Current Experience with Application of Metal-based Nanofertilizers

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Abstract. Agriculture is one of the many fields in which nanotechnology is currently applied. At the nano-scale, materials exhibit different properties mainly due to the reduced molecular size which allows different interactions between molecules. Nowadays, the agricultural sector demands methods that not only increase crop productivity, but are also sustainable and produce less environmental impact. Large-scale application of chemical fertilizers is common in farming with the aim of increasing productivity. The use of large doses of fertilizers, however, causes more harm than good. Chemically intensive agriculture disturbs the soil-mineral balance, pollutes soil, water and air, and makes lands less fertile in the long-term. Metal-based nanofertilizers allow effective and precise nutrient management due to their high reactivity, enhanced bioavailability and bioactivity. This paper presents the results derived from the application of metal-based nanofertilizers in different crops of economic relevance, displaying their importance in sustainable agriculture. The trials showed that the metabolic reactions in the plants are enhanced by providing them with the optimum amount of trace elements, which also improves the rate of photosynthesis, increases productivity, and prevents biotic and abiotic stress.

1 Introduction

Along with the increase of the population worldwide, the demand of food is increasing year after year, which thus compels agriculture to be more efficient. In search of increasing crop productivity, agriculture uses intensive fertilization. Using large amounts of fertilizers, however, does not guarantee better results and furthermore, such practices are not friendly to the environment. The application of large quantities of chemical products in the soil leads to problems such as pollution of soil and water resources, alteration of soil composition, erosion, etc. Therefore, the agricultural sector is currently looking for more modern technologies that help to increase productivity and efficiency, but at the same time cause the least environmental impact.

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Agriculture is one of the many fields in which nanotechnology has become present. Nano-scale fertilizers allow the optimized application due to the fact that the reduced size of its components allow better absorption by the plants, and at the same time enable a significant reduction in the amount of material that needs to be applied.

Little is known so far about experiences with the use of nanofertilizers. Therefore, this article shows the results obtained in different crops in which metal-based nanofertilizers have been applied and their advantages.

2 Problems with intensive fertilization in conventional agriculture

Conventional agricultural practices today use chemical fertilizers intensively. In accordance with Qureshi *et al.* [1], there is the tendency of increasing the use of chemicals in order to control diseases, insects and weeds, as well as applications that serve for plant nutrition to get maximum production per unit area; practices that disregard the care of the land and its natural resources. Some of the problems of an excessive use of conventional fertilizers are:

- Soil erosion
- Contamination of surface and underground water
- High transport costs of the large quantities of fertilizers
- Chemical forms of nutrients that are not available for uptake by plants
- Overdose and waste of fertilizer material

Considering all these problems and more, there was the need to develop new fertilization materials that, as indicated by Solanki *et al.* [2], poses improved smart properties which are specifically directed to cover the needs of the plants, can be released systematically and are applied in a small scale. Materials with such properties can be obtained with nanotechnology.

3 Nanotechnology in agriculture

According to Qureshi *et al.* [1], a nanoparticle can be defined as a small particle which has a dimension less than 100 nm (1 nanometer = 10^{-9} m = 1 billionth of a meter). Solanki *et al.* (2015) [2] define products within this nanometer range and that deliver nutrients to crops as nanofertilizers. In accordance to Hediat and Salama [3], nanofertilizers are modified forms of conventional fertilizers intended to improve soil fertility, quality and productivity of the agricultural goods, which are synthesized by physical, chemical or biological methods with the use of nanotechnology. The enhanced properties of nanofertilizers as opposed to the conventional ones are:

- Site-targeted delivery due to small size and high mobility
- Improved solubility and dispersion which makes them more bioavailable for the plants
- Reduced loss rate of nutrients into soil by leaching or leaking
- Efficient nutrient uptake by the plant due to the small size
- Saving fertilizer material resources
- Effective permanent nutrient release
- Low impact on the ecological balance of the soil

The enhanced properties present in nanofertilizers is achieved because of the different characteristics that the materials exhibit at the nano-scale. The higher surface area of the materials provides more reaction site among the molecules, which facilitates the metabolic reactions in the plant system. According to Lin and Xing (2007) [4], the reduced size of the particles allows more opportunity of contact per unit area, which leads to more penetration into the plant and uptake of nutrients.

4 Development of metal-based nanofertilizers by B+H Solutions GmbH

According to Marschner [5], plants require, besides sunlight, water and CO_2, additional components to fulfil their nutritional requirements. These chemical elements are taken up through the soil and the aerial parts. The chemicals present in the soil receive the name of mineral nutrients. The mineral nutrients required in high concentrations are called macronutrients (N, P, K, Mg, Ca, S, Si), the ones that are needed in low amounts are called micronutrients (Fe, Cu, Zn, Mn, B, Mo, Ni, Na, Cl) and all of them are essential for the right balance and proper functioning of the plant metabolism. Even when the micronutrients are needed in low quantities, these elements are essential for the healthy development of the plants. Lack of Fe and Cu has caused symptoms such as chlorosis, lack of strength and brightness, necrotic spots, susceptibility of infection, etc. and these effects mean great loss for the farmers. Such deficiencies can be corrected with fertilizers, but as indicated above, the farmers seeking the best for their crops apply immeasurable amounts of products and overuse fertilizers, causing more harm than good. Efficient fertilization in the precise amount can be achieved with nanotechnology.

In accordance to Solanki *et al.* [2], the cell wall of the plants has a diameter between 5 and 20 nm. By providing the plants with particles equal in size or smaller than the cell wall, the uptake and the ability to reach the plasma membrane can be assured. The exact mechanisms of nanoparticle uptake and translocation by the plants are still being elucidated, but studies demonstrate that the nanoparticles can reach the aerial parts of the plants by penetrating the roots and afterwards translocated via xylem tissue to the rest of the plant or directly via the leaves.

B+H Solutions GmbH is a nanotechnology company that has put effort into the development of products with nano-scale materials for plant application. B+H Solutions GmbH has developed, among others, metal-based nanofertilizers which possess elementary nanoparticles of copper (Cu) and elementary nanoparticles of iron (Fe). These products are used to provide the plants with the necessary amounts of copper and iron, which, thanks to their physical and chemical properties, provide more surface area and are more bioavailable for the plants. Commercial brands of the nanofertilizers are AgroFerrum® and AgroCyprum® for the nano-iron and nano-copper fertilizers, respectively.

The fertilizers, registered in Europe as CE fertilizers in accordance to the Reg. (CE) no. 2003/2003, developed before the first trials corresponded to both fertilizers with 3% elementary nano copper (See Fig. 1) and a fertilizer with 2% elementary pico iron.

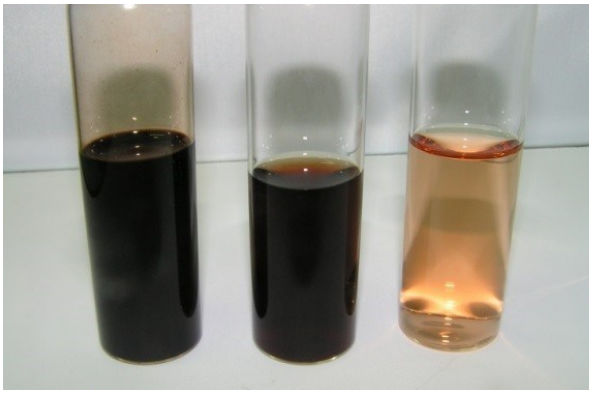

Fig. 1. Fertilizer with elementary 3% nano copper (left) and diluted 1:100 (center) and 1:1000 (right)

5 Application and experiences

The dosages of application of the copper and iron nanofertilizers were determined on the basis of already-existing respective fertilizers with the goal of achieving the same or better performance using a significantly less amount of material. The use of the fertilizers was evaluated in different crops of economic importance and the treatments were done as foliar applications as well as over the roots per irrigation. A summary of the performed trials can be seen in Table 1 and Table 2 for the nano-iron and nano-copper fertilizers, respectively.

Table 1. Trials with the nano iron fertilizer

Crop	Location	Time period	Details and results
Clementines	Agadir Kagabe, Morocco[1]	20.04.2015 – 20.05.2015	2 treatments with 600 ml per hectare cured severed chlorosis
Tomato	Biougra Soyma, Morocco[1]	05.08.2015 – 15.04.2016	20 ml per day and hectare of the nano-iron fertilizer successfully replaced 300 ml of the conventional iron fertilizer
Tomato	Almeria, Spain[2]	28.10.2015 – 30.04.2016	pH value of the soil made commercial conventional fertilizers difficult to correct severe chlorosis. 2 foliar treatments, 1 L per hectare were able to completely eliminate chlorosis
Raspberries	Agadir Kagabe, Morocco[1]	20.02.2015 – 30.06.2015	20 ml per day and hectare of the nano-iron fertilizer successfully replaced 1,5 L of the conventional iron fertilizer per week
Romaine lettuce	Lustenau, Austria[2]	15.08.2015 – 15.10.2015	Significantly more harvest due to more fruit mass, less biotic stress for *Alternaria*
Golf lawn	Lindau, Germany[2]	15.08.2015 – 15.11.2015	1 L per hectare shows positive results. Optimized state of the lawn
Grapevines	Treviso, Italy[2]	05.07.2015 – 01.07.2016	1 foliar application in Oct 2015 and 3 additional sprays between Mar and Jun 2016 resulted in no visible chlorosis.

Crop	Location	Time period	Details and results
			Chlorophyll content of the treated leaves is 10 mg/kg (Control = 8mg/kg)
Grapevines	Remshalden, Germany[2]	20.05.2016 – 26.07.2016	600 ml per hectare applied via leaves cured a heavy chlorosis that could not be cured with other conventional iron fertilizers
Grapevines	Pfalz, Germany[2]	20.04.2016 – 26.07.2016	600 ml per hectare applied via leaves cured a heavy chlorosis that could not be cured with other conventional iron fertilizers

Responsible person: Hakim Oujlouq[1], Elmar Buder[2]

Table 2. Trials with the nano-copper fertilizer

Crop	Location	Time period	Details and results
Grapevines	South Tyrol, Italy[2]	05.06.2016 – 31.10.2016	Test series of 5, 10, 30 and 100 ml of the nano-copper fertilizer. 5 ml supply all the necessary amount of copper
Tomato	Biougra Soyma, Morocco[1]	01.09.2015 – 15.10.2015	Infection with *Pseudomonas syringae* was cured with the nano-copper fertilizer in combination with 1ppm silver nano-particles
Golf lawn	Weißenberg, Germany[2]	14.04.2016 – 31.05.2016	Lawn infected with *Microdochium nivale* was controlled as well as with a commercial fungicide

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As shown in Table 1 and Table 2, the new developed nanofertilizers demonstrated similar and better performances in comparison with conventional iron and copper fertilizers.

While conventional iron fertilizers (eg., iron chelate 6% eddha products) recommend large applications to cover deficiencies, the developed nano-iron fertilizer could perform better with a fraction of the dose. The high solubility of the nanofertilizer allowed an enhanced effective concentration to be achieved that successfully covered the iron needs of the plant. More chlorophyll production and a healthy green color was noticeable in the plants treated with the nano-iron fertilizer. By having an optimized photosynthetic effect, a plant with more internal energy and an active metabolism will produce more leaves and fruit mass, which explains the better harvest in the crops. It was important that the pH-value of the soil did not affect the uptake of iron unlike conventional iron fertilizers. This is the result of the immediate and constant deposit of elementary iron on and within the plant cells, that are always available to fulfill the needs of the plant and maintain an active metabolism. Similar findings where shown by Rui *et al.* [6] comparing the effect of iron oxide nanoparticles as fertilizer with traditional EDTA-Fe fertilizer in peanut plants. The study showed that the nano-iron fertilizer improved the development of roots, plant height and biomass in the plants by regulating phytohormone contents and antioxidant enzyme activity. Other advantages were more efficient absorption on sandy soil, less leaching, and higher availability, thus, it was recommended that the nano-iron fertilizer could replace traditional iron fertilizers.

A reduction of infection by pathogens was also achieved with the use of nanofertilizers. By having a plant with an active metabolism and a correct balance of trace elements, the immune system will always be ready to respond quickly under an attack. As shown in Table 2, application of the copper nanofertilizer, in combination with silver nano-particles, helped the crops to have less pathogen infections. The better response of the plants under stress due to pathogens can be explained because the metal-based nanoparticles act as elicitors. According to Naik and Al-Khayri [7], elicitation occurs when the plant is actively stimulated to induce a desired chemical response. An elicitor is a substance applied in small quantity to a plant that induces or improves the biosynthesis of a specific compound and has an important role in the plant's response under stressful conditions. Elicitors can be divided into two types according to their origin. Biotic elicitors come from biological origin, while abiotic elicitors are substances of nonbiological origin. By this means, metals such as copper and silver act as abiotic elicitors that induce the production of secondary metabolites with a major role in the immune response of the plants, and they help the plant to be ready to respond to challenging external influences. Several studies have demonstrated the induction of secondary metabolites in plants by silver compounds and nano-silver, such as in Zaker, *et al.* [8], Cai, *et al.* [9], Shakeran *et al.* [10] and Li *et al.* [11] and by copper as in Furze *et al.* [12] and Sharma *et al.* [13]. Some of the secondary metabolites induced by the presence of these metals are: tanshinone, cryptotanshinone, tanshinone IIA, resveratrol, atropine, bacoside, sesquiterpenoid and other phytoalexins. These metabolites occurred naturally in plants and possess antimicrobial and antioxidant activity, and therefore play a significant role in the plant's immune response. Even though there is evidence that copper and silver act as elicitors, the exact mechanism is not yet fully understood. Nevertheless, the nano-copper fertilizer as well as silver nanoparticles have shown great potential as elicitors and in preventing biotic stress in plants.

6 Conclusion

It has been demonstrated that nanofertilizers have a great result in enhancing crop production by minimizing the amount of applied material, with more efficient uptake and translocation. The nano-scale fertilizers are an alternative that help minimize pollution, being an option suitable for sustainable and precise agriculture, that allow better nutrient control.

The trials with the use of nanofertilizers in different crops of economic importance showed that nano-iron and copper fertilizers helped to improve nutrient deficiencies, achieve better production yield and have a better plant response under biotic stress.

More crop production with the use of nanofertilizers would help to improve the current knowledge on the potential of the use of these materials and could lead to improvements on formulations, dosage and application methods for new crops.

References

1. A. Qureshi, D.K. Singh, S. Dwivedi, Int.J.Curr.Microbiol.App.Sci **7(2)**, 3325-3335 (2018)
2. P. Solanki, A. Bhargava, H. Chhipa. N. Jain, J. Panwar, *Nanotechnologies in Food and Agriculture*, 81-98 (2015)
3. M.H. Hediat, Salama, IRJOB **3**, 190-197 (2012)
4. D. Lin, B. Xing, Environ. Pollut. **150**, 243-250 (2007)
5. H. Marschner, *Mineral nutrition in higher plants*, 889 (1995)
6. M. Rui, C. Ma, Y. Hao, J. Guo, Y. Rui, X. Tang, Q. Zhao, X. Fan, Z. Zhang, T. Hou, S. Zhu, Front Plant Sci. **7**, 1-10 (2016)

7. P.M. Naik, J.M. Al-Khayri, *Abiotic and Biotic Stress in Plants – Recent Advances and Future Perspectives*, 249-255 (2016)
8. A. Zaker, C. Sykora, F. Gössnitzer, P. Abrishamchi, J. Asili, S.H. Mousavi, C.Wawrosch, Ind Crop Prod **67**, 97-102 (2015)
9. Z. Cai, A. Kastell, C. Speiser, I. Smetanska, Appl Biochem Biotechnol. **171(2)**, 330-340 (2013)
10. Z. Shakeran, M. Keyhanfar, G. Asghari, M. Ghanadian, Turk J Biol. **39(1)**, 111-118 (2015)
11. B. Li, B. Wang, H. Li, L. Peng, M. Ru, Z. Liang, X. Yan, Y. Zhu, Protoplasma **253(1)**, 87-100 (2016)
12. J.M. Furze, M.J.C. Rhodes, A.J. Parr, R.J. Robins, I.M. Withehead, D.R. Threlfall, Plant Cell Rep. **10(3)**, 111-114 (1991)
13. M. Sharma, A. Ahuja, R. Gupta, S. Mallubhotla, Nat Prod Res. **29(8)**, 745-749 (2015)