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A Review on Effect of Copper and Iron Nanoparticle on Agricultural Crop

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Abstract

Nano materials are used in practically every aspect of modern life, including agriculture. The conventional fertilizer is replacing by nano fertilizer due to its less quantity required for plant growth and development. Copper and Iron elements are essential micronutrient for plant. Nano Cu and Fe are playing an important role for various attributes such as growth yield, quality, and biochemical parameter. Late blight of potato caused by fungus activity of *Phytophthora* hence antifungal activity and phytotoxicity improved by the nano Cu. Enzymatic activity (ascorbate peroxidase (APX), catalase (CAT), superoxide dismutase (SOD), glutathione reductase (GR), and lipid peroxidation) and photosynthesis component (chlorophylls a, b and carotenoids) of plant are much influenced by application of Nano Cu and Fe.

Keyword: Nanomaterials, enzymatic activity, photosynthesis components

Nanotechnology may be defined as the manipulation of matter through a materials numbers and / or processes material to manufacture products with specific characteristics that can be implemented in several of applications (Usepa *et al.* 2007). Nanoparticles size range upto 1 to 100nm in a dimension. Nanoparticles have contain special properties, special extraction, thermal and electrochemical, *etc.* compared to bulk materials (Panigrahi, *et al*. 2004).

The problem of Fe and Cu deficiency has been noted and is the most serious micronutrient after Zn deficiency. The micronutrient of copper and iron were govern many important role in plant as well as human being such as increase the growth, yields and quality contents of plant, while in human body Cu and Fe are incorporated into various protein and metallo-enzyms, improved the levels of leghemoglobin, O_2 transferring in your blood and its necessary for the proper all over growth, developments and bone, brain and other body organs maintenances. Despite all these, the amount of major nutrients is added to the soil more than the micronutrients, due to which the fertilizer balance of the soil is deteriorated with low nutrients use efficiency the micro nutrients are unavailable for the plants, as well as the high concentration macro minerals were accumulate in food chain due to which diseases like cancer are born in human being. Generally nutrient use efficiency of micro nutrient is 3-5%. Fertilizer use efficiency can be enhanced by reducing the amount of fertilizer with the help of nanotechnology.

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Copper is playing very much important role in growth and developments of plant and it's positively effect on crop productivity (Karamanos *et al.* 2004). Additionally, Cu is essential to the plant growth, it is active several enzyme processes, and play an important role for formation of chlorophyll component (Viera *et al.* 2019). The CuO nanoparticle priming plants showed that enhanced drought tolerance indicated by their higher leaf water content and plant biomass as well as plants increased anthocyanin, chlorophyll and carotenoid contents compared under drought as compared with water-treated plants Nguyen *et al.* (2020). Nano Cu was positively influcence of germination seedling growth as well as biochemical attributes such as protein and sugar content Singh, *et al.* (2017). Nair and Chung (2014) CuO-NPs were applied that NPs could have vascular tissues translocated and their subsequent Cu ions dissolution could have rise to the observed. Application of Cu-NPs leads to increased lignification in the pericarp cell walls of the fruit due to which the firmness of tomato fruits is increased. In particular nano Cu based materials are positively developed specifically for applications in agricultural and food preservation based on the antifungal and antimicrobial properties of Cu^{+2} (Montes *et al.* 2015; Majumder and Neogi, 2016), and nanopesticides are based on Cu-NPs (Keller *et al.* 2017).

Iron is play major role in growth, yield and biochemical function of various agriculture crops. Generally iron (Fe) is an essential nutrient for all organisms (Zuo and Zhang, 2011). Soil particles are fixed large amount of Fe content (Mimmo *et al.* 2014; Bindrabanetal., 2015). High soil pH and aerobic condition cause Fe insoluble form Fe_3C in the soil and the available form, Fe^{2+} (Ye *et al.* 2015). Fe elements are participate in many physiological processes such as chlorophyll biosynthesis, respiration, and redox reactions (Mimmo *et al*. 2014; Ye *et al*. 2015; Zargar *et al.* 2015). Fe deficiency not olny affects the growth and development of plants but also affect the animal and human activity and created diseases anemia (Guerinot and Yi, 1994; Li *et al*. 2014).

Function and Deficiency symptoms of Cu and Fe

Copper (Cu)

The essential micronutrients of copper is absorbed in form of Cu^{+2}. Generally sufficient range of Cu for plant tissue is between 5 to 20 ppm and the concentration below 5 ppm deficiency symptoms appear on young leaves.

Functions

1. Major important role of Cu for the synthesis of lignin in plant. Lignin is constituent of the cell walls that provide strength and rigidity of cell wall and essential for plant erect stature.
2. Cu is part of the several enzyme activity such as cytochrome oxidase that catalyzes electron transfer in the transfer of electrons in respiration.
3. Important in carbohydrate and lipid metabolism.

Deficiency symptoms

1. Young leaves become yellow and stunted.
2. In advanced stages, necrosis along leaf tips and edge appears.
3. Lodging, wilting and increased incidence of disease is observed due to reduced lignification with low Cu.

Iron (Fe)

The Iron micronutrient are absorbed in form of Fe^{+2} and Fe^{+3} by plant root and sufficiency range upto 50 and 250 ppm. When the Fe concentration of below 50 ppm plant appearance deficiency symptoms on young leaves because it is immobile in plant.

Functions

1. Fe is major component of the porphyrin molecules, cytochrome, heme protein, Fe-S protein and leg-haemoglobin. It also involved in respiration and photosynthesis for oxidation-reduction reactions.
2. In the chlorophyll biosynthesis Fe is working as catalyst agents. It is key role in enzyme activity such as nitrogenase.

Deficiency symptoms

1. Young leaves develop interveinal chlorosis, progressing rapidly over the entire leaf.

2. In severe cases, leaves turn entirely white and necrotic.

Application of Cu and Fe nanoparticles on various agricultural crops

Effect of nano Cu and Fe on growth and yield attributes

Nguyen *et al.* (2020) studies that application of nano Cu on maize crop enhances several growth and yield parameter under stress condition and normal condition. Shoot biomass days after 14 & 21 days and shoot height of 14 days after sowing of the priming plant by Nano CuO @ 4.444 mg L^{-1} expressed higher than that of water-treated plants. There are any non significantly difference were found between other tested CuO-NPSs and control treatments. The shoot biomass of treated plant by Nano Cuo was showed (Fig. 1) less effect by drought stress as comparison with water-treated plants. plants were nano CuO treated showed that reduced the level of chlorophyll and carotenoids compared with CuO-NPs treated non stressed plant but in case of water treated plant were sharp decline in the levels of chlorophyall content and carotenoids under drought stress groups as compared with water-treated non-stressed group. Sheykhbaglou *et al.* (2010) studies that the nano FeO at the concerntration of 0.75g L^{-1} were increased leaf + pod dry weight while the application of 0.5gL^{-1} FeO-NPs gave highest grain yield in comparison with control. Tyagi *et al.* (2016) interaction of ZnO and FeO gave significant root and shoot growth of plants, supply plant nutrient and increasing cell permeability of the plants.

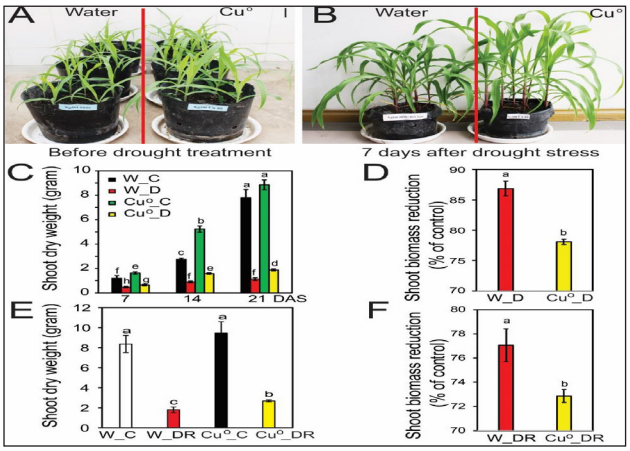

Fig. 1: Drought tolerant phenotype of the copper nanoparticle priming in maize

Armin *et al.* (2014) studies that the foliar application of Nano-Fe were significantly increase yield and yield components of wheat crop. The different concentration of Nano Fe_2O_3 (50–1000 mg kg^{-1}) positively affect showed (Fig. 2) on dry weight, branches number, height of shoot, root length and phenotypic parameter of peanut crop Rui *et al.* (2016).

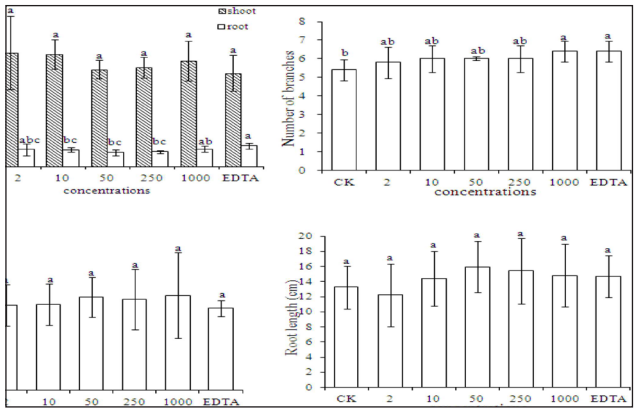

Fig. 2: Effect of Fe_2O_3 NPs or EDTA-Fefertilizer on dry weight **(A)** No. of branches, **(B)** Plant height, **(C)** Root length, **(D)** andphenotypic image, **(E)** of peanut

Effect of foliar spraying Cu-NPs and Fe-NPs on the quality content

Vargas *et al.* (2018) Tomato fruit quality such as firmness, pH, electrical conductivity (CE), Total soluble solids (TSS) and Titratable Acidity (TA) showed statistical influenced by spraying of several concentration of Cu-NPs The fruit firmness were increased with all foliar spraying of Cu NPs (50, 125, 250, and 500 mg L^{-1}) with respect to the control treatment. Juarez-Maldonado *et al.* (2016) found similar result firmness of tomato fruit were increased 9% with the application of the application of Cu NPs + chitosan. The foliar application at the rate of 125 and 50 mg L^{-1} gave significantly higher fruit pH than that of the control while decrease in the titratable acidity (TA) was found in the application of 125 mg L^{-1} Cu NPs as comparison to the control. Generally tomato pH range is found between 4.0 to 4.5. Fruit pH is highly influued of fruit quality and less acidic fruit are more favourable by consumers for their better Anthon *et al.* (2011); Jones, (2007). The Cu-NPs application was increased the electrical conductivity of tomato fruit. The lowest value were found in control treatment while application of Cu NPs @ 250 mg L^{-1} showed increases in EC of tomato fruit. In bioactive compounds which total proteins, Vit

C and flavonoids were significantly influenced by various concentration of Cu-NPs. Foliar application of Cu-NPs 50 mg L^{-1} were observed higher total protein content and content of flavonoids while the highest increase fruit vitamin C (121.97%) was found in the application of 250 mg L^{-1} of Cu NPs compared to the control. Foliar spraying of Nano Fe significantly increase protein content in *Phaseolus vulgaris* (Jahanara *et al.* 2013).

Effect of Cu and Fe nanoparticles on photosynthesis index

Wang *et al.* (2019) Reported that the application CuO-NPs mixed with the soil were no significant change in Chl a content, intercellular CO_2 concentration or photosynthetic rate in leaves of lettuce while Cu-NPs @ 200 mg/kg were found Chl b in the lettuce leaves is decreased as compared with control. Cao *et al.* (2018) revealed that the chlorophyll pigments were severely reduced by the excessive Cu (120 μM as $CuSO_4$) resulting the lower stomatal conductance and photosynthetic rate.

Mushinskiy and Aminova (2019) studies were carried out of the various size and concentration of nanoparticles such as Fe (90-110 Nm), Cu (50-110 Nm) and Mo (100-120 Nm) nanoparticles were applied in four concentrations with a geometric progression (0.0125; 0.025; 0.05 and 0.1 M). The application of different concentration of nanomaterials was significantly influenced biochemical parameter (Fig. 3). We know that chlorophylls a, b and carotenoids are playing a major role in the photosynthetic processes. Fe nanoparticles at doses of 0.0125- 0.1 M gave positive effect on the level of Chl a and Chl b in sprout of potato due to iron ions isolated from their composition.

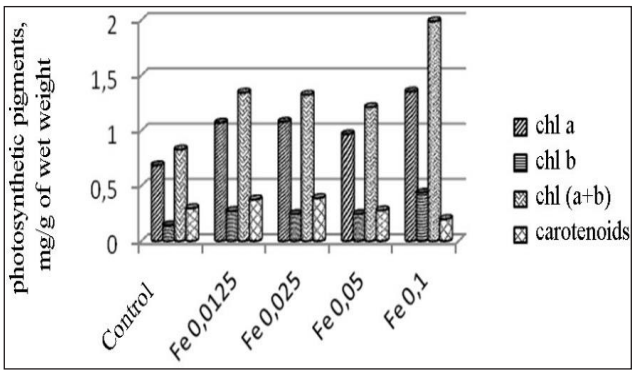

Fig. 3: The content of photosynthetic pigments in of *Solánum tuberosum* L. sprouts treated with suspensions of iron nanoparticles

Effect of Cu and Fe nanoparticles on enzymatic activity

Ogunkunlea *et al.* (2018) studies that the nano Cu was significantly impact on several enzymatic activities of *Vigna unguiculata* plant. The major enzymes such as activity of ascorbate peroxidase (APX), catalase (CAT), superoxide dismutase (SOD), glutathione reductase (GR), and lipid peroxidation in leaves and roots APX activity of enzyme was significantly increase recoded in the concentration of nano Cu 25 nm as compare to control in leaf and root tissues both while CAT activity in leaf tissue of plants exposed to 25 nm Cu-NPs decreased with compared to control, but in case of CAT activity in root, was positively increased at all the 60–80 nm nano-Cu concentration as compare to control (Fig. 4). Shaw and Hossain (2013) and Hong *et al.* (2015) similar evidence of the increases activity of APX in leaves by the application of nano Cu in *Oryza sativa* and *Lactuca sativa* respectively. Rao and Shekhawat (2016); Dimkpa *et al.* (2012) reported that application of nano CuO at the doses of 1000 mg/L and 500 mg/kg gave significantly increase CAT enzymatic activity in *Brassica juncea* and *Triticum aestivum*. In addition, Trujillo-Reyes *et al.* (2014) in the root CAT activity was increased with the applied of nano Cu treatment but decrease APX activity in root of *Lactuca sativa*. All over view results showed that various activity of antioxidant enzymes deponds on plants species. Iron is a key role in structural component in many enzymes such as catalases and peroxidases as well as flavoproteins (Boorboori *et al.* 2012).

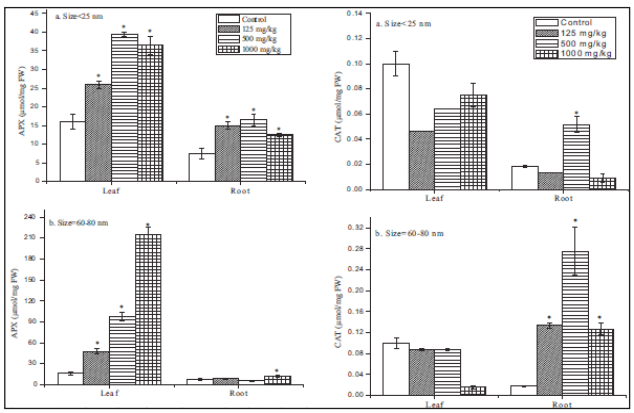

Fig. 4: APX and CAT activity in leaves and roots of cowpea plants grown for 65 days in soil treated with **(a)** 0 (control), 125 mg/kg, 500 mg/kg and 1000 mg/kg nano-Cu (< 25 nm), and **(b)** 0 (control), 125 mg/kg, 500 mg/kg and 1000 mg/kg nano-Cu (60–80 nm)

Effect on Cu based NPs on Antifungal activity and phytotoxicity

Giannousi *et al.* (2013) the synthesized Cu-NPs by hydrothermally method using sereval chemical compound such as copper(II) nitrate trihydrate, hydrazine hydrate and polyethyleneglycol. NPs were characterized by X-ray powder diffraction (XRD), TEM images, elemental composition of the samples was tested by inductively coupled plasma atomic emission spectroscopy (ICP-AES), Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Average particles size of synthetic Cu-based NPs of 11–55 nm (Fig. 5). *Phytophthora infestan* caused late blight of tomato a well known threat to one of the major agricultural products world-wide. The efficacy of the nanomaterials Cu/ Cu_2O composite NPs, Cu_2O NPs and CuO NPs were evaluated of the anti antifungal activity against *Phytophthora infestans* and crop safety on protected tomato plants. Plant treated with the application three different Cu-based NPs resulted significantly protection from the fungal disease infection from *P. infestans* on leaves as comparison to the negative control treatment. Petzold *et al.* (2012); Akhavan and Ghaderi (2010) studies that matallic Cu-NPs were found more bioreactive as compared to Cu_2O and CuO NPs, and its more effective against *Escherichia coli* bacteria and antiviral activity.

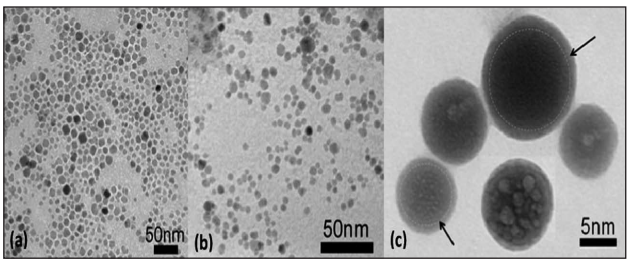

Fig. 5: TEM images of samples CuO-NPs **(a)** Cu_2O NPs **(b)** and **(c)** Cu/ Cu_2O composite NPs

CONCLUSIONS

Nano Cu and Fe were gave a lot of opportunity for plant nutrient due to smart delivery system nanofertilzer more available as compassion to conventional fertilizer. Copper (Cu) and iron (Fe) nanoparticles were enhance crop productivity due to its improved the photosynthesis pigmentation and development much quantity of biomass. Nano Cu and Fe formulation using various agricultural area such as antifungal (nano fungicides) and antibacterial activity etc. Enzymatic activity of several crop were also influenced by the application of nano Cu and Fe due to more reactive specific surface area.

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