Chapter

# Application of Nanotechnology Solutions in Plants Fertilization

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## Abstract

Post-modern society is viewed nowadays as a technologized society, where the great solutions to human problems can be solved by the progress of technology in economics from classical industry to communications. In the last years, nanotechnology is called to play an important part in the global food production, food security and food safety in the sense that the use of nanoscale micronutrients conduced to suppressing crop disease and the relationship between nutritional status and plant diseases is investigated. Nanomaterials are capable to penetrate into cells of herbs; they can carry DNA and other chemical compounds in the cells extending the possibility in plant biotechnology to target special gene manipulation. It is important to note that the concentration, plant organ or tissue, exposure rate, elemental form, plant species, and exposure dosage (chronic/acute) affect the plant response and in particular the distinct stress response. The complex process of utilization nanoparticles in agriculture has to be monitored to a level that avoids further environmental contamination. The present and future use of nanoparticles as micronutrients is affected by different risks related to nanotoxicity of micronutrients, a problem to be solved by an appropriate and safe circuit of nanoparticles in soil, water, plants and at last in human organism.

**Keywords:** nanotechnology, nanoparticles, micronutrients, fertilization, nano-toxicity

## 1. Introduction

Post-modern society is viewed nowadays as a technologized society, where the great solutions to human problems can be solved by the progress of technology in economics from classical industry to communications. In this regard, nanotechnology was viewed from the beginning as the manipulation of matter at atomic, molecular and supramolecular scale leaved the established field of microfabrication, semiconductor physics, energy storage to extended surface science, organic chemistry and molecular biology applications. Nanotechnology presents the ability to create new materials with dimensions on the nanoscale together with a large range of applications in new domains as nanomedicine, nanoelectronics or biomaterials. From this point of view, in the last years nanotechnology is called to play an important part in the global food production, food security and food safety in the sense that the use of nanoscale micronutrients conduced to suppressing crop disease and the relationship between nutritional status and plant diseases are investigated. The large use of nanotechnology raises the problem of the toxicity of the new materials involved and their use in economics, this problem is associated with a poor legislation in the field regarding accidental release, atmospheric deposition, deliberate disposal in the environmental as pesticides, remediators, including the use of soil amendments containing nanomaterials (manuers, sludge) or water contamination for irrigation. In spite of this toxicological concern, the agriculture-nanotechnology is viewed as a solution, as a technological advancement in order to use efficiently the natural agriculture resources, i.e. water, nutrients or chemicals while farming. Besides the possible benefits of enhancing the crop yield, nanotechnology presents itself that having the ability to maximize the benefits of natural agriculture resources, through efficient products in the form of pesticides for pest and disease management and for sensors that monitors the soil quality and plant health, in the other words to solve a problem of environmental pollution. In this regard, over the last decade an important number of patents have been proposed and different products on the market that incorporated nanomaterials have been used in agricultural practice, e.g., nanopesticides, nanofertilizers or nanosensors.

As a general aspect, of world-wide society characterized by a constantly growing of population number, there exists the most important challenge that of higher agriculture yields. The aim of application of nanomaterials in agriculture is to reduce the applied amount of plan protection products, to minimize nutrient losses in fertilization and increased the yields through an optimized nutrient management. Classical active substances used nowadays can be lost during application due to different processes as runoff, evaporation, photolysis, and hydrolysis or micro-organisms degradation. Different nanomaterials used as additives are characterized by large surface area and as a consequence they are appropriate to sorption process minimizing in this way the losses by reducing runoff and decreasing releases kinetics. Special designed nanoparticles can protect the active ingredients from photodegradation or can enhance uptake into leaves and other parts of the plant. Nanomaterials characteristics conduced to the substitution hazardous organic solvents present in some plant protection products and can reduce the application rates through their enhanced reactivity. As it was expressed before, despite of these positive impacts some nanomaterials have properties that classified them as potentially hazardous. The use of nanomaterials in agriculture and especially in plant protection and fertilization may pose unpredictable risks due to the fact that their application is accompanied by an intentional input of nanomaterials in the environment. In this regard, the human and environmental exposure due to nanomaterial residues in crops and soil might increase due to bioaccumulation of nanomaterials in the environment and food chain [1]. The requirements of a growing food market implied the existence of an urgent demand for products containing nanomaterials due to a process of regulation. At the beginning of twenty-first century the most popular agriculture application of nanotechnology is focused on plant protection and fertilization. It is stated [2] that higher plants have an ability to develop mechanisms to perform satisfactory under hard atmospheric and soil conditions. In order to help plants growth one of the novel methods is the use of nanomaterials that possesses physicochemical characteristics to enhance the metabolism of plants. In this view, the fertilization that used nanotechnology can amplify the plant production by delivering the micronutrients on request and control the development of plants. Nanomaterials are capable to penetrate into cells of herbs, they can carry DNA and other chemical compounds in the cells [3], extending the possibility in plant biotechnology to target special gene manipulation.

One of the most serious and important problems of agri-nanotechnology is the absence of analytical methods to quantify the concentration of nanomaterials in water, soil and air, in order to define an exposure limit. Part of difficulties is related to extraction and separation from soil matrix and interfering constituents, and the presence of very low concentrations, more over for metallic nanomaterials there exist different natural constituents as counterparts. However, the analysis techniques indicates possibility to extract these low concentrations by processes as X-ray based techniques, chemothermal oxidation, thermogravimetry or mass spectrometry, these techniques been used generally coupled on a measurement line. The evaluation risk of organic compounds used in plants protection products, namely the evaluation of persistence, bioaccumulation and toxicity is based on specific end points and parameters obtained from laboratory and field experiments. For instance, the persistence is evaluated considering the dissipation of 50% of initial concentration, bioaccumulation properties are measured of octanol-water partition coefficient and the evaluation of toxicity is based on aquatic toxicity namely the intrinsic toxicity of the compounds.

In the agri-nanotechnology the enhanced yield is related to the potential nutritional value of nanomaterials, especially for the essential micronutrients necessary for host defense. The permanent search for new solutions to global food problem conduced to the application of nanotechnology to enhance the efficiency and sustainability of agriculture practice.

## 2. Nanomaterials in plant growth

The increase requirement of global food production is related nowadays with the necessity of application new technology for enhancing crop yield in order to satisfy the global food security. As a modern trend in this view, the application of nanotechnology solutions can bring a response to grave problem of different deficiencies in human population as deficiencies of iron, zinc, selenium, calcium, phosphorus or vitamin A. The nanotechnology can offer solutions as micronutrients in agriculture in order to optimize the deficient presence of these substances in soil, by their use in fertilization. Besides the possible studied benefits, it is stated [1] that the nanomaterials use in agriculture may pose unforeseeable risks due to the intentional input of nanomaterials in the environment that can led to human exposure related to bioaccumulation in crops and soil and as a consequence in the food chain.

The great challenge of modern agriculture related to the use of nanotechnology is to regulate the products with the nano content in the condition where the nanomaterials pose problems to the regulatory bodies and on the other hand there is a lack of knowledge to the possible effect on the plant growth, i.e. to the genetics of plants. The possible use of nanomaterials in agriculture is a new nanotechnology solution under development now for a dozen years [4, 5] as studies regarding the use of nanoscale nutrients (metals, metal oxides, carbon) to suppress crop diseases [6]. In this view, the problem of agriculture in managing the crop disease is related to different attempts as genetic breeding, new pesticides products or new eradication protocols with the effect of the development of host plant resistance. Genetically modified plants raises different ethical problems related to the effect to the metabolism of human body, and this is a serious public concern.

A possible alternative for suppressing crop disease is the managing of plant nutrition statue and in this perspective the major limitation is that different crops have different nutrients requirements and the nutrient interacts with the level of plant disease in variable ways. As an example, the micronutrients are critical in the defense against crop disease where tissue infection induced reactions that conduced to the production of inhibitory secondary metabolites. These metabolites are generally generated by enzymes that requires activation by micronutrients cofactors, e.g. Mn, Cu and Zn as activating host defense enzymes i.e. phenylalanine or ammonia lyase. The availability of micronutrients level is related to soil characteristics, e.g. Fe, Mn, Zn are deficient in alkaline soils which limit uptake by roots and by consequence exposed roots to infections. Another way for enhancing disease defense is connected to non-essential elements, e.g. Al or Si, that offers resistance to a number of foliar and root pathogens although their presence in soil (e.g. Si) is frequently limited. As regarding Al, its application has been limited due to the fact that the over-application can cause significant crop damage and yield reduction, and insufficient presence modifies the acidity of soil [7]. The important characteristics of the nanoscale metals and metal oxides is the greatly their availability and translocation within plants. In the process of producing nanomaterials to be applied in agriculture there are used besides chemical and physical methods for synthesis the biosynthesis using plant extracts. The traditional method is the synthesis on chemical route, namely the reduction in liquid phase with common reducing agents as; citric acid, hydroxylamine, cellulose, hydrogen peroxide, sodium carbonate and sodium hydroxide. In the solutions are added stabilizing agents in order to assure uniform particle distribution and dispersion, agents such as: polyvinyl alcohol and sodium polyacrylate. The physical methods for synthesis include laser ablation, chemical vapor deposition (CVD), sonochemical reduction, supercritical fluids or gamma radiation. In the case of carbon, the fullerene synthesis is realized in arc discharge or gas combustion and carbon nanotubes are produced by CVD in the decomposition process of gaseous hydrocarbons. Different nano products that can be used as fertilizers have been patented in the last years as: active nano-grade organic fine humic (CN 1472176-A, Wu et al.); oxide nano rare earth (CN1686957-A, Wang et al.), carbon nanomaterials (US 0174032-A1, Lui et al.); nanosilver (KR 000265-A, Kim et al.); nano diatomite and zeolite (US 0115469-A1, Yu et al.), nano-selenium (US 0326153-A1, Yin et al.) or nano-silicon carrier (US 0225412-A1, Sardari et al.). The high-surface area nanoscale materials conduced to a more efficient retain of nutrients and represents a stable reservoir to plants [8], raising the potential for enhanced plants growth. The use of traditional is characterized by fertilizers with active ingredients that have low water solubility, the result being an inefficient availability to plants and furthermore a lack of control to pathogen agents. The nanofertilizers offer controlled release and synchronization of the nutrient flux over time with the uptake, minimizing the wasteful interactions with soil or air that conduced to nutrients loss. From the roots of the plants the nanomaterials as ZnO, $TiO_2$, $CeO_2$, $Fe_3O_4$, $Ni(OH)_2$, $C_{70}$ fullerenes, Al, Cu, Ag, carbon nanotubes (CNT), are uptake and translocated to plant stem where partly are deposited ($C_{70}$, $Fe_3O_4$,$CeO_2$, $Ni(OH)_2$) or partly are foliar deposited (Al, Ag, Cu, Zn, ZnO, $CeO_2$, $Fe_3O_4$, $C_{70}$). The root cell of a plant has different absorption zones for different kinds of nanomaterials, for instance $Fe_3O_4$ has absorption areas in epidermis, cortex and cambium; $Ni(OH)_2$ in epidermis, cortex, cambium and metaxylem, Ag in epidermis and cortex or $Ag^{2+}$ in epidermis, cortex, endodermis, and metaxylem.

Regarding nanomaterials exposure there exists a positive experience impact on crop growth and pathogen inhibitions, as related to antimicrobial activity for Ag, ZnO, Mg, Si or $TiO_2$. The effect on different plants of the foliar exposure to nanomaterials as ZnO conduced to increase in shoot length (15.1%), root length (4.2%) [9], increase in chlorophyll (24.4%) soluble leaf protein (38.7%) or increase in acid phosphatase (76.9%), alkaline phosphatase (61.7%) and phytase (>3x). The effect of tobacco culture cell exposure to MWCNT (multiple wall carbon nano tubes) conduced to enhanced cell growth and regulate cell division by activating water channel protein [10] and the effect of 50 μg/ml on tomato roots to MWCNT conduced to enhanced fresh and dry mass besides changes in gene expression (water channel protein) [11]. The foliar and root application of nanoparticles of $Fe_2O_3$ conduced to the increasing of root elongation and to the increase of photosynthetic parameters by foliar application [12]. The application of Mn in concentration 0.05–1 mg/L on Mung bean roots in a Hoagland culture solution conduced to an increase in shoot and root length, dry and fresh biomass and rootlet number [13]. The effect of spinach roots exposure to $TiO_2$ nanoparticles present in soil conduced to an enhanced growth rate and chlorophyll as well as an enhanced rubisco activity and photosynthetic rate [14]. The silver nanoparticles exhibit an intense inhibitory activity to microorganisms, in this regard Ag NPs damaged and penetrate the cell membrane subsequently reducing the infection [15]. Another nanomaterial with intense antimicrobial activity is ZnO NPs that is effective to pathogen control growth, also characterized by a lower toxicity in comparison to Ag and with benefits on soil fertility. The application of ZnO NPs conduced to systemic disruption of cellular function of pathogens as *Botrytis cinerea* or *Penicillium expansum* resulting in hyphal malformation and fungal depth [16]. Another promising amendment is $TiO_2$ NPs due to their combined photo-catalytic and antimicrobial activity, e.g. application of $TiO_2$ NPs reduced *P. cubensis* infection of cucumber by 91% and increase photosynthetic activity by 30% [17]. One of the most popular cultures is that of wheat, in this case the foliar application of Ti NPs at 20 g/l it increased stem elongation, biomass, flowering, ear mass and seed number [18]. Nanomaterials fertilizing activity is influenced by the chemical and physical characteristics of the environment soil, air and water. The initial properties of NM can suffer different transformations due to the interactions with both biotic and abiotic soil components and these modifications can influence the stability of NPs, transport and aggregation and availability to plants. Necessary micronutrients as Cu, Fe, Mn or Zn become less availability from the soil when pH is approaching to the limit of 7.0 and subsequently there exist a lower uptake to plants roots and compromising the nutritional status [19]. It is reported [20] a pH-dependence of humic acid adsorption onto nanoparticles of $TiO_2$, $Al_2O_3$ and ZnO where the electrostatic interactions and ligand exchange with $SiO_2$ is responsible for selective adsorption onto oxide surface. Due to different limitations related to soil characteristics and their content in macro and micro nutrients, it became important the foliar applications of fertilizers, in particular the nanomaterial nutrients. The entrance gate for micronutrients is the leaves through stomata and cuticle structures as the studies in literature have presented [21]. In case of watermelon [22] the pathway leaf-to-root translocation of nanomaterials after a foliar application presented an important content of Ti, Mg or Zn nanoparticles that exist in root tissue a fact that shows the effective action of foliar application of nanomaterials. The possible route of biosynthesis of nanoparticles, e.g. ZnO by extracellular secretions of *Aspergillus fumigatus* TFR-8 and their applications as a foliar spray conduced in case of bean plants [23] to an increase of physiological parameters i.e. biomass, shoot/root length, root area or chlorophyll content and on the other hand the residual protein from fungal extract increased nanoparticle stability. Regarding $TiO_2$ nanomaterials is stated [24] that the application on different crops, e.g. wheat or soybean has increased the yield and reduced the pathogenic diseases, these effects being based on surface properties of $TiO_2$ nanoparticles as their photo-catalytic characteristics. Another nanomaterial applied to cucumber leaves is $CeO_2$ [25] in nano-powder form, showed a high leaf-to-root translocation suggesting a phloem-based transport throughout the plant. Foliar applied nanoscale amendments dedicated to pathogen control are related to antifungal activity of $CuO_2$ nanomaterial or Ag nanoparticles. Tested on tomato infected with *Phytothphora infestans* the effect of $CuO_2$ nanomaterial [26] showed an increased protection (73.5%) as compared to bulk amendment (57.8%) promoting the use of nanoscale amendments both to suppress disease and enhanced the nutrient action of nanomaterials. The antifungal activity of Ag nanoparticles is based on the accumulation in the fungal hyphae that disrupted cellular function, an intense process related to a higher ion release on the increased nanoparticle surface area [27]. It is worth to mention that the problem of *in planta* translocation, i.e. the way that the foliar application of nanoscale nutrients affects root pathogens, is still under research in the sense that pathogens can be released after shoot-root transfer or the induced host resistance. A non-classical nutrient besides metal and metal-oxides there is based on carbon nanomaterials in the forms of $C_{60/70}$ fullerenes, carbon nanoparticles, or single/multiple wall carbon nanotubes (SWCNT/MWCNT). An extended study [11] in literature upon the action of MWCNT, SWCNT, graphene and bulk activated carbon onto tomato plants grown in artificial medium revealed an enhancement of biomass by stimulating the growth. The molecular analysis upon the action of MWCNT has shown a stimulation of cell division and plant growth due to the activation of water channels (aquaporins) and regulatory genes for cell division and extension. Carbon nanomaterials exposure can alter the different co-existing organic contaminants in various kinds of soils. In this regards, carbon nanomaterials presents toxicity to soil microorganisms, with accent to SWCNT including fungal community. Carbon nanomaterials have potential to enhance plant growth, nutrient uptake, seed germination or fruit yield the most promising one being MWCNT with positive effects on different crop species. The large inters in the use of nanomaterials is based on the increase global production of nanomaterials and their possible application in agriculture with hazards and risks to be investigated. An exposed [28, 29] "realistic exposure scenario" for $TiO_2$, Ag and carbon nanotubes proposed the doses of 0.4, 0.02 and 0.01 μg/kg/year although the relationship between these values and the actual concentration in the environment is not known.

It is worth to mention, that in general the discussion to nanomaterials in agriculture refers also to a most prominent fraction of nanomaterials that are non-solids comprising nanoscale structures that can encapsulate an active ingredient in plan protection product. Generally active substances have poor solubility in water and at room temperature are brought to solution with organic (co)solvents. In order to avoid the use of organic (co)solvents one solution is stated [30] the use of oil/water emulsions. Generally the physical appearance of non-solid nanomaterials are lipid base in liposomes, micelles or cochleates, in polymer based in micelles, nanosphere, nanocapsules and polymersomes or in emulsions base as liquid crystals and micro-emulsions. The nanomaterials in non-solid forms enhance the solubility and the coverage of the hydrophobic leaf surface together with the penetration of the active substances through the cuticula.

As presented, the characteristics of solid and non-solid nanomaterials have been investigated in the last decade in order to understand the effect of nanonutrients in culture fertilization as well as in plant protection with promising results together with various studies regarding the toxicity of nanoparticles in the environment.

## 3. Nanoparticles and their action on plants

The nanotechnology application in agriculture is for our world one of the most important domains of study due to the possibility of increasing for different culture production and assisted plant protection against pests and diseases together with the monitoring of pathogenic agents. In this regard, the application of nanotechnology in the control of crop yield and crop protection is relatively recent compared to organic or chemical nutrients and different drug delivery or pharmaceuticals [31, 32].

One of the most important nutrients for humans and plants is iron (Fe) where iron deficiency is common in nowadays human diet affecting over 2 billion people in the world [33] Iron is essential for plant development and plays an important part in photosynthetic process being implied in redox reaction as well as generating reactive oxygen species [34]. Due to its properties iron containing nanoparticles have been used as nano-fertilizer for nutrition of plants. As an example there was observed [35] a positive effect of nano-FeO and nano-ZnCuFe oxide on the growth of mung (*Vigna radiata)* seedling, as well a positive influence on leaf and pod dry weight on soybean yield and quality [36]. The problem of high rate of accumulation of iron oxide nanoparticles in plants that conduced to precipitation in gravitational field can be solve by surface-coating materials [37], a promising way to improve the agronomic traits. Surface iron coating materials as nano-$Fe_2O_3$ coordinated with humic acid improved the mobility of iron in peanuts [38] or water-based ferrofluids stabilized with citric acid on the growth of maize [39]. In this spirit, in literature [40] there are data regarding the action of nono-iron fertilizer capped with ethylenediaminetetra acetic acid (EDTA) upon sunflower(*Helianthus annuus)* by foliar and soil application. An important parameter in studying the functional biology is plant biomass, in this regard the effect of applied nano-fertilizer by foliar treatment is the improving of aerial organ dry biomass while the effect on soil application of nano-Fe-EDTA is not conclusive. Regarding aerial organ fresh biomass both foliar and soil addition of nano-Fe-EDTA had the effect of increasing aerial organ fresh weight of the plants as compared to classic fertilizer. In this method of applying nano-Fe-EDTA there exists an increasing of leaves number in percentage by 21.42% as compared to control plants [40]. As regards, the plant height the application of nano-Fe-EDTA is effective also in foliar and soil treatment and taking into account these experiments the general growth of sunflower is influenced by iron oxide nanoparticles. The nano-fertilizer that treated the plan influenced also the physiological parameters in the sense that all treated plants had a higher chlorophyll content, the most important pigment, level than the test plants i.e. from the total level of 2.69 mg/g and 2.34 mg/g belongs to chlorophyll to the treated plants with nano-Fe-EDTA through soil absorption, indicated the translocation of coated nanoparticles from roots to the aerial parts. This treatment method implied penetration points on the leave surface i.e. stomata and subestomatic chambers which means hydrophobic penetration of nanoparticles through these pores. Another problem for foliar application of nanoparticles is the possibility for their accumulation in cells from epidermis of petiole near the application point limiting in this way their possible contribution to plant growth or photosynthesis reaction. However, the effect of an organic shell around nano-Fe made these nanoparticles more compatible for entering and translocation in the plant [40]. Another direction to suppress iron deficiency common in human diet is to use iron fertilizers based on humic substances extracted from lignites, such as leordine, it is stated [41] that this kind of fertilizer is more ecofriendly than synthetic iron chelates as discussed above, but they are less efficient in suppressing iron chlorosis. Low concentrations of superparamagnetic Fe-nanoparticles increased significantly the chlorophyll contents in sub-apical leaves of soybeans under hydroponic conditions. The plants fertilized with the leonardite humates accumulated slightly higher fresh weight than those fertilized with the iron chelate, the humic substances generally increase the shoot and root growth by 15–25% and the accumulation of total iron in pods for soybean plants reaches 50 mg/kg under conditions of sufficient nourishment [41]. The applied nanoparticles of $Fe^{57}$ were capable to supply the $Fe^{57}$ deficiency in plant and it was transported from root to shoot and reaches the pods, this iron humate was prepared taking into account its maximum complexing capacity in order to avoid the iron flocculation in calcareous conditions [41]. As a remark, in the context of sustainable agriculture, the Fe-nanoparticles can be considered as a part of novel technology in line with the politics of precision and sustainable agriculture.

One of the elements that results from the rapid industrialization is cadmium-Cd and as a consequence there exists an irreversible exposure in the environment, especially in the soil. The Cd absorption in the plants from soil or air through aerial deposition and its transfer into different parts of the plants can cause several abnormalities in plants as reduced growth and yield [42]. The major entry gate of Cd in plants is the roots while the toxic element entry in the human body is the consumption of contaminated food. The excess of Cd in plants affected the plant growth by reducing the production of reactive species, electrolyte leakage, hydrogen peroxide and malondialdehyde concentrations in plants [42]. As a solution to reduce the Cd content in soil is the application of biochar, as a carbon rich pyrolyzed organic biomass that is effective in reducing bioavailability of metals in soil [43]. These properties are based on biochar high pH, cation exchange capacity, nutrient retention capacity including water retention capacity and lower bulk density [44]. The use of nanotechnology in agriculture can rise different problems as the role of foliar application of ZnO nanoparticles combined with soil applied biochar in Cd accumulation by plants [45], in this regard it was stated that compared to other cereals maize (*Z. mays*) plant has a higher ability to take up Cd and its translocation to the aerial parts that conduced to Cd accumulation in grains. The effect of applied ZnO nanoparticles alone or combined with biochar enhanced the chlorophyll concentrations and gas exchange parameters in leaves of maize [45]. On the other hand, the effect upon on malondialdehyde, hydrogen peroxide, electrolyte leakage and antioxidant enzyme activities in maize leaf and roots are in the sense that the nanoparticles reduced these contents applied alone or with biochar. Experimental application of ZnO-nanoparticles improved the activities of antioxidant enzymes in leaves and roots [45]. As it was presented [45] the application of ZnO nanoparticles and biochar reduced the Cd concentration in maize shoots and roots. Generally the revealing that ZnO nanoparticles with effect in maize biomass and growth is expressed by accelerated exogenous application of nanoparticles further enhanced with biochar application in combination to nanoparticles. It was observed [45] that the lower biomass in control plants is associated with higher Cd concentration in maize which reduced the chlorophyll concentration in leaves, or due to the increased levels of malondialdehyde, hydrogen peroxide and electrolyte leakage in the belowground and aboveground tissues. Lower concentration of ZnO nanoparticles have positive impacts on plants [46] in the sense that the height of the plants increased and the biochar application decreased the soluble Cd in soil, meanwhile nanoparticles increased the Zn level in the plants [45]. Exogenous application of ZnO nanoparticles improved the chlorophyll concentration and as a consequence improved photosynthesis and with applied amendments might reduce the oxidative stress in maize plants. It was suggested [47] that ZnO nanoparticles can be considered as slow-release for Zn fertilizers which is advantageous to avoid sudden absorption of Zn by plants as the higher concentrations of Zn absorbed by the plants also conduced to toxicity in plants. It was stated [48] that a proper amount of Zn in the soil or plants may interfere with Cd and could reduce the Cd accumulation by plants due to the antagonistic effects of these metals on each other and furthermore biochar application in combination with ZnO nanoparticles further deceased Cd concentration in maize plants. As a solution to Zn malnutrition, the strategy of using ZnO nanoparticles combined with biochar in cereals growth, in particular in maize, conduced to the enhancement in plant biomass with decreased Cd concentration in cereals. A proper concentration of Zn is benefic to plant organism because Zn is necessary for the activity of enzymes such as dehydrogenases, aldolases, isomerases, transphosphorylases and RNA and DNA polymerases, as well as in synthesis of tryptophan, cell division, maintenance of membrane structure and photosynthesis and acts as a regulatory cofactor in protein synthesis [49].

For example in coffee plants although Zn is required for optimal metabolism, yet deficiency is prevalent partly due to the inefficient absorption of this micronutrient combined with a deficiency in translocation [50]. Zn fertilization improves the production and quality of coffee beans by positive impact on polyphenol oxidase activity, color index, sucrose content, caffeine and trigonelline content and chlorogenic acid [49]. One of the most efficient ways of suppressing Zn deficiency is foliar fertilization a method that avoids toxicity symptoms and reduce fertilizer-related pollution and in this perspective the foliar fertilization using micronutrients as Zn nanoparticles is the advanced solution proposed by nanotechnology. In spite of positive physiological impacts of nanoparticle fertilizers on crop growth, the properties of nanoparticles can induce oxidative stress and toxicity in plants and other organisms in ecosystem [51]. It was observed [52] the effect of ZnO nanoparticles application on coffee plant on its positive part, i.e. the fresh weight of roots and leaves are increased in percentages of 37% (root) and 95% (leaves) and no effect on the stem as compared to control. The net photosynthesis rate did not vary over time for ZnO nanoparticles treated plants and as regards zinc assimilation ZnO nanoparticles treated leaves contained a higher content of Zn compared to classical nutrient $ZnSO_4$ treated plants [52]. As regards, the zinc assimilation in stems and roots there does not exist significant differences between the treated plants with ZnO nanoparticles and zinc sulfate at the same content of Zn in the soil. The treatment of coffee plants with ZnO nanoparticles positively affected plant biomass, with a major effect on fresh and dry weight. Part of so-called photosynthetic machinery was improved when coffee plants were exposed to ZnO nanoparticles, there exists a positive interaction between ZnO nanoparticles and net carbon assimilation rate and stomatal conductance, confirming the role of Zn as a cofactor of carbonic anhydrase that increases the content of $CO_2$ in the chloroplast and thus also increases the carboxylation capability of the Rubisco enzyme [53]. It is important to state that although Zn is an essential element, in an impropriate quantity it can reduce plant health and performance at phytotoxic concentrations. Symptoms of Zn toxicity are reduced growth and plant biomass, inhibition of cell elongation and division, wilting, curling and rolling of young leaves chlorotic and necrotic leaf tips and root growth inhibition [54].

The effect of nano-boron (B) fertilizer on the mineral nutrition and fruit yield was put into evidence by on pomegranate trees culture [55]. It was observed that a foliar spray of nano-B (concentration 6.5 mg $BL^{-1}$) in combination with nano-Zn increased significantly the fruit yield up to 34% depending on treatment, with an accent to nano-B fertilizer. Also, the foliar application of these nano-fertilizers increased the number of fruits per tree, without an effect upon fruit cracking. As regards the fruit size physical parameters as fruit diameter, fruit calvyx diameter or average weight, they are not affected significantly for the treated trees, but the pH pomegranate juice increased to 0.62 pH units under fertilization. Concentrated nano-B foliar application caused small (1%) but statistically constant changes in the amount of total phenolic compounds in pomegranate juice whereas the antioxidant activity is not affected. The total amount of sugar in pomegranate fruit juice increased up to 4.6% at discussed nano-B concentration with no significantly increase in total anthocyanins under treatment. The action of nano-B fertilizers is also efficient in fruit crops as almond, apple, pear, persimmon or peach.

Calcium (Ca) is an important macro-element that plays an important role in plants including structural functions of cell walls, stabilization of cell membrane, maintenance of cell turgor pressure and counter-ion for inorganic and organic anions in vacuoles, as well as cytoplasmic messenger. Calcium cannot be transferred through from the older tissue to other parts of plant on the basic phloem pathway and Ca xylem translocation depends on unidirectional transpiration stream [56]. Studies of foliar application of nano-Ca on pomegranate trees shows no significant effect on fruit yield and to the number of fruits per trees [57]. Nano-Ca fertilization increased the Ca leaf concentration, whereas the foliar treatment decreased significantly pomegranate fruit cracking. The total phenolic compounds in pomegranate fruit juice is decreased in nano-Ca fertilization but with no significant effect on antioxidant activity and total anthocyanin content. Foliar application of Ca reduces the fruit cracking due to its role on cell wall, in enhancing the mechanical properties of plant tissue. However, the foliar fertilization of Ca had no significant effect on yields for kiwifruit, strawberry, grape and cherry.

Manganese (Mn) is a micronutrient required by most of the plants die to its implication in biochemical reactions, as those required by dehydrogenases, decarboxylases, kinases, oxidases, peroxidases enzymes and to their role in fighting oxygen reactive species in plants. Plants required 20–40 mg Mn/kg of dry weight for its various functions e.g. in tricarboxylic acid cycle, oxidative and non-oxidative decarboxylation reactions and for different synthesis as carotenoids, sterols or gibberellic acid. The most important process of photosynthesis, implied the final conversion of absorbed light to energy via enzymatic reactions. Among them, a studied Mn-containing enzyme, is found in PSII oxygen evolving complex, a multi-step enzymatic pathway where Mn is required, as a cofactor in both lower and higher plants for the Hill reaction-the water splitting and oxygen evolving system [58]. Mn plays an important role in the synthesis of fatty acids and carotenoids, as well as in cell division and elongation. A normal function of the plant as biological system is affected by abiotic stress defined any adverse force or condition that affects its normal functioning. Abiotic stresses as drought, flood, salinity or harsh temperature conduced to an excessive amounts of reactive oxygen species that potentially injure proteins, membrane lipids, carbohydrates and DNA. The application of Mn increased the leaf area, photosynthesis rate and stomatal conductance in drought stress conditions, reducing the production of reactive oxygen species in plants. These reactive species also accumulated in inside the plants under thermal stress as harsh temperatures, that causes damage to cellular compounds and metabolic processes. It was suggested [59] that salinity inhibits the uptake of Mn inside plants inducing deficiency, in this case the foliar application increased stem diameter, fresh and dry biomass, number of seeds and different biochemical parameters as total protein or Hill reaction activity. The application of Mn nanoparticles on wheat applied by foliar exposure or soil amendment showed [60] no inhibition of vegetative or reproductive development, further more Mn nanoparticles significantly reduced Mn accumulation in shoots but increased the translocation efficiency in grains compared to classical Mn fertilizers due to a greater reactivity and non-toxicity due to a slower and a continuously availability of soluble Mn from Mn nanoparticles as compared to ionic Mn salt. The Mn nanoparticles greater photophosphorylation and oxygen evolution compared to bulk Mn suggested its novel potential nano modulator of the photochemical pathway in agriculture [61]. Furthermore Mn nanoparticles are viewed as a stimulant of plant growth and of metabolic processes as alkaloids production. In infested soils, foliar exposure to Mn oxide nanoparticles reduces disease up to 28% as compared to controls [62], the plants can have cross-tolerance between abiotic and biotic stresses, and in this regard stress tolerance can help plants to form faster and more resistant manner to additional environmental changes. The propose mechanism for the distribution of Mn nanoparticles through the plant incudes transportation from the root through the vascular system, a process considered as active-transporting as long as includes signaling, recycling and plasma membrane regulation. Generally the excess amounts of Mn in plants is not benefic to their health by interfering with the uptake, transport and utilization of other minerals as Ca, Fe or Mg as being competitive for the same ion transport.

Copper nanoparticles at low concentrations ($<0.25$ mg $L^{-1}$) stimulated plant photosynthesis in a percentage of 35% on waterweed (*Elodea. densa planch*) compared with control plants [63]. It was stated [64] that soil amendments with metallic Cu nanoparticles up to 600 mg $kg^{-1}$ increased significantly 15-day lettuce seedling growth up to 91% without toxic effects. Higher concentrations up to 1000 mg $L^{-1}$ of metallic Cu nanoparticles conduced to toxic effects on seedling growth of mung bean and wheat [65] and can reduce the biomass of zucchini by 90% as compared to control. The optimal concentration for aqueous copper for proper plant growth is in the range of only 0.02 mg $L^{-1}$ due to the effect of phytoxicity at higher levels [66].

Magnesium (Mg) is essential for plant growth as it plays an important role in the photosynthesis process as central component of chlorophyll and also acts as a phosphorus carrier as an important element for phosphate metabolism. Mg is necessary in cell division and protein formation in activation of several enzyme systems and is essential for plant respiration. The effect of foliar application of magnesium and iron nanoparticles solutions upon black-eyed pea (*Vigna unguiculata*) combined in a concentration of 0.5 g $L^{-1}$ enhanced the 1000-seed weight by 7% in comparison with regular application of Fe and Mg [67]. The Mg nanoparticles application improved the uptake of Mg in plant stems and leaves compared to the use of regular Mg salts, a fact related to the higher mobility of Mg nanoparticles. Magnesium deficiency conduced to a slow growth of plant and to leaves problems due to the development of internal chlorosis and that is why Mg important in crop yield.

Silver (Ag) is known as an element with antiseptic characteristics and it is important to understand its effect upon soil microbial community. Microorganisms are key regulators of biogeochemical recycling of nutrients in the environment and assist in maintaining the overall health and function of ecosystems [68]. The soil is regarded as a complex system and its physicochemical characteristics as pH, texture and organic matter content can influence the nanoparticles properties introduced in it, a fact that can conduce to an increased or a decreased bioavailability and toxicity of nanoparticles. The effect of Ag nanoparticles on the microbial diversity and enzyme activity of soil is regarded as a significant decrease in microbial mass as a function of increasing Ag nanoparticles concentration. [69]. Ag nanoparticles had impact on vascular plants, presenting positive or negative effects on seed germination, root growth and plant biomass [70]. In Ag nanoparticles application on wheat plants, there was not observed a significant effect with the exception of root fresh weight and root length that presents a negative response at 75 ppm treatment while in cowpea and *Brassica* there was observed a positive response to Ag nanoparticles. In cowpea plants a 50 ppm concentration of Ag nanoparticles conduced to growth promotion and increased root nodulation suggesting that Ag nanoparticles treatment improved the growth by modulating the antioxidant action of nanoparticles. Increased nodulation is supposed to be related to nitrogen-fixing bacteria as long as root exudation pattern is dependent to Ag nanoparticles concentration. In soil, total bacteria count improved in 50 ppm treatment and nitrogen fixer bacteria are sensitive toward 75 ppm treatment. In cowpea, the total bacteria count declined with increasing Ag nanoparticles concentration, with an increase of diversity index of total bacteria population was observed in 50 ppm treatment whereas the diversity of nitrogen fixers decreased in the 75 ppm treatment. The impact of Ag nanoparticles on soil bacteria diversity is dependent on Ag nanoparticles concentration and on the other hand on the plant species grown in that soil, a specificity related to the different root exudation patterns of different plant species. The antimicrobial properties of Ag nanoparticles may be altered when released in soil due to the complex system of biotic and abiotic processes, e.g. pore-water harbors a range of electrolytes that increase the aggregation of Ag nanoparticles in soil, thus reducing its size-dependent toxicity. The plants cultured in artificial soils compared to agar conditions in addition to higher concentration of $Ag^+$ ions the plants exhibited some characteristics: (a) the apparent toxicity observed in the soil was attributable to the particle toxicity; (b) lower rates of nanoparticles dissolution can be attributed to the reduction in the surface and greater soil aggregation; (c) the agar and soil have different mechanisms for sorption of the dissolved $Ag^+$ ion and the Ag nanoparticles. The application of Ag nanoparticles in real soil improved the bactericidal and fungicidal effectiveness of silver against most important plant pathogenic fungi.

Titanium oxide ($TiO_2$) mineral is naturally occurred in four natural polymorphs: akaogiite (monoclinic), brookite (orthorhombic), anatase (tetragonal) and rutile (tetragonal). $TiO_2$ nanoparticles are explored due their use as an antimicrobial agent and photocatalyst in order to remove organic compounds from contaminated air, soil, and water. Ti is not an essential element for plants, therefore $TiO_2$ nanoparticles are not viewed as plant nutrients but plays a potential role in plant protection and at lower doses its effective to its properties as a photocatalysts or an UV protector. It was stated [71] that exposure of naturally aged spinach seeds to $TiO_2$ nanoparticles (rutile) at concentration of 250–4000 mg $L^{-1}$ significantly increased the germination rate, the germination index, the dry weight of seedlings and vigor index of seeds. It was observed that under hydroponic conditions on agar, $TiO_2$ nanoparticles generally cause positive or non-consequential effects on plant growth for different food crops. For example, in hydroponic conditions it was observed a significant increase in the root and shoot length of *Brassica juncea* seedling treated with $TiO_2$ nanoparticles at concentrations: (0, 200, 500, 1000 and 1500 mg $L^{-1}$). An important factor is the lack of toxicity of $TiO_2$ nanoparticles due to their rapid agglomeration and consequently formation of larger hydrodynamic particles that are not available to plant and have no effect on plants, this is a property of rutile form that presented the characteristic of lipophilicity. It was observed [72] that $TiO_2$ in anatase form are toxic at high concentrations and due to their antimicrobial properties a significant growth of the roots was observed.

Selenium (Se) is an essential trace element for humans and animals and is beneficial for plants at low concentrations particularly under stress conditions acting like an antioxidant. Cereals are a good source of Se as it is present in the form of Se-methionine [73]. The total concentration of Se in most of soils is 0.1–2 mg $kg^{-1}$, with factors that affects Se solubility as: soil pH, redox potential, calcium carbonate level, cation exchange capacity, organic carbon, iron and aluminum level as well as the plants capability to produce root exudates. Selenium is most available in alkaline soils in the form of selenite, in acidic poorly aerated Se occurs in insoluble selenide forms, the lower limit for Se concentration in soil is 0.5 mg $kg^{-1}$. Selenium fertilization rate and its chemical form directly influenced Se grain concentration affecting the yield, its application form being foliar or liquid on the soil surface. Low concentrations of Se had a positive effect on growth of ryegrass, lettuce and potato due to its antioxidant action. It was stated [74] that 10 g Se selenite per ha can increase wheat Se concentration from a base level of 30–100-200 μg $kg^{-1}$ to recommended level of 300 μg $kg^{-1}$ as a minimum target. Agronomic use efficiency is higher for foliar application than soil application. Agronomic bio-fortification is an inexpensive method for the increase of Se intake by humans but the limited Se resources indicated that fertilization strategies had to increase agronomic use efficiency in environmental conditions by improving agro-technical measures.

Silicon dioxide ($SiO_2$) is a form of silicon oxide that had abundance in environmental mostly in the soil. Lower amounts of nano-$SiO_2$ increased germination of seeds in tomato [75], or of *Lycopersicum esculentum* seeds germination in concentration of 8 g $L^{-1}$ nano-$SiO_2$ for a percentage of 22.16%. The same concentration increased the fresh weight of seedlings by 116.58% and seedlings dry weight by 117.46% compared to control, with an important action upon root and shoot growth. Nano-$SiO_2$ amplified various factors of the growth and conditions of seedlings, i.e. height, diameter of root collar, main length of roots, seedlings lateral root number as well as induction of chlorophyll synthesis. Under abiotic stress nano-$SiO_2$ increases seeds germination in tomato [76] and in saline conditions nano-$SiO_2$ maximized the fresh and dry weight of leaves confirmed that the increment in the proline accumulation, unattached amino-acids, nutrient quantity and antioxidant activity of enzymes increased plant's level of endurance to environmental stress [77]. The chlorophyll content developed on nano-$SiO_2$ treated plants grown in salt-stressed conditions, the application of 1 mM silicon dioxide could alleviate the side effect of salt stress on percentage of germination, length, of root and shoot, weight of seedling, mean germination rate see vigor index and cotyledon reserve mobilization of *Lens culinaris* [78]. Nano silicon dioxide developed the growth of the plant, net rate photosynthesis, level of transpiration, conductance of stomata, rate electron transport and photochemical quell [79].

Regarding the nanotoxicity of nanoparticles action, the involved mechanism is not entirely understand, this mechanism is assumed in the sense by the changes related to the chemical structure, particles size and active surface area of nanoparticles. It is stated [80] that the toxicity action is focused on two directions: i.e. (a) a chemical toxicity based on the chemical composition as the released of toxic ions and (b) stress or stimuli caused by the surface, size or shape of particles. As viewed from chemical physics processes, the solubility of oxide nanoparticles affects the cell culture response and nanoparticle mediated toxicity is partly explained by the release of dissolved components of them [81]. In comparison to metal toxicity in plants and animals, the nanoparticles pathway is different, a problem solved by the introduction of different parameters in experimental tests to evaluate the nanoparticles dynamics. In a plant culture exposed to nanoparticles, the gain and losses related to the development, growth and productivity are not exclusively part of nanoparticles effect but they can be viewed as a participation of the primary ions to biological processes active in plants. Regarding the presence of nanoparticles in soil, as culture area for plants, had to be considered the interaction with the microorganisms in soil because they can positively interact with plants e.g. arbuscular mycorrhizal fungi [80]. The nanoparticles interaction with plants e.g. accumulation in plant biomass affects their fate and transport in the environment. There exists a first report [82] in 2007 regarding the negative effects of nanoparticles upon several plants as corn, cucumber, soybean, cabbage and carrot at relatively low dosage. At microscopic scale, the analysis of the chromosome morphology showed a relation between increased number of aberrations and the increased concentration of nanoparticles e.g. the appearance of stick chromosomes [83]. The phyto-toxicity was observed at molecular and nuclear cell level because the occurrence of stick chromosomes might be related to the degradation or de-polymerization of chromosomal DNA [80]. The extended development of modern agriculture brings besides some true benefits regarding crop productivity increasing problems related to environmental contamination with toxic elements e.g. metals or pesticides compounds and from this point of view nanoparticles used can aggravate the situation. The process of heavy metals accumulation by plants is related for the large majority of plants to roots accumulation and only a small part is translocated to the aboveground of the plants [84]. There are evidence [85] to a translocation process from the roots to the fruits, without the existence of changes due to biochemical processes. It is important to note that the concentration, plant organ or tissue, exposure rate, elemental form, plant species, exposure dosage (chronic/acute) affects the plant response and in particular the distinct stress response. This is the reason why the complex process of utilization nanoparticles in agriculture has to be monitored to a level that avoids further environmental contamination i.e. soil, water and air.

## 4. Hydroxyapatite and essential oils

One of the essential problems that limits crop production is the low availability of phosphorous (P) in many agricultural regions. In order to increase the phosphorous content in the soil it is necessary to apply P fertilizers, because phosphorous is an essential element for plant growth. Besides classical fertilizers, nanotechnology can offer a solution to supply the micronutrients deficiencies for plants development. In this regard, it was suggested [86] the use of hydroxyapatite nanoparticles $Ca_{10}(PO_4)_6(OH)_2$, nano-HAp, as potential fertilizers. Tests on the potential use of nano-HAp (15 nm) on soybean (*Glycine max*) [87] conduced to the conclusion that plants which received the nano-fertilizer produced greater biomass yield and seed compared with the plants fertilized with conventional water-soluble phosphorous source. It was stated [88] that nano-HAp might enhance P fertilizer efficiency in acidic and strongly P absorbing soils through the better mobility of nano-HAp in the soil potentially reaching plant roots. The experiments showed that the application of conventional triple superphosphate and HAp treatment conduced to an significantly increased the plant dry matter yield compared to control depending on soil characteristics e.g. Greenwood soils. The application of conventional fertilizer conduced to significant increase in shoot uptake of phosphorous in all types of soils in the range (0.1–1.4 mg P plant$^{-1}$), in peculiar the application of nano-HAp increased the plant uptake to a maximum value of 0.4 mg P plant$^{-1}$, indicating a contribution uptake in percentage (40–61)%. These results suggesting that nanoparticles could possibly have a benefit over water-soluble P conventional fertilizers in the very strongly absorbing soils since the opportunities for P fixation in the soil is minimized.

Among other important plants for the use in medicine are those conducted to the extraction of essential oils as basil and lavender. Essential oils are complex biostructures and contain a lot of chemical compounds from different classes as: terpenoids, ketones, aldehydes and esters with a composition depending on the plant's origin and quality, harvest time, climate, soil and extraction method. About 90% of the bioactive components of essential oils are monoterpenes and in the oxygenated form the bioactivity is enhanced. The medical use of essential oils is based on their properties such as antibacterial, antifungal and their characteristic to prevent the growth of different pathogens. The antibacterial activity of HAp samples and HAp samples coated with essential oil of basil and lavender was tested on methicillin_resistant *Staphylococcus aureus* (MRSA), *Staphylococcus aureus* 0364 and Gram-negative bacteria *Escherichia coli* ATCC 25922 as presented in [89]. As observed in **Figure 1(a–c)** there exists a slow decrease in MRSA growth for HAp-B and HAp-L samples at different concentrations—**Figure 1(a)**.

The evolution in the cell growth of *S. aureus* is observed in **Figure 1(b)**, an evolution that indicates a decrease in the cell growth starting from the low level concentration of 0.01 mg mL$^{-1}$ in the presence of the HAp-B sample. The HAp-L inhibited *E. coli* (**Figure 1c**) starting with the concentration of 0.02 mg mL$^{-1}$. Taking into account that MIC is the lowest concentration of the chemical that prevents visible growth of bacteria, the lowest concentration of HAp-L nanopowders at which the visible inhibition of MRSA bacterial growth was observed was 0.039 mg mL$^{-1}$, and for HAp-B was 0.625 mg mL$^{-1}$. In the same conditions for *S. aureus* we have for HAp-B MIC value of 0.313 mg mL$^{-1}$ and for *E. coli* HAp-L

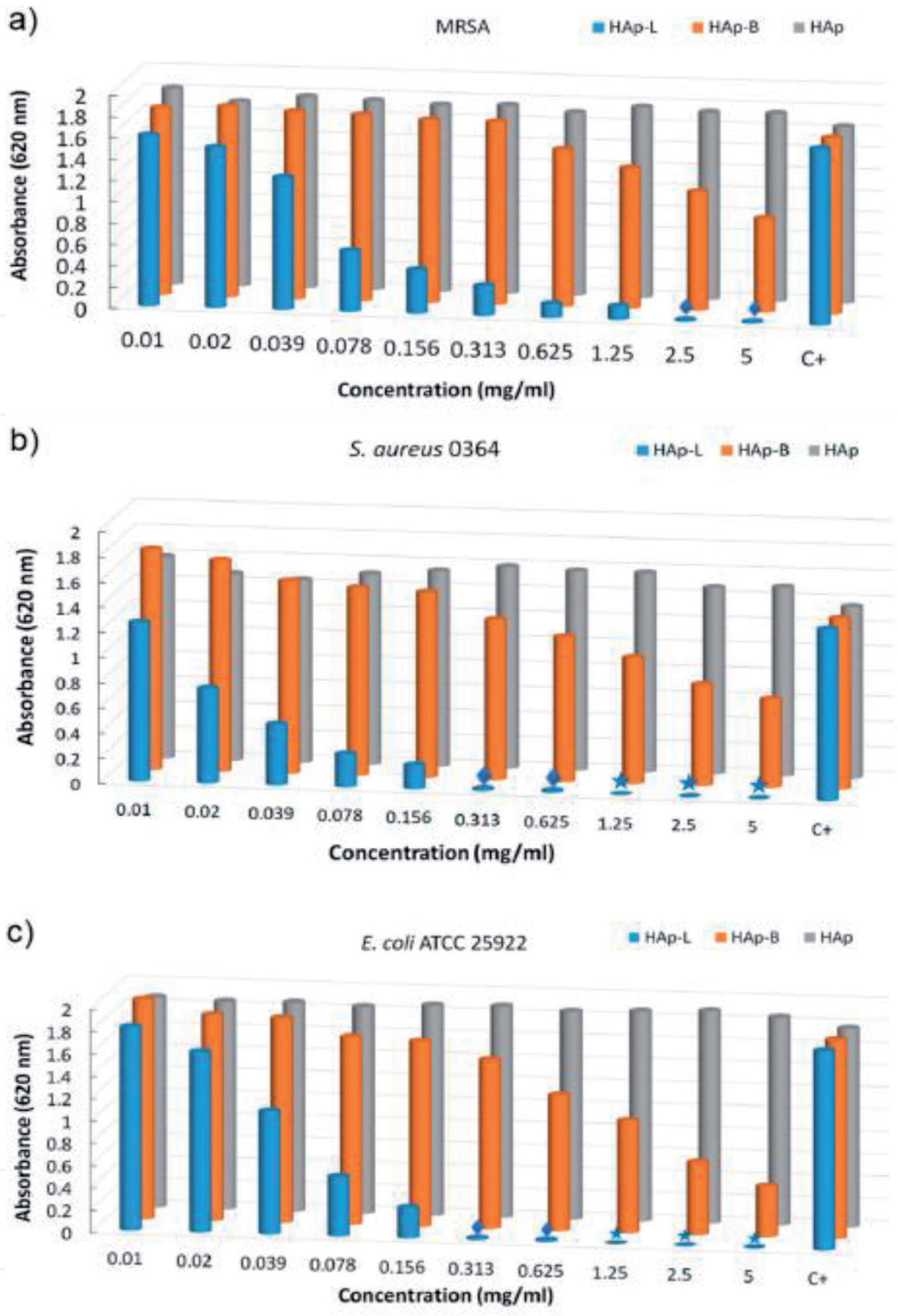


**Figure 1.**
*Graphic representation of absorbance values of the microbial culture obtained in the presence of the plant EO-coated HAp on different bacterial strains MRSA (a),* S. aureus *(b) and* E. coli *(c) quantified by A620 nm values.*

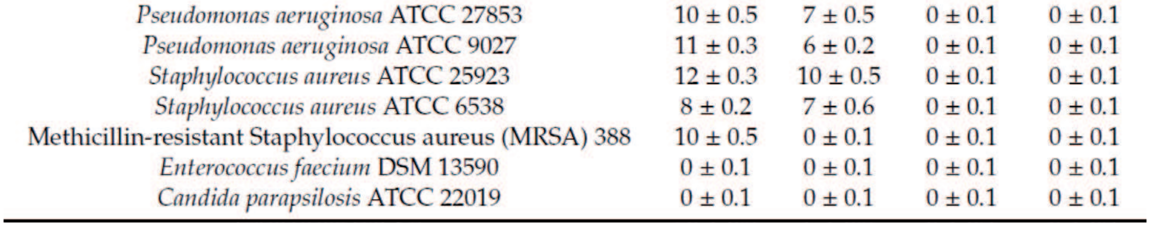
MIC value was 0.039 mg $mL^{-1}$. The antimicrobial properties of materials based on hydroxyapatite coated with essential oils can be explained for HAp-B samples on the major component of hydroxyapatite as the basil essential oil was poorly adsorbed onto the surface of hydroxyapatite nanoparticles.

*Mentha* species are one of the most used medical herbs due to their chemical constituents as menthol and menthone. Peppermint (*Mentha piperita*) essential oils are used as remedies in coughs, colds, mouth sinuses, pain relief and headaches, with properties related to antiviral activity against influenza, herpes and other viruses. The influence of peppermint essential oil (P-EO) on the surface of hydroxyapatite nanoparticles was studied [90] related to their morphological, physicochemical and antimicrobial properties. The results of the qualitative antimicrobial properties of P-EO and HAp-P are presented in **Table 1**.

Antimicrobial qualitative assay revealed that the peppermint had a significant inhibition effect on the microbial growth of the tested microorganisms, with the inhibition diameter ranging from 6 to 22 mm. The solvent DMSO did not affect the growth on solid media of any tested microbial strains. HAp had no inhibitory effect on the growth of the tested microorganisms and the most pronounced inhibition was observed in the case of *E. coli* tested strains in its two forms. The diameter of the inhibition growth area was 22 mm to 20 mm in the case of P-EO and a smaller inhibition zone of 8 mm for HAp-P. On *S. aureus* the inhibitory effect was related notably for P-EO and HAp-P with an inhibition zone in the range 7–8 mm. Essential oil extracted from peppermint contains active constituents that are responsible for eliminating bacterial pathogens, i.e. P-EO and HAp-P presented significant antibacterial activity with constituents acting on the cell membrane causing important morphological damage and destabilization of microbial membrane. Due to the worldwide emergence of *S. aureus* and *E. coli* strains which are resistant to conventional antibiotic therapy, there have been major concerns in public health area that conduced to the necessity of the developing of new antimicrobial compounds. Nano-sized powders of HAp doped with several metal ions that are known to possess antimicrobial properties as silver, zinc or cerium are used together with HAp in combination with essential oils. The effect of plants EOs and plants EOs-HAp combination regarding the antimicrobial activity is presented [91] in **Table 2** related to the diameter of inhibition zone-inhibition growth of tested bacterial strains.

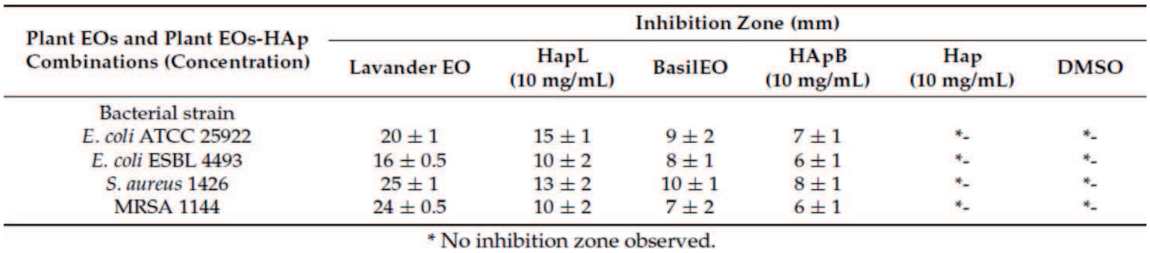
The lavender EO inhibited the growth of all tested bacterial strains, as indicated the formation of inhibition zone ranged from 16 mm (*E. coli* ESBL 4493) to 24 mm (MRSA 1144). The HAp-L material was active against tested bacterial strains compared to HAp. The basil EO and HAp-B samples exhibited a lower inhibitory effect against the tested bacteria. On the other hand, HAp material had no effect on the growth of the selected bacteria.

The possibility of covering hydroxyapatite with different molecules, e.g. essential oils offer a solution to apply in food industry, in the idea that HAp is an essential component of human organism. In this regard, the potential use in medicine e.g. bone reconstruction could help the reducing of postoperative infections after different implants. In the case of hydroxyapatite nanotechnology have opened the gate to different applications in agriculture, food industry, medicine with the final target of improving human health and resistance to a continuous modification of pathogen agents.



| Microbial Strains | P-EO | HAp-P | HAp | DMSO |
|---|---|---|---|---|
| *Escherichia coli* ATCC 25922 | 22 ± 0.2 | 8 ± 0.2 | 0 ± 0.1 | 0 ± 0.1 |
| *Escherichia coli* C5 | 20 ± 0.3 | 7 ± 0.3 | 0 ± 0.1 | 0 ± 0.1 |
| *Pseudomonas aeruginosa* ATCC 27853 | 10 ± 0.5 | 7 ± 0.5 | 0 ± 0.1 | 0 ± 0.1 |
| *Pseudomonas aeruginosa* ATCC 9027 | 11 ± 0.3 | 6 ± 0.2 | 0 ± 0.1 | 0 ± 0.1 |
| *Staphylococcus aureus* ATCC 25923 | 12 ± 0.3 | 10 ± 0.5 | 0 ± 0.1 | 0 ± 0.1 |
| *Staphylococcus aureus* ATCC 6538 | 8 ± 0.2 | 7 ± 0.6 | 0 ± 0.1 | 0 ± 0.1 |
| Methicillin-resistant Staphylococcus aureus (MRSA) 388 | 10 ± 0.5 | 0 ± 0.1 | 0 ± 0.1 | 0 ± 0.1 |
| *Enterococcus faecium* DSM 13590 | 0 ± 0.1 | 0 ± 0.1 | 0 ± 0.1 | 0 ± 0.1 |
| *Candida parapsilosis* ATCC 22019 | 0 ± 0.1 | 0 ± 0.1 | 0 ± 0.1 | 0 ± 0.1 |

**Table 1.**
*The diameters of inhibition growth zones (mm).*



| Plant EOs and Plant EOs-HAp Combinations (Concentration) | Inhibition Zone (mm) | | | | | |
|---|---|---|---|---|---|---|
| | Lavander EO | HapL (10 mg/mL) | BasilEO | HApB (10 mg/mL) | Hap (10 mg/mL) | DMSO |
| Bacterial strain | | | | | | |
| *E. coli* ATCC 25922 | 20 ± 1 | 15 ± 1 | 9 ± 2 | 7 ± 1 | *- | *- |
| *E. coli* ESBL 4493 | 16 ± 0.5 | 10 ± 2 | 8 ± 1 | 6 ± 1 | *- | *- |
| *S. aureus* 1426 | 25 ± 1 | 13 ± 2 | 10 ± 1 | 8 ± 1 | *- | *- |
| MRSA 1144 | 24 ± 0.5 | 10 ± 2 | 7 ± 2 | 6 ± 1 | *- | *- |

* No inhibition zone observed.

**Table 2.**
*Antimicrobial activities of plant EOs, HAp-B and HAp-L against Gram-positive and Gram-negative bacteria.*

## 5. Conclusions

As it was presented, in the last few decades, nanotechnology reveals its benefit usage in different activity fields and in particular in biotechnology and agriculture. Fertilizer compounds are essential for our quality of soil and water for the development of plants in order to increase the crops in order to cover what is needed to sustain the food necessities all over the world. Therefore there exist a necessity to decrease nutrient casualties in fertilization, and to amplify the plant product by the operation of novel uses with assistance of nanotechnology and nanomaterials. This type of fertilization delivers the nutrients on request, control the use of chemical fertilizers that regulate growth and development of plants and raise the activity of target vegetal organism. In this regard have been presented the effects of different nanomaterials and nanoparticles upon selected plants culture as wheat, maize, soybean, etc. taking into account their growth morphological parameters and the nanoparticles influence upon plant metabolism. The present and future use of nanoparticles as micronutrients is affected by different risks related to nanotoxicity of micronutrients, a problem to be solved by an appropriate and safe circuit of nanoparticles in soil, water, plants and at last in human organism. In this regard, it is important to quantify nanomaterials concentration in water, soil and air, where the concentration of relevant nanomaterials is essential to define exposure, a problem to be solved by the modeling of environmental concentrations. Due to the rapid development of manufactured nanomaterials it is important to evaluate their environmental and health impact, and it was stated to assure a safe circuit from micronutrients used for plants crop increasing to the beneficiaries of these plants, i.e. animals and humans. The present work is an approximately extensive presentation of the present status of the application of nanomaterials and nanoparticles in agriculture i.e. in plants fertilization with accent to the plants growth parameters, possible toxic risks and application to the antimicrobial activity.

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