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INFLUENCE OF CERIUM OXIDE NANOPARTICLES AND NPK NANOFERTILIZERS ON GROWTH AND YIELD OF CABBAGE PLANT

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ABSTRACT

This works has been carried out in the experimental field, Abu Ghraib region, Baghdad to investigate effect of use CeO_2 (100 mg/L), NPK nanofertilizers (30g, 48g, 100g) and NPK chemical fertilizers (840g, 420g, 840g).The most important results indicated that the two types of nanofertilization treatments were superior to the chemical fertilization treatment in plant height, head weight, external leaves weight and total plant yield. The highest total plant yield was in NPK+ CeO_2 NPs treatment (72 ton/ha) followed (68.704 ton/ha) in NPK nanofertilizer treatment. Plants which fertilized with NPK, NPK+CeO_2 give high chlorophyll content compared to the plants that fertilized with NPK chemical fertilizers and CeO_2 NPs.

Keywords: Cerium oxide nanoparticles, NPK, nanofertilizers, Cabbage plant

Introduction

Cabbage *Brassica oleracea var. capitata L.* is one of major winter leafy vegetable which belong to cruciferae family. It is well grown in cool humid weather and grown for the leafy head grown a row and the end bud. The leaves were used row or in pickle or cooked. Cabbage crop can be grown in middle region of Iraq especially in Baghdad region in large scale (Hasan and Solaiman, 2012). The area cultivated with cabbage in Iraq (1187.5 ha) with a productivity of (12.725 ton.ha^{-1}). The productivity of cabbage in Iraq is very low when compared with other countries (AL-Ubaidy *et al.,* 2019). Agricultural sector faces nowadays great challenges in seeking for the sustainability. These challenges include the ability to provide safe and enough nutrition for the global population and at the same time the conserving or maintaining of the agroecosystem services (Agyin-Birikorang *et al*., 2018). Therefore, several approaches have been adapted for conservation and management of biological diversity to sustain and increase crop productivity as well as to enhance agroecosystem services (El-Henawy *et al*., 2018). The use of more efficient mineral fertilizers is necessary to achieve the increased food production needed to feed this increased population and support economic development. In addition, the intensive application of conventional fertilizers over long periods of time has caused severe environmental stresses around the world, including pollution of groundwater, eutrophication of water, degradation of soil quality, and degradation air pollution. (Congreves and Van Eerd, 2015). The limited efficiency and environmental constraints associated with the use of chemical fertilizers remain a major problem and an obstacle to achieving reasonable sustainability in agriculture. In addition, the cost increases resulting from excessive application of chemical fertilizers will reduce the profit margins of producers. Low nutrient utilization efficiency is usually the result of high release of conventional fertilizers exceeding the actual rate of nutrient uptake by plants, processing of fertilizers, nutrients into forms that are not bioavailable for crops (H. Chhipa, 2017). Nanotechnology plays an important role in increasing production and improving the quality of food produced by farmers. Many believe that this new technology will ensure the growing world's food needs as well as provide a range of economic and environmental benefits. Nanotechnology has proven its position in agricultural sciences and related industries as a multidisciplinary technology and pioneer in solving problems (Mousavi and Rezaei, 2011). Nanotechnology is considered a tool that helps in solving challenges facing farmers in managing crops by obtaining high producing crops and minimizing the use of synthetic chemicals (Kumar, 2013; Prasad *et al*., 2014). Nanomaterials are defined as materials their minutes are between 1 to 100 nanometers, and because of their tiny size nanomaterials are defined as materials their minute sizes are between 1 to 100 nanometers, they behave in a way differs from the traditional materials of big size molecules as well as differ from them in the physical and chemical properties (Mazaherinia *et al*., 2010; Ghorbani *et al*., 2011). Artificial fertilizers are inorganic fertilizers prepared in ideal concentrations of macro and micro nutrients. Nitrogen is an important nutrient that is essential for plant growth. The most widely used source of water soluble nitrogen is urea (46% N). The nitrogen concentration in the soil decreases due to leaching. Therefore, the NUE (nitrogen utilization efficiency) is low. Urea modified hydroxyapatite particles have been used in agriculture; due to its higher NUE and slow release of nitrogen into the soil, this helps to maximize NUE by plants and minimize adverse effects on the environment (Subbaiya *et al*., 2012). Phosphorus plays an important role in several physiological processes in the plant, such as photosynthesis, energy storage, transfer and respiration, cell enlargement and cell division. In addition, phosphorus is an important structural component of many biochemical coenzymes such as nucleic acids (DNA, RNA), nucleotides, sugar phosphate and phospholipids. It stimulates root growth, fruit flowering and seed formation. Potassium is considered essential in photosynthesis, nitrogen metabolism, sugar translocation, enzymatic activation, water relationship, stomatal opening and growth of meristematic tissues, it acts as a policeman of the chemical circulation, root propellant, stem strengthener, respiration regulator and protein builder and delays disease, but it is not effective without its coefficient such as N and P (Merghany *et al*., 2019).

Cerium oxide NPs has been studied, they can act as direct antioxidants and scavengers of free radicals, depending on the size, surface properties, exposure period and age of the plant. CeO_2 NPs in low concentration give positive effect in growth and photosynthesis, growth parameters and chlorophyll contents were increased at low concentrations of CeO_2 NPs. CeO_2 NPs affected the radical scavenging ability of the antioxidant enzyme (catalase, superoxide dismutase, ascorbate peroxidase, guaiacol peroxidase and glutathione reductase and non-enzymatic antioxidants (thiols, glutathione, phenolics, ascorbate and proline) which they help to scavenge generated reactive oxygen species (ROS) in plants (Jahani *et al.,* 2019; Rico *et al.,* 2013).

The aim of this work is to investigate the improvement of cabbage growth and yield when fertilized by chemical NPK fertilizers and nano NPK fertilizers along one season of implantation and enhanced by CeO_2 NPs prepared by laser ablation in liquid.

Materials and Methods

Nano fertilizers (N, P, K) were purchased from Al-KAZRA company- Iran, while CeO_2 NPs was prepared by laser ablation. A two months' cabbages (*Brassica oleracea* var. *capitata L.*) Yarbouz category had been obtained from local farms in Iraq. NPK chemical fertilizers were obtained from ARD company- Iraq.

Preparation of cerium oxide nanoparticles by PLAL

The cerium oxide disk (1 cm^2, 5 g) was prepared by compressing of CeO_2 powder, and burning in furnace at 1500 $^{\circ}C$ for 2 hr. Stuck solution of CeO_2 NPs was generated by ablation by Q-Switched Nd: YAG laser. Subsequently, 10 ml of distal water was added to the sample and ablated under energy of 500 mJ. Furthermore, two wavelength of 532 and 1064 nm of Nd:YAG laser with 1000 pules and 3 Hz were utilized. The NPs structure was assessed by X-ray diffractometer (Shimadzu, 6000, Japan, Mashad, Iran).

Characterization of nanoparticles

Cerium oxide had been characterized field Emission Scanning Electron Microscope (FE-SEM) was used to determine the particles size and morphology of CeO_2 and fertilizers NPs.

Land preparation and soil analyzing

Land preparation was conducted in the winter season (2019-2020) in one of the Abu Ghraib fields in Baghdad. A plot of 100 m^2 was prepared, plowing, leveling, and smoothing operations were performed. The land was divided into terraces 10 meters long and 75 cm wide and at three replications per-transaction. Cabbage plant were planted in 1/10/2019 on both sides of water flow and a distance of 30 cm between one plant and another. All the recommended agricultural service operations were performed for all seedlings in a similar manner for all plants such as weeding, control and irrigation, depending on the method of irrigation by drip. The study included 5 simple transactions, each treatment is three replicates, and contain 45 plant. The experiment was conducted according to the design of the complete randomized design. Pre planting soil samples were collected randomly from the experimental area at a depth of 30 cm for physical and chemical analysis. Soil samples were bulked, air dried and ground to pass through a 2 m sieve. The particle size of soil was determined according to (Black, 1965). Spectrophotometer had been used to determine phosphorus, iron and zinc in soil according to Olsen (1982) and Jones (2001), while nitrogen was determined by Kjeldahl digesting method (Blak, 1965) and potassium was estimated by flame photometer according to Page (1982). On the other hand, soil pH and electrical conductivity (EC) were also measured table (1).

Table 1 : Chemical and physical properties of the soil before cabbage implantation.

Properties		Value and type
Electrical conductivity (E.C)		4.4
Soil pH		7.2
Soil particles	Clay	3%
	Silt	32.6%
	Sand	64.4%
Soil tissue type		Sandy mixture
Nitrogen		**21**.4
Phosphor		6.2
Potassium		**170**

Fertilizers application

The fertilization of seedling was started after one week of plantation. A mixture 100 g of nanonitrogen, 48 g of nanosphosphorus and 30 g of nanopotassium were taken and dissolved in 9 L of D.W as recommended by manufacturer while, 840 g of N chemical fertilizers, 420 g of P chemical fertilizers and 840 g of K chemical fertilizers were taken and dissolved in 9 L of D.W as recommended by manufacturer. Then 200 ml of mixture was added to each plant contentiously every 21 days. On the other hand, 100 mg / liter CeO_2 NPs was added directly to the plant a month after planting in a quantity of 10 ml for each plant (S. Jahani *et al*., 2019).

Cabbage harvesting and growth parameter estimation

The cabbage harvested after the completion of fertilization program during one agricultural season (from the 1^{st} of October 2019 to the 1^{st} of January 2020). Growth parameters include fresh head weights, height, number, external leaves weight, plant head height and head circumference were measured before and after harvesting. Furthermore, plant leaves samples were collected to estimate the total content of chlorophyll.

Chlorophyll determination in cabbage leaves:

One gram of dried leaves was mixed with 10 ml of 80% acetone and crushed well in a ceramic mortar. The filtered volume was complete to 100 ml with acetone, and absorbance was measured at 645 and 633 nm by spectrophotometer. The amount of the dye was calculated according to the method described by (AL-Ubaidy *et al.*, 2019).

Statistical analysis

The data were statistically analyzed using a program Gensatst 2012, and the means was compared using L.S.D. at 0.05 level of significant to compare the arithmetic averages (Steel and Torrie, 1960).

Results and Discussion

Characterization of nanoparticles

Cerium oxide revealed spherical nanoparticles with diameter average of 16.69 – 25.58 nm, as shown by FE-SEM figure (1). FE-SEM images of N, P, K nano fertilizers revealed particles size range between 12.17 to 36.89 nm figure (1).

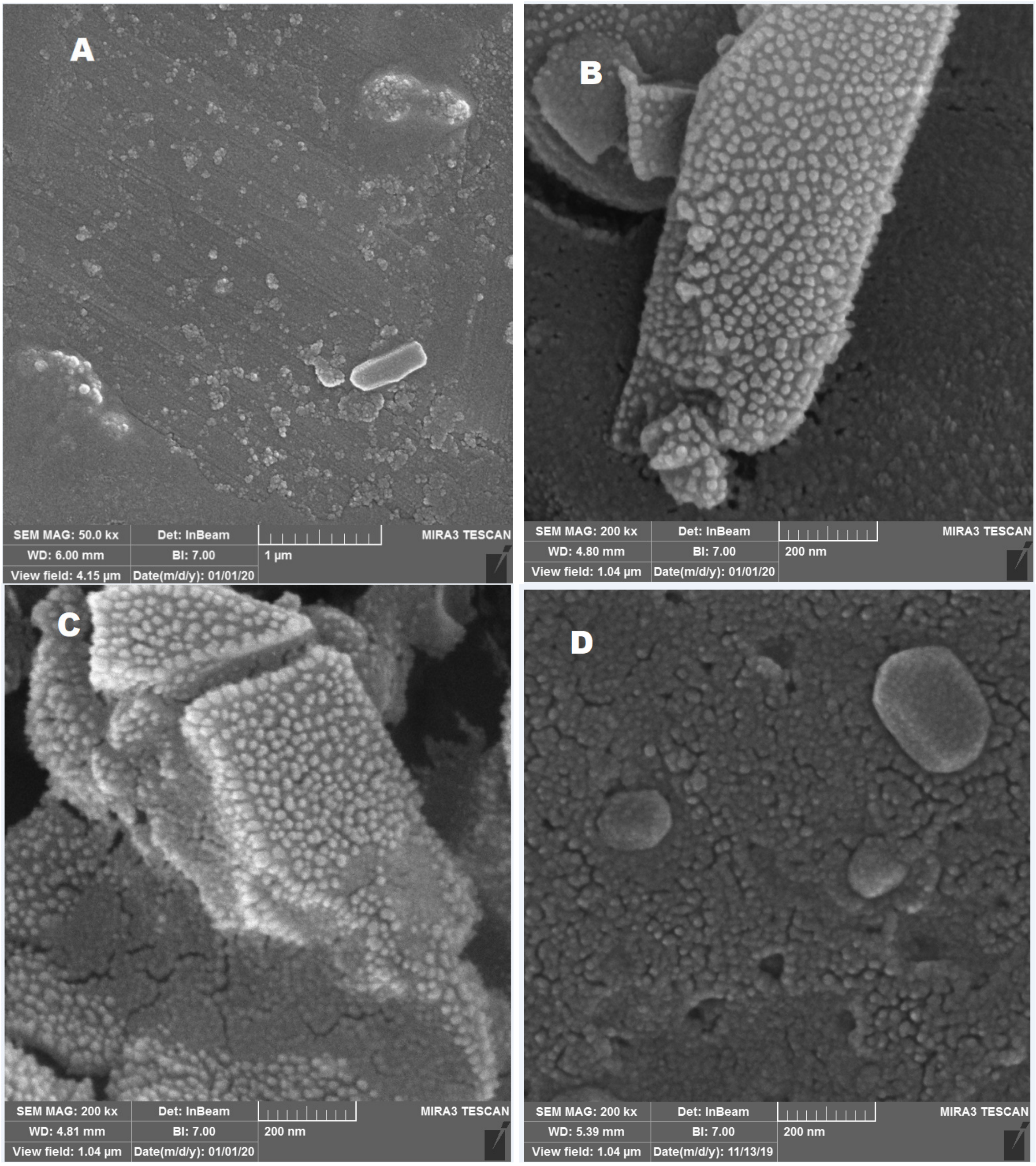

Fig. 4: FE-SEM images of nano fertilizers A. Nitrogen, B. Phosphorus, C. Potassium, D. CeO_2.

Growth parameters and cabbage yield

Variation in growth parameters had been observed when different types of fertilizers applied to the cabbage than in control plants table (2). The average number of external leaves was high in control plants (19.67) than in when the plants were fertilized by NPK nano fertilizers (17.41), while the higher average weight of non-wrapped external leaves (0.867 Kg/plant) was observed with plants that fertilized with NPK nanofertilizer. Furthermore, cabbages that fertilized with nanofertilizers, except CeO_2 NPs, revealed higher circumferences (not less 49.42 cm) when compared with control (28.17 cm). High average (55.56 cm) of head circumference was observed when plant fertilized with NPK nano fertilizer, while (48.11 cm) was observed with plants that fertilized with NPK chemical fertilizers. Moreover, cabbages show height head 16.56 cm when plant fertilized with NPK+CeO_2 nano fertilizer, while plants that did not receive any fertilizers, as control observed 10.67 cm. Finally, the average of higher cabbage head weight reached 1.88

Kg/plant when the plant fertilized with NPK + CeO_2 NPs table (2), while the NPK chemical fertilizers was 0.747 Kg/ plant within 90 days. On the other hand, table (2) illustrated that treatment fertilized by NPK nano fertilizers with CeO_2 NPs had remarkable increased the total plant yield to (72.164 ton/ha). While NPK nanofertilizers alone, NPK chemical fertilizers, CeO_2 NPs alone and control produced (68.704, 61.692, 34.722 and 27.507 ton/ha) respectively Significant differences were obtained between the higher values and others.

Table 2 : Determination of cabbage Growth parameters in one season.

Fertilization type	Average of external leaves number (Leaves/plant)	Average of external leaves Weight (Kg/plant)	Average of head circumference (cm)	Average of head height (cm)	Average of head height (cm)	weight average of plant head per treatment (Kg/plant)	Total plant yield (Ton/ha)
NPK chemical fertilizers	17.77	0.752	48.11	15.22	1.227	0.747	61.692
NPK nano fertilizers	17.41	0.867	55.56	15.67	1.790	0.957	68.704
NPK+ CeO_2 NPs	17.56	0.861	49.42	16.56	1.889	1.082	72.164
CeO_2 NPs	17.83	0.502	36.89	10.16	0.639	0.520	34.722
Control	19.67	0.457	28.17	10.67	0.513	0.413	27.507
L.S.D (0.05)	2.36	0.173	7.04	1.18	0.087	0.103	7.657

Despite the positive effects of cerium oxide NPs in growth and photosynthesis, it can be act as antioxidant. CeO_2 NPs affected the radical scavenging ability of the antioxidant enzyme which they help to scavenge generated reactive oxygen species (ROS) in plants. CeO_2 NPs catalytic trapping of ROS can protect the light and carbon reaction of photosynthesis in plants by minimizing oxidative damage to chloroplast photosystems, pigments, lipid membranes and enzymes involved in carbon binding. CeO2 NPs are therefore well positioned to protect plant photosynthesis against the effects of ROS accumulation. ROS can protect the light and carbon reaction of photosynthesis in plants by minimizing oxidative damage to chloroplast photosystems, pigments, lipid membranes and enzymes involved in carbon fixation. Thus CeO_2 NPs are well positioned to protect plant photosynthesis from effects of ROS accumulation (Jahani *et al.,* 2019). Moreover, Rico *et al.* (2014) demonstrated that CeO_2 NPs significantly improve wheat growth and shoot biomass in potted plants grown in green house conditions. Jahani *et al.* (2019) confirmed that the low concentration of CeO_2 (50 and 100 mg/L) induced *C. officinalis* growth parameters.

According to the previous result, the weight of cabbage external leaves of cabbage in nano fertilization treatments than others treatments, this indicates the effectiveness of the nano fertilizers in increasing the absorption of nutrients necessary for increasing the vegetative growth of cabbage plant. It is confirmed with El-Henawy *et al.* (2018) which was used nano fertilization application to enhancing plant growth in red cabbage and broccoli. In another study, a patented nano composite consist of N, P, K have been shown ti increase the uptake and utilization of nutrients by grain crops (Tapan and Sivakoti, 2019).

Chlorophyll amount in cabbage leaves

Chlorophyll amount had been determined in cabbage leaves after harvesting. Chlorophyll amounts estimated in all fertilized cabbages leaves were higher than control (65.57 mg/100 g leaves). Chlorophyll amount in cabbage leaves fertilized with nano fertilized, except CeO_2 NPs, was higher than in cabbage leaves that fertilized with chemical fertilizers, as shown in figure (5). The higher amount of chlorophyll in cabbage was 131.22 mg / 100 g of leaves after fertilized with NPK+CeO_2 NPs, and significant differences were determined when compared with other fertilizers.

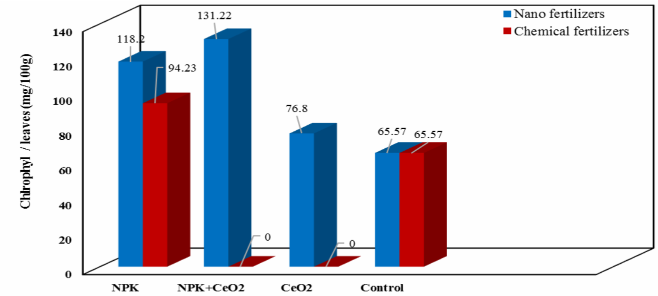

Fig. 5: Chlorophyll amount in cabbage leaves.

According to the result, the content of chlorophyll was increased in cabbage leaves that fertilized with NPK nanofertilizers supported by CeO_2 NPs. Low concentration of NPs showed a stimulates effect on the content of chlorophyll, because cerium can act as a catalyst in the production of chlorophyll and it can maintain the structure of the chloroplast which conducts photosynthesis and performs a number of other functions including the synthesis of fatty acids and amino acids in the plant (Shyam and Aery, 2012; Milo and Phillips, 2015; Jahani *et al.,* 2019). Similarly, Gui *et al.* (2017) reported the enhancement of chlorophyll content by low concentration of CeO_2 NPs (10, 50, and 100 mg/Kg). Moreover, Yang *et al.*(2017) showed that the total chlorophyll content of *Arbidosis thaliana* was not effected by 500 mg/L of CeO_2 NPs but it was significantly decreased at higher concentration (≥1000 mg/L). In another study, the CeO_2 NPs significantly affected the chlorophyll content when it was used in concentration 125 mg/L on rice (Rico *et al.,* 2013).

On the other hand, the increasing of chlorophyll content in the presence of low concentration of CeO_2 NPs is due to the ROS low production and less lipid peroxidation, while the high ROS level lead to damage in chloroplast structure, change in pigment protein complexes, degradation and inhibition of photosynthetic pigments synthesizing (Garcia-Sanchez *et al.,* 2002). Therefore, the increasing of chlorophyll content, in the present study, in the presence of low concentration of CeO_2 NPs may due to the ROS low production and less lipid peroxidation.

Furthermore, NPK nano fertilizers effected the content of chlorophyll in cabbage plant due to the role of these elements in the increasing of cell division and cell size. In same context, the nitrogen element interferes with prophyrine formation which is participates in chlorophyll pigments formation (AL-Taey *et al.,* 2017; Al-Ubaidy *et al.,* 2019). The results in this study was agreed with results obtained by Olaniyi and Ojetayo (2011), when they used NPK fertilizers for cabbage (*Brassica oleracea L.*).

Conclusions

Nanofertilization supported with nano particles has provided the plant's need of necessary nutrients as well as giving it result higher than chemical fertilization and superior to most of the measured vegetative characteristics. The nanofertilization gave the cabbage plant a high nutritional value as the percentage of elements present in the leaves of the plant is high compared to chemical fertilization.

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