-655.

كفاءة رش بعض الجسيمات النانوية على جودة ثمار نخيل البلح "الزغلول" وتقييم مدى تراكمها على صحة الإنسان

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الملخص العربي

أجريت هذه التجربة لدراسة تأثير الرش ببعض الجسيمات النانوية قبل الحصاد وهي، أكسيد الزنك والماجنتيت والسيلينيوم والفضة بتركيزات (٣٠، ٦٠، ٩٠ جزء في المليون) لكل مادة. تم رش جميع المعاملات على السوباطات وتم تنفيذها ثلاث مرات في بداية النمو وبعد عقد الثمار وبعد شهر واحد من العقد. تم حصاد الثمار المرشوشة في مرحلة الخلال في شهر سبتمبر، وتم دراسة تأثير هذه المعاملات على خصائص المحصول و تحسين الجودة في يوم الحصاد. أظهرت النتائج أن جميع المعاملات قد أدت إلى زيادة المحصول كمًا ونوعًا، وبدراسة خصائص الجودة وجد أن أفضل معاملة كانت جزيئات أكسيد الزنك النانوية بتركيز ٩٠ جزء في المليون والتي أدت إلى زيادة المحصول ووزن السوباطات ووزن الثمرة ووزن اللحم وزيادة صلابة الثمرة أيضاً أعلى نسبة من المواد الصلبة الذائبة الكلية والسكريات الكلية والمحتوى الكلي من الأنثوسيانين أيضًا أعطت أقل نسبة من وزن البذرة، علاوة على ذلك، وجدت تركيزات المعادن في الثمار المرشوشة ببعض الجسيمات النانوية ضمن الحدود المسموح بها للمعايير الصحية. بالإضافة إلى ذلك، كان مؤشر المخاطر الصحية لجزيئات الزنك والماجنتيت والسيلينيوم والفضة النانوية أقل من ١، مما يدل على أن ثمار نخيل "الزغلول" المرشوشة بـ ZnONPs و Fe_3O_4NPs و SeNPs و AgNPs خالية من المخاطر الصحية على الإنسان ويمكن اعتبارها إستراتيجية مناسبة لتحسين المحصول والحالة التغذوية وجودة نخيل البلح صنف الزغلول.

الكلمات الدالة: نخيل التمر، الجسيمات النانوية، أكسيد الزنك، الماجنيتيت، السيلينيوم، الفضة، مؤشر المخاطر الصحية.