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Effect of pre-seed and foliar treatment with nano-particle solutions on seedling development of tiger nut (*Cyperus Esculentus* L.) plants

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Abstract. Micronutrients are part of enzymes and play an important role in plant germination. Purpose of our study was to establish the effect of pre-seed treatment of chufa tubers with metal nanoparticles on the growth of the root system and seedlings in the early stages of development. Laboratory tests were performed on seed of tiger nut cultivar Pharaoh. Experiment involved two methods of treatment: pre-sowing treatment of seeds with nano-particles solutions of manganese, zinc, copper and iron with a concentration of 60 ppm and re-application of these solutions after seedling emergence. The weight of seedlings and roots was determined at 3rd and 10th days after emergence in treated and untreated variants. Pre-sowing treatment of chufa tubers with all forms of micronutrients significantly increased the weight of the plant (excluding the weight of seeds), and the most effective were treatments with copper and iron. Treatment with copper colloidal solution increases in root weight at 3rd day on 156% compared to control without treatment and this dynamic stayed at 10th day. Most affective treatment is iron colloidal solution. This treatment gives +99% of root weight at 3rd day and 194% at 10th day after germination compared to control in same time. Colloidal forms of manganese, copper and iron also significantly increased the weight of the shoot. Increase in the mass of roots, shoots and plants is observed in plants with foliar fertilizing, but a few variants have an insignificant difference or inhibit the assimilation processes of plants. Pre-sowing treatment with zinc citrate at 60 ppm decreased root and shoot weight in chufa.

Key words: citrate, chufa, colloidal, copper, iron, manganese, solution, zinc.

INTRODUCTION

Tiger nut or chufa (*Cyperus Esculentus* L.) is a highly productive crop that accumulates nutrients in the tubers (Mokady & Dolev, 1970). Tubers are used for planting, so the content of nutrients in the tuber significantly affects the initial growth and formation of plant productivity. Accumulation of dry matter in chufa occurs exponentially up to 90 days, while in the initial stages the leaves and roots grow. Formation and accumulation of dry matter in the tubers of chufa occurs only

1.5–2 months after germination (Pascual-Seva et al., 2009). Stimulation of root and leaf surface growth at the initial stages of development will allow to form a more efficient photosynthetic system (leaf) with increased drought resistance (root).

Requirement for macro- and micro-nutrients in plants is fully covered by the reserves of tubers in the first 15 days. Content of micronutrients in the tubers varies significantly and depends on the region of cultivation. iron content in the tubers can be from 2.00 mg per 100 g (Arafat et al., 2009) till 6.18 mg per 100 g of tuber (Salama et al., 2013), but a greater extent Fe is concentrated in the inner part of the tuber (Ekeanyanwu & Ononogbu, 2010). Zinc content is 2 times lower than iron and is on a par with copper, and the manganese content differs significantly from the place of cultivation and the method of establishing the content (Arafat et al., 2009, Ekeanyanwu & Ononogbu, 2010). Copper content in the tubers is on average 4 times lower than iron and varies much less (Suleiman et al., 2018).

Soil factors can complicate the absorption of zinc and other trace elements from the salts contained in fertilizers (Alloway, 2009). 'Controlled release' property of nanoparticles allows them to include in physiological cicles in 'right dose' at the 'right time' (Kumar et al., 2014), however not all materials have this property (Deshpande et al., 2017). Main advantages of nanoparticle solution for fertilizations are control deliverey of nutrients, increase it bioavailability and reduce loss rate of nutrients (Zulfiqar et al., 2019). On the other hand, there is a risk to food safety because micronutrients are heavy metals and can accumulate in edible parts (López-Moreno et al., 2018).

Trace elements stimulate the awakening of tubers, as well as the growth of roots and stems in the initial stages (Farooq et al., 2012; Taran et al., 2016). Growth of shoots in chufa after germination is slow, so the greater the vegetative mass is formed in the initial stages, the more shoots and dry matter will accumulate in the active phase (Kelley, 1990). Effect of different micronutrients on the formation of the vegetative organs of the chufa under pre-sowing treatment with micronutrients (Mn, Cu, Zn, Fe) is poorly understood, and the effect may vary because sowing material of chufa is a tuber. Chufa tubers contain a lot of carbohydrates and fats (Pascual et al., 2000; Makareviciene et al., 2013), so their breakdown and use for the formation of roots and seedlings will depend on the enzyme system, which includes trace elements.

MATERIALS AND METHODS

Experimental conditions

Laboratory tests were performed on tubers of tiger nut variety Pharaoh. All tubers were aligned in size and shape, the weight of 1,000 tubers was 1.14 ± 0.02 g. Tubers on the day of planting were treated with solutions of nanoparticles with a concentration of 60 ppm. Tubers of chufa had planted in perlite (Fe free). Air temperature was + 22 °C. Tiger nut plants cultivated on a 12-hour light/12-hour dark cycle.

Experiment design

Scheme of research included two factors (Table 1). Factor A is nanoparticle solution: water (control, without nanoparticles), manganese citrate (Mn citrate), colloidal solution of manganese (Mn colloidal - MnO, $MnCO_3$), zinc citrate (Zn citrate), colloidal solution of zinc (Zn colloidal - Zn, ZnO), copper citrate (Cu citrate), colloidal solution of copper (Cu colloidal - Cu, CuO), iron (II) citrate (Fe citrate), colloidal solution of iron (Fe colloidal - Fe, Fe_3O_4, FeO). Factor B was treatment time. There were pre-sowing tuber treatment and pre-sowing tuber treatment + foliar fertilizing (3rd day after emergency) in treatment time. Pre-sowing treatment (spraying of tubers) was carried out at 1 hours before sowing. Rate of consumption of the solution to pre-sowing treatment was 1.2 L t^{-1} (500 mg L^{-1} of nanometal solution) of tuber and 0.2 L ha^{-1} (500 mg L^{-1} of nanoparticles) to foliar fertilizing (density is 150,000 plants ha^{-1}). Working solution to pre-sowing treatment was 10 L t^{-1} (concentration of nanoparticles is 60 ppm) of tuber and 100 L ha^{-1} (concentration of nanoparticles is 1 ppm) to foliar fertilizing. Solutions were prepared based on application rate of 100 mg ha^{-1} Mn, Cu, Zn or Fe in pre-sowing treatment and foliar fertilizing.

Table 1. Scheme of research

Factor A – nanoparticle solution	Size, nm	Factor B – Treatment time
Water (control)	–	
Mn colloidal	53	
Mn citrate	–	B1. Pre-sowing treatment of tuber (PST)
Zn colloidal	45	
Zn citrate	–	
Cu colloidal	78	
Cu citrate	–	
Fe colloidal	25–60	B2. Pre-sowing treatment of tuber + Foliar fertilizing (PST + FT)
Fe citrate	–	

'–' size is not established.

Colloidal nanoparticle solution was produced by method of metal dispersion by electric current pulses with an amplitude of 100 to 2,000 A in water (Lopatko et al., 2009). Size and other properties of nanoparticles in the experimental colloidal solution obtained by X-ray diffraction and the diffraction patterns of the specimens (Batsmanova et al., 2020). Size of nanoparticles that was obtained by physical method is showed in Table 1. Citrate forms (nanoaquachelates) was obtained by erosive-explosive method at LLC 'Nanomatherials and Nanotechnologies' (Ukraine). Citrate forms (Mn, Zn, Cu, Fe) of fertilizers are characterized by a much smaller particle size (Cao et al., 2013; Huliaieva et al., 2018).

Calculation was performed so that the rate of solution for foliar fertilizing was similar to pre-sowing treatment on one plant/tuber. Foliar fertilizing was performed on 3rd day after emergence so results on 3rd day do not include root and leaf weight by foliar treatment variants.

Sampling

Mass of roots and leaves was determined on the 3rd and 10th day after emergence. Ten plants (n = 10) from each variant were selected. Root system and leaf surface were weighed separately, the weight of the tuber was not taken into account (Fig. 1).

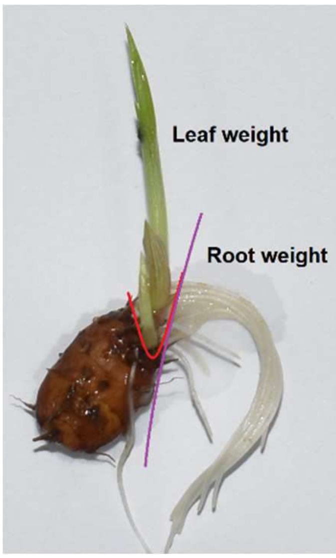

Figure 1. Chufa plant on 3rd day after emergence.

Statistical analysis

Suitability of the sample for statistical analysis was evaluated according to the *Shapiro-Wilk test*. Effect power on 3rd day was assessed by one-factor *ANOVA*, and on 10th day by two-factor *ANOVA*. Difference between the variants was assessed by *Tukey post-hoc test*.

RESULTS AND DISCUSSION

Effect of pre-sowing treatment on 3rd day after germination

Root weight

Colloidal forms of micro elements had a significant effect on the mass of the root system on day 3 after germination (Fig. 2). The highest mass of roots was formed by pre-sowing treatment of tubers with a colloidal solution of copper. Pre-sowing treatment with copper citrate did not differ significantly from the control variant. Effect of treatment with manganese solutions on the growth of the root system differed significantly from the type of the solution. Treatment with a colloidal solution of manganese allowed to form 0.282 g of roots. which did not differ significantly from the value of treatment with colloidal solution of iron and iron citrate. Iron citrate was more effective than colloidal solution, but only on 8.8%. Treatment with colloidal zinc solution had the least effect among colloidal solutions, but gave a significant increase compared to control variant.

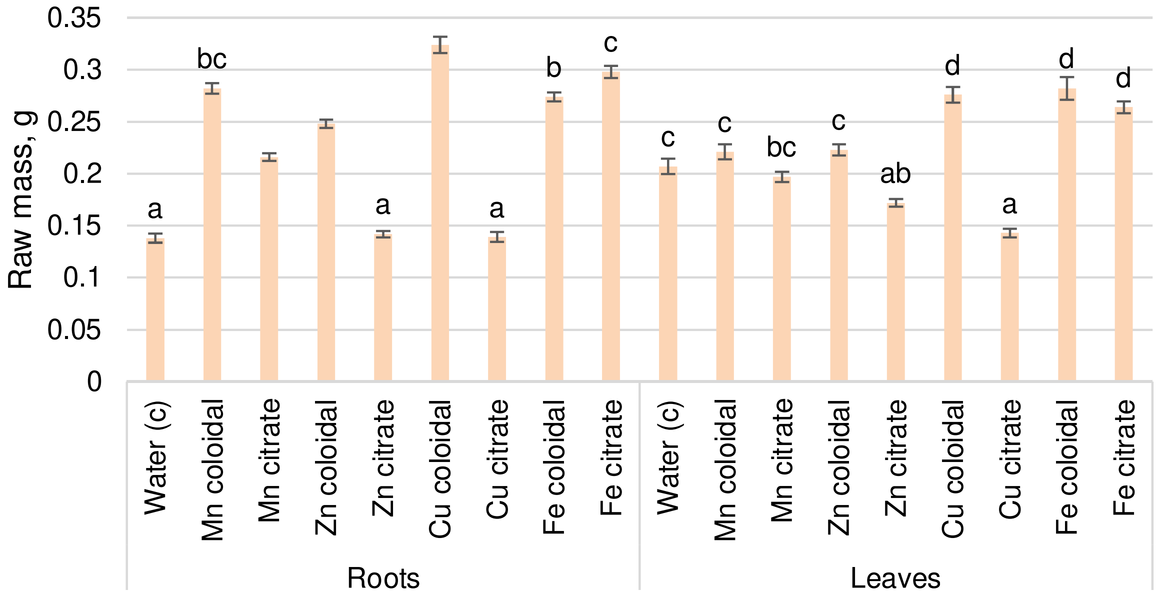

Figure 2. Raw mass of chufa plant components (n = 10) on 3rd day after emergency depends on pre-sowing seed treatments with nanoparticle solutions of metals (different superscripts denote statistical significance at $p \leq 0.05$ by *Tukey`s post-hoc test*; leaf and root weight were analysed separately).

Leaf weight

Effect of seed treatment with trace elements was manifested on the leaf surface differently than on the roots. The largest raw mass of leaves was in the variants by treatment of tubers with colloidal solution of iron, iron citrate and colloidal solution of copper. Pre-sowing treatment of tubers with manganese solutions and colloidal zinc solution did not significantly affect the weight of seedlings compared to control variant. Variants by treatment with zinc citrate and copper citrate formed a significantly lower mass of seedlings than without treatment, because phytotoxicity may occur. These variants also formed the root system at the level of control variant, therefore the total weight of the plant was less than in the control.

Pre-sowing treatment with solutions of iron (colloidal and citrate form) and colloidal solution of copper were the most effective in assessing the weight of roots and leaves on 3rd day after germination. Mass of roots and leaves at the initial stages of development in chufa allows us to assess the effectiveness of the use of spare substances of tubers and their utilization for the formation of vegetative organs.

Greater efficiency of colloidal forms than conventional fertilizers may be due to the size of nanoparticles and their neutrality to the environment (Batsmanova et al., 2020). At the same time, the particle size depends on the form of nanoparticle, and therefore their permeability to the tuber will be different (Wong et al., 2016). High effect of iron treatments may indicate the favour of chufa to this element because a similar effect was observed in other plants (Cifuentes et al., 2010). Effect of iron citrate on the growth of vegetative mass in *Chlorella vulgaris* was manifested on the second day, and the effectiveness depended on the concentration, therefore its effect in plants may be similar, but with a slower manifestation (Golub et al., 2018).

Effect of pre-sowing treatment on 10th day after germination

Root weight

Mass of the root system on 7th day after the previous sampling (10th day after germination) increased, and the effect of pre-sowing treatment of tubers and foliar fertilizing (3rd day after germination) had a significant effect on the variation of this parameter (Fig. 3).

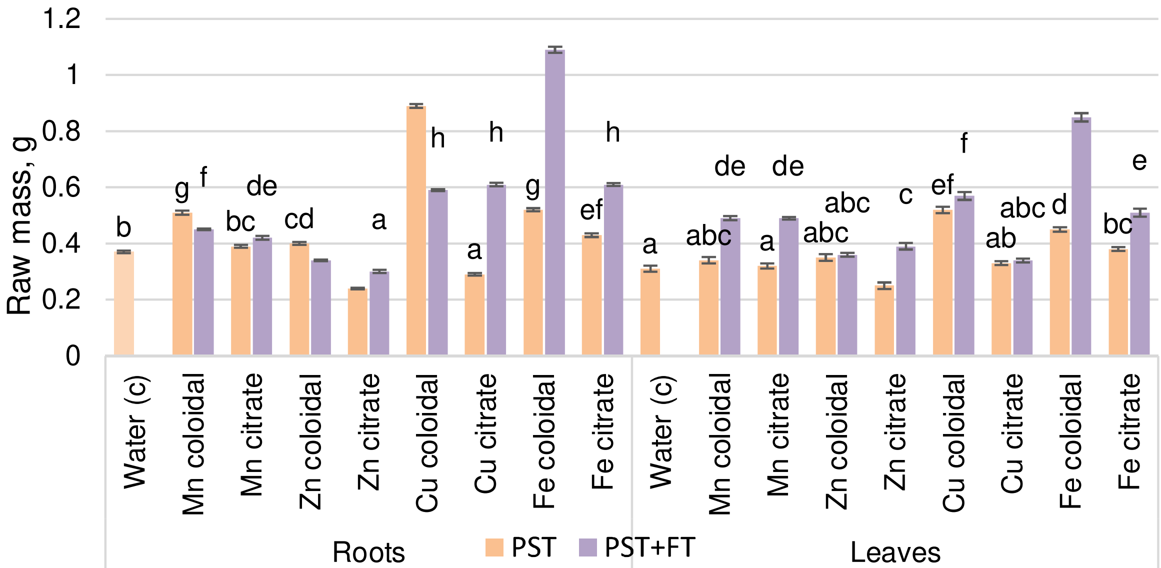

Figure 3. Raw mass of chufa plant components ($n = 10$) on 10 day after germination; PST – pre-sowing treatment; PST + FT – pre-sowing treatment+ foliar treatment (3rd day after emergence); different superscripts denote statistical significance at $p \leq 0.05$ by *Tukey`s post-hoc test*; leaf and root weight were analysed separately.

Difference in root weight between the variants of treatment with colloidal solution of manganese (Mn) and manganese citrate decreased, but colloidal solution of manganese stayed more effective. Mass of the root system of variant with foliar fertilization by colloidal solution of manganese was significantly reduced compared to the variant without foliar fertilization, while this figure increased in treated variant with manganese citrate. Response to foliar fertilization is more pronounced on the leaves because manganese is one of the main trace elements involved in photosynthesis and can accumulate in the plant in significant quantities without phytotoxicity (Fernando et al., 2010). Manganese can slightly increase the weight of the plant but increases the oil content and diversity of fatty acid fractions (Stepien et al., 2019).

Similar trend was for treatments with colloidal solution of zinc (Zn) and zinc citrate. Variants treated with zinc citrate were characterized by significantly lower mass of the root system compared to the control without treatment. This may indicate a long-term aftereffect of pre-sowing treatment of tubers with this compound and phytotoxicity, which persists for a long time (Cuypers et al., 2002). Zinc is a very highly toxic element, regardless of the form of fertilizer (Bandyopadhyay et al., 2015), so the development of forms that release it slowly may be one way to reduce its toxicity (Shcherbakova et al., 2018). Foliar fertilization with zinc citrate allows to significantly increase the weight of the root system compared to the variant where it was not carried out, but this is still not enough to overcome the negative impact. Zinc citrate is characterized by higher absorption capacity than other forms (Montanha et al., 2020), so it could exhibit phytotoxicity at this concentration (Chaney, 1993). Mass of the roots in the variant of leaf treatment with colloidal solution of zinc was significantly lower than variant without such treatment and compared with the control variant. Worse root development after colloidal zinc treatment at 10th day after germination may be due to the formation of excess ROS, which affects the formation of root cells (Ahmed et al., 2018).

Variant with pre-sowing treatment of tubers with colloidal solution of copper (Cu) was characterized by the highest root mass among all variants without foliar fertilizing. Mass of the roots on 7th day after foliar treatment with a colloidal solution of copper was significantly less than in the variant where this treatment was not performed, but this variant had 1.5 times more root mass than the control one. Absorption of copper nanoparticles by the root system is much better than the leaf surface, so the concentration of Cu increases much faster (Nath et al., 2018). Copper regulates photosynthesis and redistribution of carbohydrates, so the vegetative part grows faster (Fernandes & Henriques, 1991; Yruela, 2005). Similar mass of the root system had a variant with copper citrate treatment in pre-sowing application and foliar fertilizing, but variant without foliar fertilizing with copper citrate was characterized by a significantly lower root mass compared to control. This may indicate the phytotoxic effect of copper citrate on the treatment of tubers, which can be overcome by the application of copper citrate in foliar fertilizing. Treatment with copper nanoparticles is more efficient than other types of fertilizers, which leads to greater accumulation of copper in the plant (Zulfiqar et al., 2019). Copper nanoparticles can improve root growth in certain plant species (Trujillo-Reyes et al., 2014), but they are more often toxic even in relatively low concentrations (Zuverza-Mena et al., 2015).

Treatment of chufa plants with iron (Fe) nanoparticle solutions had the most stable effect on the growth of the root system. Weight of the root system of plants was 0.52 g per plant in a variant where the tubers were treated with colloidal solution of iron. Foliar fertilizing of plants with colloidal solution of iron allowed the plants to form root weight to 1.09 g. This parameter is 2 times higher than the variant with pre-sowing seed treatment of tubers and 3 times the control variant. The effect of treatment with iron citrate was generally high, but nothing special stood out. On the other hand, iron citrate is mobile, so the effect of its introduction may appear later (Starodub et al., 2014; Flis et al., 2016; Malhotra et al., 2019).

Leaf weight

Pre-sowing treatment of chufa tuber in most cases had little effect on the variation in the weight of the leaves. Treatment of the tubers with colloidal manganese solution, manganese citrate, copper citrate and zinc colloid gave a slight increase in leaf weight. Weight of the leaves of variants with pre-sowing treatment by zinc citrate was significantly lower (0.25 g) than in control variants, because phytotoxicity, which was on 3rd day after germination remained on 10th day. Pre-sowing treatment of tubers with iron nanoparticle solutions significantly increased the weight of the leaves compared to the control variant (0.31 g), but the greatest effect among variants without foliar fertilization was in colloidal solution of copper (0.52 g). Foliar fertilizations significantly increased the weight of the leaves compared to the variants where they were not carried out, except for copper solution (colloidal and citrate form) and colloidal solution of zinc. Concentration of Cu in the leaf mass in untreated plants is high, so foliar fertilizing of Cu is not highly effective, ZnO nanoparticles may be dissolute in hydroponic median so they efficiency can decreased too (Nath et al., 2018). Foliar treatment of iron colloidal solution also had a huge impact on leaf growth similar to the root system one. Treated variants with iron have a long-term effect of gradual growth of the chlorophyll index, regardless of the form of iron (Son'ko et al., 2013; Islas-Valdez et al., 2020).

Plant weight

Total weight of the plant (excluding tubers) allows to assess the effect of pre-sowing treatment with solutions of nanoparticles (Table 3). Comparison with the control variant (treatment with water) indicates the effectiveness of the use of tuber substances for the formation of vegetative organs.

Effect of pre-sowing treatment of chufa tubers with nanoparticle solution is manifested on the 3rd day. It was found that the total plant weight in the variants with treatment with zinc citrate and copper citrate is significantly lower than in control variant without treatment with nanoparticle solutions. This indicates the phytotoxicity of these nanoparticle solutions at a concentration of 60 ppm, which is first manifested in a smaller mass of seedlings at normal root mass. However, the negative effect of these compounds remains for 10 days after germination, but also manifests itself in root and

Table 3. Raw mass of chufa plants

Nano-particle solution	Time of sampling (after germination)		
	3rd day	10th day	
	Pre-sowing	Pre-sowing	Pre-sowing + foliar
Water (control)	0.35a	0.68	0.68a
Mn coloidal	0.50	0.85c	0.94b
Mn citrate	0.41	0.71b	0.91b
Zn coloidal	0.47	0.75b	0.70a
Zn citrate	0.31a	0.49a	0.69a
Cu coloidal	0.60	1.41	1.16c
Cu citrate	0.28	0.62	0.95b
Fe coloidal	0.56b	0.97	1.94
Fe citrate	0.56b	0.81c	1.12c
Average	0.45	0.81	1.01

leaf weight. Foliar fertilizing on 3rd day after germination stimulates an increase in the mass of roots and seedlings, that allows to overcome phytotoxicity in some cases on 10th day after germination (7th days after foliar fertilizing). Some foliar treatments led to the formation of less mass than in variants where they were not performed. This effect was observed during treatment with colloidal solution of zin and colloidal solution of copper because they could significantly affect the physiological processes during formation of the vegetative part.

CONCLUSIONS

Pre-sowing seed treatment of chufa tubers with nano solutions of micronutrients has a long-term effect on growth processes in the initial stages of development. Certain elements may have a stimulating effect or exhibit phytotoxicity at relatively low concentrations depending on the form of nutrient. Pre-sowing treatment with zinc citrate and copper citrate at concentration of 60 ppm decrease formation of vegetative part on 3rd and 10th day after germination, so they need to adjust the concentration and application rate. Treatment with iron solutions gives a stable increase in the mass of roots and leaves, regardless of form, and in some cases, iron citrate or colloidal solution of iron will be more effective if the foliar fertilizing.

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