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"NANOEMULSIONS AND NANOTECHNOLOGY – INDUSTRIAL, AGRICULTURAL AND HEALTHCARE APPLICATIONS"

Review Based Book Chapter

NANOTECHNOLOGY IN AGRICULTURE: CARBON NANOTUBES FOR ENHANCED CROP GROWTH, PROTECTION, AND DISEASE MANAGEMENT

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REVIEW BASED BOOK CHAPTER

NANOTECHNOLOGY IN AGRICULTURE: CARBON NANOTUBES FOR ENHANCED CROP GROWTH, PROTECTION, AND DISEASE MANAGEMENT

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Abstract

Nanotechnology has successful application of an inter disciplinary field of science together with physics, chemistry, biology and material science. Nanotechnology can offer preferences to pesticides, such as diminishing lethality, improving the time span of usability, and expanding the solvency of inadequately water-solvent pesticides, all of which could have positive ecological effects. Nanoparticles can be used for plant illness the executives: either as nanoparticles alone working as protectants; or as nanocarriers for bug sprays, fungicides, herbicides, and RNA-interference. The nanotechnology holds the promise of controlled release of agrochemicals and site targeted delivery of numerous macromolecules required for improved plant disease resistance, increased plant growth and efficient nutrient utilization. Effect and uptake efficiency of different nanoparticles on the growth and metabolic functions vary differently among plants. Specifically, application of nanoparticle technology in plant pathology targets specific agricultural problems in pathogen-plant interactions and provide new ways for crop protection. The distinctive mechanical, electronic, and biological properties of the carbon nano-tubes have fascinated broad range of application in the field of agricultural and environment regarding the impact of carbon nanotubes (SWNCTs & MWCNTs) on growth and development of plant. The objective of this review is to evaluate the current literature, including effects of SWNCTs & MWCNTs on plants, enhanced crop yield, fruit development, and potent broad-spectrum antibacterial and antifungal activities toward pathogens. This manuscript also focused on the toxicity and mechanism of antimicrobial activities. The CNTs (SWNCTs & MWCNTs) recently gained interest due to their possible applications in the regulation of plant growth. In addition, efforts need to be focused on better understanding of the underlying mechanism of CNTs-plant interactions.

Keywords

Nanotechnology, Agriculture, Carbon Nanotubes, Crop Growth, Diseases, Protection

1. INTRODUCTION

Nanotechnology is a new rising and attractive field of science, having extensive applications in the fields of medicine, biotechnology, and agriculture due to the astonishing properties of nanoparticles which allow them to execute different functions at cellular and sub-cellular levels [1]. The integration of nanoscience and nanotechnology with other rising innovations and themes of interest like biotechnology, biomedical engineering natural remediation, molecular communication networks, quantum processing, and information-driven plans of new materials informatics have been adopted in the field of nanoscience and nanotechnology in the present year [2]. Phyto nanotechnology has rising attention in the field of agriculture due to its application of nanomaterial with target-specific delivery in plants at the cellular level resulting in boosting of plant function as well as resistance to environmental pollution. The application of nanosized fertilizer, insecticides, and pesticides has improved the ability of plants to uptake the minerals efficiently in good amounts, increasing tolerance against insecticides and pesticides [3].

2. Molecular Nanotechnology

Complex structures and atomic specifications using mechano-synthesis have been created by molecular nanotechnology. This technology is based on different nanoscale materials supported by Richard Feynman's vision of miniature factories exploiting nanomachines to create advanced products nanomachines, this advanced variety of engineering or molecular manufacturing would create the use of positionally controlled mechano-synthesis guided by molecular machine systems. The “top-down” and “bottom-up” are the two methods for the synthesis of carbon material. The top-down method is based on the large carbon materials fragmentation by oxidation of acids, discharge of arc, laser ablation, and exfoliation either by ultrasonic/electrochemical method or by hydrothermal/solvothermal method. While the bottom-up method is based on the carbonization of material by hydrothermal, microwave, and thermal lysis methods. The Raman Spectroscopy technique is used for the analysis of changes in nano-tube properties as well as procedures and conditions applied during their synthesis. This technique provides accurate and complete information about electronic and structural characterization. Atomic force microscopy (AFM) is a relatively low-cost technique for the atomic resolution of a three-dimensional sample in a short time and provides detailed information of the length and diameter of nanotube bundle [4].

3. Nanoparticles

Nanoparticles are considered as effective treatment-delivery systems in plants due to their penetration power into the plant parts with dimensions ranging from 1-100 nm. Nanoparticles have been engineered by material scientists for use as a protectant due to unique characteristics, like shape, pore size, and surface properties, or as a pesticide for precise and targeted delivery via adsorption, encapsulation, and conjugation processes. Through two different mechanisms, nanoparticles protect plants: (a) crops are providing themselves protection by nanoparticles, (b) for existing pesticides or other actives, such as double-stranded RNA (dsRNA), nanoparticles act as carriers that soak onto seeds, foliar tissue, or roots or spray. Silicon Dioxide plays an important role in the germination of seeds, root elongation, and shoot development. Nano-SiO2 with lower concentrations improved seed germination of tomatoes and in squash due to NaCl stress, the antioxidant system is activated by nano-SiO2. Nano-SiO2 is also activated in salinity stress by increasing the assembly of proline, content of nutrients, antioxidant enzymes activity, and free amino acids, and in turn improving leaf dry weight, tolerance of plants to abiotic stress and chlorophyll content [5]. Iron oxide nanoparticles have been used in different biomedical fields involving cell labeling, cancer therapy, drug delivery, hyperthermia, targeting and immunoassays, tissue repair, detoxification of biological fluids, magnetic resonance imaging, and magnetically responsive drug delivery therapy application [6]. Zinc oxide nanoparticles enhance plant development and growth. Somatic embryogenesis, regeneration of plantlets shooting, and biotic stress are controlled by the synthesis of proline and superoxide dismutase, catalase, and peroxidase activity with ZnO supplemented with MS media promoted [7]. Zinc and titanium nanoparticles are applied in the field of biomedical, ultraviolet (UV)-blocking agents, cosmetic, and various cutting-edge processing [8]. Copper and palladium nanoparticles used in batteries, polymers, plastics plasmonic waveguides, and optical limiting devices, have antimicrobial activity and several biomolecules like metabolites, nucleic acids, peptides, lipids, and fatty acids have been investigated by copper and palladium nanoparticles [9]. Gold nanoparticle's miscellaneous uses of metal nanoparticles have been investigated in biomedical, farming, natural, and environmental field. Gold nanoparticles have been exploited for tumor identification, angiogenesis, hereditary illness and disorders, photothermal treatment, and photoimaging. Limited studies have shown the contact of gold nanoparticles (AuNPs) with plants. Several researchers found that toxicity is induced in plants by inhibiting aquaporin function, a group of proteins that help in the transportation of a wide range of molecules including water, improve seed germination, the number of leaves, plant height, leaf area, chlorophyll and sugar content that lead to the better crop yield, significant role on antioxidant system in *Arabidopsis thaliana* and altered levels of microRNAs expression that regulates various morphological, physiological, and metabolic processes in plants [10]. On silver nanoparticles (AgNPs), several studies have been conducted to explain the role of the effects on plant growth, microbial and animal cells, root elongation, seed germination, and seedling induces the synthesis of protein and carbohydrate and decreased total phenol contents and catalase and peroxidase activities [11]. Silver nanoparticles have antimicrobial activities, anticancer, anti-inflammatory, and wound treatment applications [12]. Researchers have focused on the influence of titanium dioxide nanoparticles (TiO_2 NPs) on bacteria, mice, plankton, algae, fish, and rats but research focusing on the realization of the effects of TiO_2 NPs also enhances seed germination and stimulated radicle and plumule growth of canola seedlings, light absorbance, enzymes activity involved in nitrogen metabolism and acts as a photocatalyst and induces an oxidation-reduction reaction [13].

4. Nanomaterials

Nanomaterials are materials having structural components that are less than one micrometer (~0.2 nm) [14] and are made of metals, polymers, natural materials, and composites and incorporate nanofilms, nanoparticles, nanocrystals, nanorods, nanotubes, nanoclusters, nanofibers, and nanowires via a top-down and top-up nanofabrication advancements and so on). Along these lines, nanomaterials with such fantastic physiochemical properties (i.e., mechanical, electrical, optical, reactant, attractive properties) have been broadly researched in a wide scope of biomedical applications, specifically regenerative medication [15].

5. Carbon nanomaterial

Carbon nanomaterials such as graphene, graphene oxide, carbon nanotubes, and carbon nanofibers, demonstrate a noteworthy potential as desulfurization adsorbents [16]. Carbon-based nanomaterials have developed as a promising platform in many fields of science because of their distinctive mechanical, electronic, and organic properties. Fullerene, carbon nanotubes (CNTs), graphene and diamond-like carbon which are different forms of carbon nanostructures have been exhibited to have powerful antibacterial properties against many pathogens [17].

5.1. Carbon nanotubes (CNTs)

Sumio Iijima in 1991 discovered carbon nanotubes [18]. Carbon-based nanomaterials are mostly used as nanoparticles. Among different nanomaterials, carbon nanostructures (CNSs) and their subsidiaries increased huge consideration due to their remarkable properties and potential to apply in an immense number of existing and developing applications. The structure of pure carbon nanotubes (CNT) can be imagined as a solitary sheet of graphite moved to form a consistent chamber. Carbon nanotubes are significant nonmaterial due to their unique properties. Indeed, carbon can cling to itself in kind designs to shape incredibly low-measurement structures, including fullerenes (0D), nanotubes (1D), and graphene sheets (2D) furthermore, precious diamond-like carbon (3D) as shown in Figure 1. As a rule, CNSs are perceived for their astounding electrical conductivity, incomparable mechanical quality, high thermal conductivity, phenomenally high surface area, exceptional photoluminescent properties, high transparency, and basic dependability [19]. The allotropes of carbon having a length-to-diameter ratio more noteworthy than 1,000,000 belong to carbon nanotubes that have numerous applications in the field of nanotechnology. The fullerenes with a diameter < 100 nm have three-dimension structures, carbon nanotubes with a diameter < 100 nm have two-dimension structures, graphene and other associated materials with CNTs have one-dimension structures with diameter less than 100 nm [20].

Carbon Nanomaterials

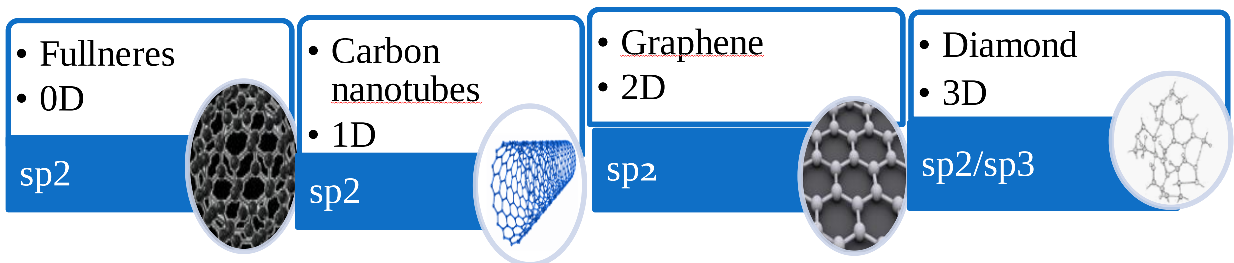

Figure 1. Different type of carbon nanostructures

Several carbon-based structures found numerous decades before are contemplated and associated with technological devices these days.

5.2. Nano Diamond (ND)

Nano diamond (ND) structure dating from the 1960s and is a nanosized (5–100 nm) carbon structure basically framed by sp3 hybridization [21]. Their optical and electronic qualities are expected to be dopants present in the structure, and the amazing surface action is relegated to basic imperfections and unsaturated compounds emerging from carbon molecules [22].

5.3. Fullerene (FLN)

The revelation of fullerene (FLN) happened in 1985 by the work of Meirzadeh et al. These are a sub-atomic allotrope of carbon having a three-dimensional shut enclosure (Cn) made of five six-membered rings with 12 pentagons and an alternate number of hexagons, contingent upon the FLN size [23].

5.4. Graphene (GPN)

The graphene (GPN) was the principal found two-dimensional nuclear gem framed by a solitary molecule layer of carbon particles organized in a honeycomb cross-section structure. Figure 1 demonstrates the different types of structures [24].

6. Carbon nanotube (CNT) types

Another carbon-based structure is a carbon nanotube (CNT) that has a place within the FLN family demonstrating a semi-one-dimensional structure (single or multiwalled CNTs). The length and diameter of carbon nanotubes differ considerably depending on the man-made procedure adopted, usually, length is tens of microns reliant on the production time while nanocarbon tubes are of smaller and longer sizes [25].

Table 1: Properties of CNTs [25]

Carbon nano tubes	Dimension	Hybridization	Specific surfaces Area m^2 g^{-1}	Thermal conductivity W $m^{-1}K^{-1}$	Electrical conductivity S cm^2	Tendency	Hardness
CNTS SCNTs& MCNTs	1 Dimensional	SP^2	~1300	3500	Structure dependent	Flexible, elastic	high

CNTs become a prominent tool over the other nanocarriers due to their biocompatibility nature, with no immunogenicity, change in size easily, better stability, and elevated drug loading potential. CNTs can be modified on an individual basis to produce a number of functional groups on internal and external surfaces of CNTs for conjugation with targeting ligands as well as drug molecules. CNTs having the hexagon shape due to sp^2 hybrid orbital and in-plane σ bonding and out-of-plane π bonding give pentagons and Pentagon structure. Defect-free nanotubes have tube-shaped structures resulting in σ-π rehybridization with a diameter as small as 0.4 nm. Defective nanotubes have pentagons and heptagon structures. The physical properties of nanotubes are affected by the orientation and diameter of the nanotubes [26]. Defect-free nanotubes either semiconducting or metallic by quantized conductance are formed due to electron movement in the tube perimeter while localized structures are produced by the pentagons and heptagons. Optical and optoelectronic properties are involved in the optical applications with a wavelength ranging possibly from 300 to 3000 nm. Magnetic and electromagnetic properties of CNTs give phenomena such as quantum oscillation and metal-insulator transition by the electron orbits circulating around a nanotube [27].

6.1. Single-walled and multi-walled carbon nanotubes

Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are two classes of CNT. SWCNTs comprises a single layer of graphene with a diameter in the range of 0.4-2 nm and a catalyst is needed for its production. SWCNTs can easily be twisted have poor purity and don't have any complex structure. The SWCNTs has arm chair, zigzag, chiral, or helical arrangements. Zigzag has a hexagon structure as one moves circumferentially around the body of the tubule. Chiral tubes may twist in either direction. The armchair is the two conformers of Cyclohexane and hexagon of carbon atoms. CNTs are obvious from carbon filaments, which are strands of layered graphite sheets instead of being single carbon atoms. The sizes of the metal NP from which they are developed control the diameter of single-walled nanocarbon tubes ranging between ~ 0.7 to 3 nm. Both SWCNTs and MWCNTs are packed together in ropes as a result of appealing van der Waals forces equivalent to forces that bind sheets of sheets of graphite [28].

6.2 Multiwalled carbon nanotubes (MWCNTs)

Multiwalled carbon nanotubes (MWCNTs) with a diameter ranging from 2-100 nm are bigger and comprise many single-walled tubes placed one inside the other having good purity with complex structure. A catalyst is necessary for its production and cannot be twisted easily as given in Table 2 [24, 29]. MWCNT has Cylindrical, polygonal, and spiral ganglion of graphene arrangements (Figure 2).

Table 2: Comparison between SWNCTs & MWCNTs

Single-walled carbon nanotubes	**Multi-walled carbon nanotubes**
Graphene Single layer diameter in the range of 0.4-2 nm	Graphene multi-layer diameter ranges from 2-100 nm
Catalyst required for synthesis	No Catalyst is required for synthesis
Have poor purity	Have high purity
Simple structure	Complex structure
Easily twisted	Not easily twisted
Arm chair, zigzag, chiral, or helical arrangements	Cylindrical, polygonal, and spiral ganglion of graphene arrangement

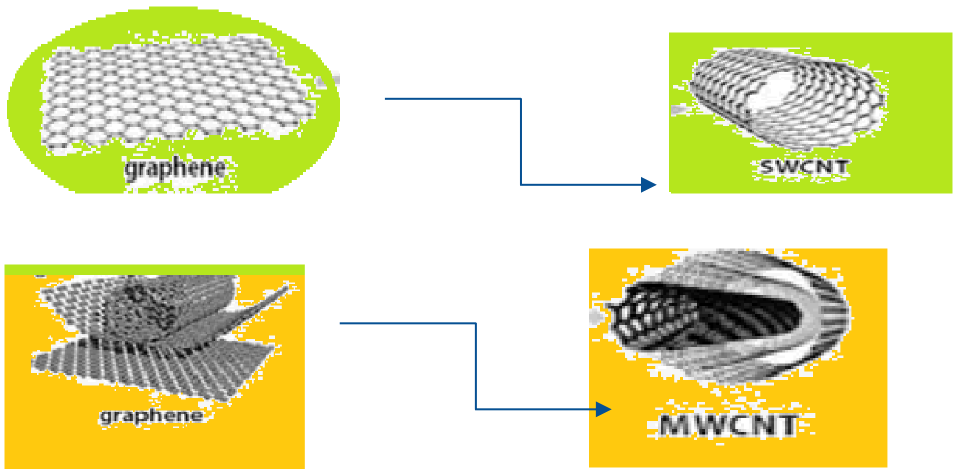

Figure 2: Structure of single walled carbon nanotubes and multi walled

7. Translocation & penetration of nanoparticles into plants

Nanoparticle entry was hindered by plant cell walls acting as a barrier for access of any peripheral mediator into plant cells. Nanoparticles with diameters less than the pore diameter (ranging from 5 to 20nm) permitted by a cell wall and finally to the plasma membrane, by using engineered nanoparticles cell wall pores size can be increased. A cavity-like structure is formed around the nanoparticles by the plasma membrane leading to the internalization occurring during endocytosis and embedded transport carrier proteins or ion channels can pass through the membrane. Different cytoplasmic organelles bind with nanoparticles and interfere with the metabolic processes at that site, in the cytoplasm. Nanoparticles enter through the stomatal openings or the bases of trichomes and then translocated to many tissues after application on the leaf. Nanoparticles may be translocated into the whole plant through short-distance transport (intercellular spaces) as well as through long-distance transport (vascular tissue). Xylem plays an important role in the translocation of NPs into plants. NPs after absorption via root enter into cell walls and plasma membranes of epidermal layers and then penetrate the vascular tissues from where; it is moved to the leaves. The cell wall is composed of polysaccharide fiber, and acts as a natural sieve, through the pores; the small-sized NPs can pass while permission is not provided by plant cells to larger NPs, thus sieved out [30]. CNTs can be up taken by cells via penetration into the cell membrane; CNTs after passing through a range of cellular barriers to be found inside cell endosomes and lysosomes and even enter the nucleus. Endocytosis-phagocytosis pathways are utilized by the cell-internalization mechanisms for CNTs after the formation of a vesicle of endosomes (Endocytosis) while Phagocytosis engulfing larger particles may be enhanced by functionalization through conjugation with phosphor-lipids [31]. A lysosomal enzyme-Myeloperoxidase (MPO) an abundant enzyme of neutrophils granulocytes found in white blood cells is used to break down the Carbon nanotubes inside the body. MPO is also used to damaging bacteria [32].

8. Nanotoxicology

Nanotoxicology is the branch of science that deals with toxicity of nanoparticles on plants, humans, microorganisms, and the environment and it mainly depends on the applied dose (concentration) of the nanomaterials. Besides the concentration of nanoparticles, other parameters that determine the poisonousness level of the nanoparticles are the size, number, surface area, reform, and accumulation of NP with other materials (Figure 3). The utilization of nanoparticles in the field of production, waste, and water management may also cause the release of nanoparticles into the environment, which may pollute the environment. There is a deficiency of information about the piousness effect of the nanoparticles on the biological organization (humans, insects, animals' fungi, etc.), so it becomes difficult to know that NP can cause toxicity when applied to the living system. The physiochemical properties like surface charge, size distribution, and morphology of nanoparticles can produce different results on modification individually in humans, animals as well as in plants. The method of synthesis of NP, time duration over the plant, mode of application on the plants, and interaction with the plant are the factors that are responsible for the toxicity of the nanoparticles. The exposure of NP on plants may include injection method on plant tissue, spray on plant leaves or other parts, introduction into plant pollens and seeds, and application of NP directly into soil or using NP as a suspension (Figure 4) [33].

Characteristic of Nanoparticles

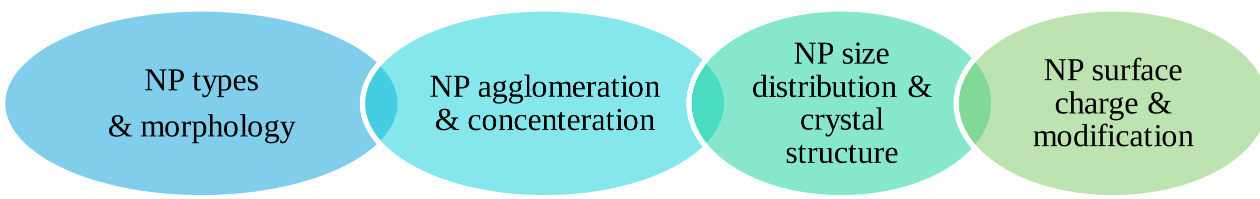

Figure 3: Fundamental properties of the nanomaterials

Exposure of nanoparticles on the plants

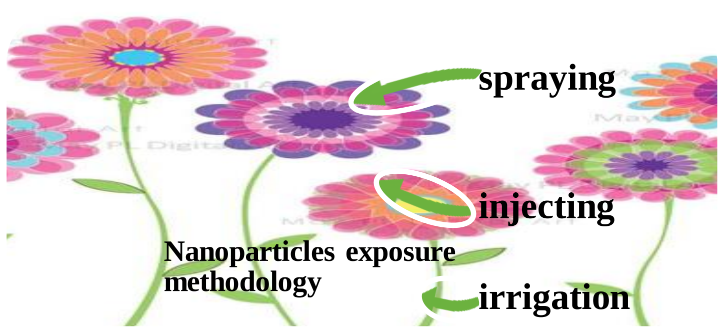

Figure 4: Different ways of application of NP on the plants

Many studies have reported about the phytotoxicity of the nanoparticles which may be caused by to accumulation of the metals or ions released from NP, dissolved into the soil, and bio-transformed into plants may result in phytotoxicity. The regulation of the gene and oxidative process of plants may be affected by the liberation of ions from NP after interaction with plant cell metabolism. Clogging and damage in roots or inside the tissue of the plant will result from the bioaccumulation of NP. The toxicity in plants may depend on plant species, plant growing media (pH & salinity, etc), and plant growing environment (soil vs agar medium) and may change the physical and chemical characteristics of NP resulting in phytotoxicity. Environmental stress may affect the rate of photosynthesis of plants and lead to the production of ROS which results in DNA damage and oxidation of proteins & lipids in plants [34].

The series of biochemical reactions taking place include lipid peroxidation (LPO), depletion of reduced glutathione (GSH), DNA damage, and mitochondrial damage which can ultimately result in cell damage by the production of ROS (reactive oxygen species) leading to the death of the cell. The production of excess reactive oxygen species (ROS) provoked by NPs is based on the mechanism underlying the toxicity of NPs, resulting in oxidative stress [35, 36]. There are four types of ROS; singlet oxygen ($^1O_2$), hydrogen peroxide (H_2O_2), superoxide ($O_2^{\bullet -}$), and hydroxyl radical ($HO^{\bullet}$) which are produced after the interaction of plants with the NPs. The ROS is the result of normal metabolic pathways in organelles such as mitochondrion, peroxisomes, and chloroplasts in normal conditions while severe oxidative damage to plant biomolecules through electron transfer is induced by ROS under stress conditions [37]. Many nanoparticles are observed to be genotoxic which after a threshold concentration causes chromosome aberrations, DNA damage, and ultimately cell death. The exact mechanism by which nanoparticles cause DNA damage is still unknown but it has been proposed that oxidative stress plays a significant role in nanotoxicity.

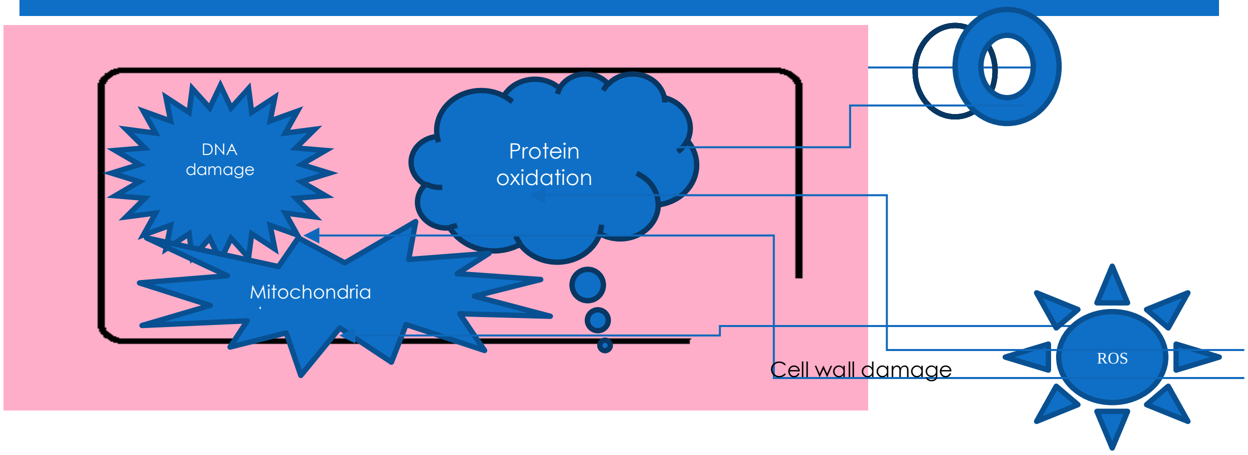

Figure 5: This figure describing those ions released from NPs interacts with protein, DNA and Mitochondria, resulting in the generation of ROS which will damage the cell wall, proteins, DNA, and Mitochondria of the cell

Mitochondria, is a cellular compartment that is involved in many cellular processes i.e., cellular differentiation, cell growth, signaling, ATP generation and supply, and apoptosis. After interaction with NP, mitochondria are declared to be a very important indicator of toxicity of exogenous materials. Moreover, the intracellular ROS buildup is associated with mitochondrial damage; this imbalance of ROS can disrupt mitochondria structurally. Excess ROS buildup can lead to respiratory chain disruption, DNA damage, alteration in the permeability of mitochondrial membrane, and arrest of the cell cycle (Figure 5). In addition, protein families such as Bcl2 and CytC are involved in apoptosis of the cell induced by mitochondria [38].

The detrimental effect of nanoparticles is because of the high surface area and intrinsic toxicity of the surface. The toxicity of nano-sized particles depends on physiological properties, retention time with the cellular contact [39]. It is important to find out the toxicity of nanoparticles because of their increased use of nanoparticles and liberation in the surroundings. The toxicity of CNTs in different organs of the body depends on the concentration, constituents, structure, size, and functionalization of CNTs. Due to excess utilization of carbon nanotubes, they exert toxic effects on different body parts of the human lungs, liver, dermal and subcutaneous, central nervous system, kidney, cardiovascular, spleen, and eye [40].

The way of liberation of CNTs into the lungs is by directly inhaling the fine NPs and causing respiratory toxicity. Due to the physical characteristics and physiochemical properties (particle size, functionalization, and dispersion) of MWCNTs and SWCNTs, they exert toxic effects on the lungs by accumulation in alveolar and intratracheal tissue walls, resulting in the tumor formation in the inner walls of respiratory tracts by accumulating of SWCNT & MWCNTs as clumps in lungs [41]. Various metabolic pathways are carried out by the liver, SWCNTs increase enzyme levels, and enhance the proliferation as well as inflammation in the liver while the MWCNTs induce the coagulation of blood, inflammation, and affect the kupffer cells which are macrophage cells as shown in Figure 6.

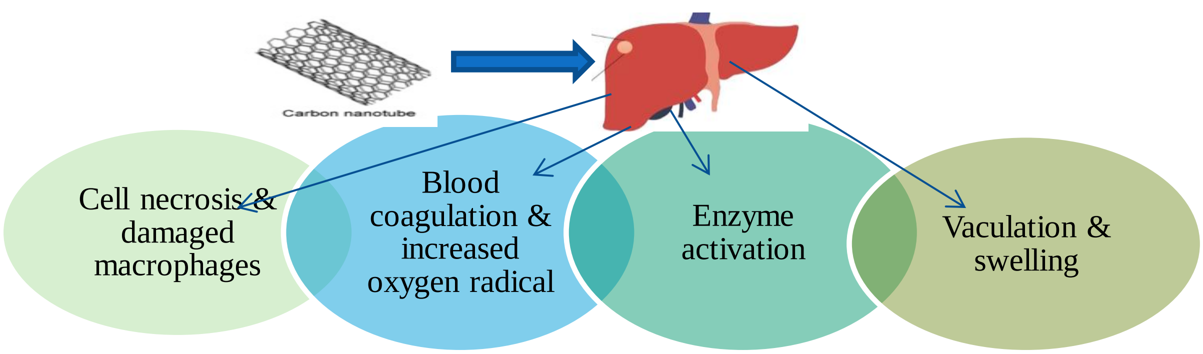

Figure 6: Toxicity effect of CNTs on the liver

Skin is damaged by CNTs due to direct interaction Different Researchers have conducted *in vitro* and *in vivo* studies, of skin tissues by well-engineered artificial methods and mice skin to lessons the toxic effects of SWCNT and revealed that SWCNTs for the dermal tissue have toxic effects and produced oxidative stress and inflammation in skin cell. Keratinocytes interact with the CNTs resulting in the induction of genotoxicity, and inflammation and also reducing the viability of cells as shown in Figure 7 [42].

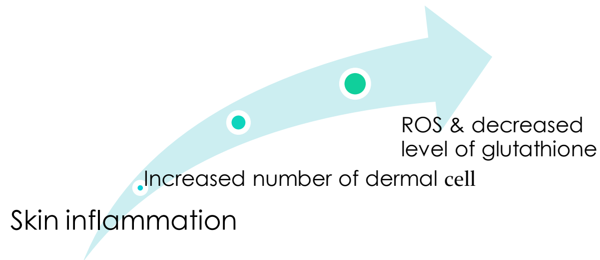

Figure 7: Representation of effects of CNTs on the skin

The toxic effect of CNTs on brain cells results in chemicals released from the microglia and astrocytes which in turn enhances the oxidative stress in the brain through the mechanism of endocytosis/pinocytosis (Figure 8). CNS has been altogether investigated by researchers due to its exceptional connection with the neurons and sensory system.

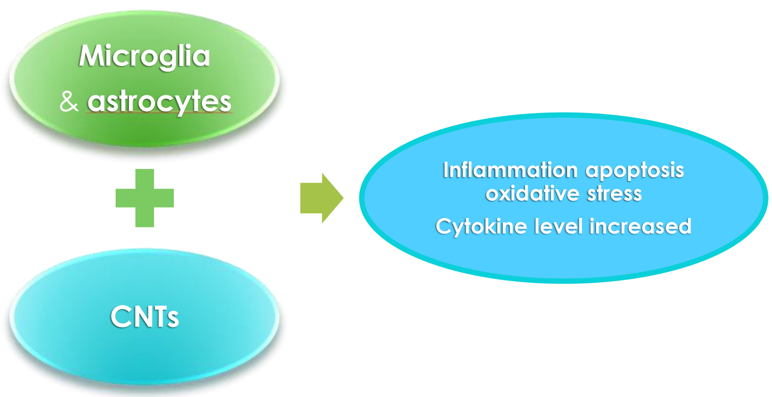

Figure 8: Neurotoxicity interaction of CNTs with brain

The organs engaged with the discharge of poisons (kidney) are at a higher danger of CNTs getting gathered, reports recommend kidney is in danger for CNT aggregation and may prompt renal lethality as given below in Figure 9 [43].

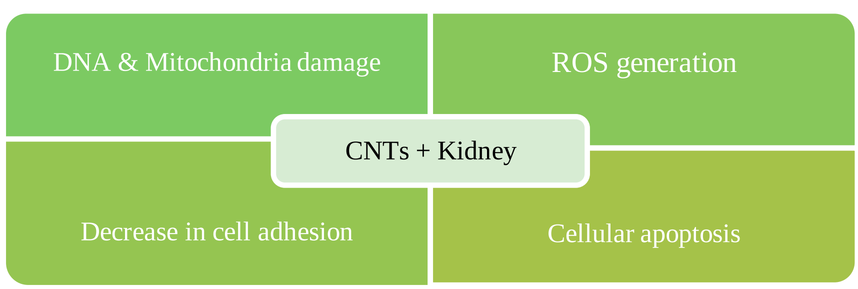

Figure 9: Toxicity effects of carbon nanotubes on kidney

Nanoparticles showed inflammation in the mouse spleen. Cardiovascular toxicity is caused because of the association of CNTs with the heart muscle cells. This association instigates harm to the heart and causes cell multiplication, oxidative stress, inflammation, muscle harm, and obstacle in the blood stream just as vascular atherosclerosis. The interaction of the eye with CNTs depends on exposure time. Experiments were conducted and their results showed that SWCNTs have no toxic effects but MWCNTs have soft irritation to the eyes. The carbon nanotubes are examined in different in vitro and in vivo studies to lessen the lethal effects of CNTs as well as to achieve target-based precise effect [44].

9. Application of the CNTs (SWCNTs & MWCNTs)

Carbon nanotubes have exceptional properties like thermal, electrical, optical, and mechanical and may be used in the environment for production, utilization, reuse, demolition, and transportation in plant systems and applied in plant science for changing the plant production system, detoxification of chemicals by using as pesticides and fertilizer and act as plant growth regulator as well as disease resistance (Figure 10) [45].

Figure 10: Application of carbon nanotube in different fields

9.1. Agricultural application

Inexpensive nanotech applications are used by nanoscience scientists for improvement in seed germination, plant growth, development, and acclimation to environments. The seed germination (sensitive phase) is influenced by the environmental factors, genetic traits, moisture, and fertility of soil [46]. The mechanisms of stimulating germination by nanomaterials are still unclear. The capacity of absorption and utilization of water is improved after entering of nanomaterials into the seed coat of the plant, resulting in an enzymatic system of the plant is activated which in turn enhances the germination and seedling growth [47]. The Nano formulation or nanoencapsulation of pesticides containing the active ingredient of pesticides as well as engineered nano-particles has updated the plant protection sector. The chemical composition of nanomaterial produces different effects on the growth of plants and varies from plant to plant. The carbon nanotubes act as a fertilizer and enhance the plant growth of bioenergy crops (sorghum and switch grass which increases the crop production, used as plant defense by acting as a pesticide [48] and herbicide [49] and care of farming by the optimization of agricultural procedures [50]. The carbon nano-material also improved the fruit quality, nutrient uptake, plant growth, and germination of [51] carbon nanotubes are used as a macronutrient and micronutrient carrier fertilizer [52].

9.2. Biomedical application

The carbon nanotube's biomedical application includes neuron regeneration, bone regeneration, gene delivery [44] protein, and targeted drug delivery as a biosensor along with their imaging [53]. Multi-walled nanotubes used for the absorption of antibiotic [54] for the removal of herbicides from the aqueous solution [55] as well for the removal of nitrogen and phosphorus from wastewater [56]. Malfunctioning, damaged tissues in the body can be replaced and repaired by using a rapidly growing tissue engineering approach. Carbon nanomaterial-based frameworks are a key model, and show noteworthy capacity to influence bone tissue recovery, effective cell multiplication, and osteogenic separation. Essentially, scaffolds are laid out for the development, proliferation, recovery, adhesion, and separation procedures of bone stem cells. The beating heart of tissue engineering is known as scaffold. The CNTs have vast applications in the field of tissue engineering even for direct use as scaffolds, biosensors for enhancing the electron transfer in NADH and hydrogen peroxide reaction [57] drug delivery for doxorubicin, cisplatin, genes including plasmid DNA, small-interfering RNA, oligonucleotides and RNA/DNA aptamers, proteins and cancer cell death [58] Carbon nanotubes with distinctive morphology and properties of surface regarded as well-known nanomaterial with the most important functions in the field of drug delivery, tissue, and plant technology [59].

9.3. Senor application

The assurance of sustainable development of crop and soil health becomes possible with the application of nano-sensors in the agriculture field. The nano-sensors are used to examine crop growth and soil, deficiency of nutrients, toxicity, diseases caused by pathogens, and the release of agrochemicals to the environment to improve the safety of plants as well as the safety of the environment. Under in vivo conditions augmenting photon absorption of SWNTs into plants enhances the electron transfer rate of light-adapted chloroplasts by 49% as a result ROS production is also inhibited and plant yield as well as photosynthetic efficiency is improved. High stability and long lifetime are displayed by MWCNT-ionic liquids/ tyrosinase which are enzyme-based biosensors i.e., glucose detection is based on enzyme biosensors determine the concentration of blood glucose level in the human body [60]. Non-enzymatic glucose biosensor is formed by the deposition of gold nanostructures onto the CNT electrode showing significant performance in Non-enzymatic glucose biosensors [61]. An enzyme aflatoxin-oxidases adsorbed onto chitosan-SWCNTs modified gold electrode used for the detection of sterigmatocystin. In medical diagnostics, forensic science, agriculture, or environmental clean-up efforts, DNA biosensors are used. In clinical medicine, immunosensors formed by amplified electrochemical are used for extremely sensitive recognition of cancer biomarkers in serum and tissue lysates based on SWCNT immobilized on the multi-label secondary antibody-nanotube forming bioconjugates. Ultra-sensitive immunosensors have been applied for the discovery of pesticides such as atrazine. The application of the biosensors involves intensive care of food traceability, quality, protection, and nutritious value [62] finding a variety of chemical and biological toxic mediators for use in pacemakers which are artificial implantable devices [63].

9.4. Electronic Applications

Increased speed and efficiency of electronic devices can be achieved now by elevated integration density. CNTs are seen to have amazing roles in electronics field too. For the development of current devices, CNTs electronics provide capacity and in energy storage. Properties of CNTs such as great mechanical power, good characteristic ratio, sharp tip, chemical constancy make them suitable to be used for gas discharge tubes, X-rays, field emission electron sources and flat panel displays. Furthermore, CNTs emitters are comparably better than thermo-ionic emitters as these doesn't need pre-heating for the electron emission from cathode surface and they display steady operation and are better energy savers as well [45].

10. Role of CNTs (SWNTs & MWNTs) as an antimicrobial agent

Carbon-based nanomaterials exhibit unique characteristics related to biological, sensing, drug delivery, and strong antibacterial activity towards killing the pathogen microorganism. There are two mechanisms (physical & chemical) involved in the bactericidal action of carbon nanostructures. Physically mechanism based on the cell wall & cell membrane destruction of pathogen. The chemical mechanism is based on the production of oxidative stress (ROS) due to electrons released from the outer surface of the pathogen that leads to pathogen death [64]. CNTs, among all carbon nanomaterials particularly SWNTs show greater antimicrobial activity. Saleemi et al. principally studied the antimicrobial effect of SWNTs and MWNT. SWNTs have higher antimicrobial activity than MWNTs, due to their smaller size which contributes to membrane disruption and provides a larger surface area [65]. The antimicrobial effectiveness of CNTs may be affected by the dissolving ability of CNTs in polar and nonpolar solvents while the interaction of CNTs with target pathogens should be direct [66]. The bactericidal action of CNTs may be improved by purification of CNTs and functionalization [67]. Nanomaterials possess broad-spectrum antimicrobial activity against gram + and gram – bacteria while this activity is different from nano-particle nano-particles to other nanoparticles due the to the mechanism involved of microbes. The membrane of the bacteria is disrupted by the structure of the nanoparticles and ROS-independent oxidative stress is caused when metal ions of the bacteria are released from the nanoparticle surface as shown in the figure. The antibacterial activity is affected by variables like the size of a particle, form, metal potential, and low surface to volume enhance the greater interaction of microbes with the nanoparticles as a result of reactive oxygen species being produced. The powerful antimicrobial activity is shown by the single and multi-walled carbon nanotubes and it is dependent on length, diameter, catalyst, electronic surface, functional group present on the surface, and coating factors. The reactive oxygen species, ROS, are produced due to the combination of carbon nanotube particles with the microbes and cause toxicity. The numerous factors like length, type of functionalization, concentration, time-span of exposure, the approach of exposure, the concentration of the solubilizing agent, and the surfactant are associated with the toxicity of the carbon nanotubes on plants that have been studied in vivo and in vitro experiment [68].

The potent bactericidal properties against pathogenic microbes have been shown by the carbon-based nanomaterials which depend on the composition and surface variation, the nature of target microbes, and the surroundings in which CNSs interact with the cell resulting in the inactivation of the microbes. The antimicrobial activity of single-walled, double, and multi-walled against Gram-positive *Staphylococcus aureus*, Gram-negative *Pseudomonas aeruginosa* and the opportunistic fungus *Candida albicans* was investigated. Results show CNTs have colony-forming unit capacity and generation of ROS in all the microbial species [69]. CNTs have been successfully engaged as an antibacterial agent as explained in having potent antibacterial activity against *E.coli, S. epidermidis, B. subtilis, S. aureus,* and *S. typhimuriu,* microorganism while the MWCNT have minor antibacterial activity against *E.coli, S. epidermidis, B. subtilis, S. aureus* and *S. typhimuriu.* The positive cationic structure of CNTs is increased due to the side amino group, which also increases the interaction between the CNTs and the negative charge on microbes. The hydroxyl group and carboxyl group on SWCNTs involved strong antimicrobial activity against gram (+) and gram (-) bacteria while MWCNTs do not show any antibacterial activity as shown in the below table [70, 71].

Another study conducted by the Liu, S represented that SWCNTS with diameter d= 0.83 nm have a strong antimicrobial effect against gram-positive and gram-negative bacteria in dispersed form as compared to aggregation form. SWCNTS in solution form are known as "nano dart" and destroys the cell membrane which results in oxidative stress and leads to the death of the cell [66, 72]. The bacterial colonies, and biofilm formation can be minimized by the coating the antibacterial agents with the polymer. Electrospun SWCNTs- PSf (weight loadings (0.1, 0.5, and 1.0 wt %) having diameter 0.8nm were introduced into electrospun polysulfone due to its excellent thermal & chemical stability against E. coli. They showed that antibacterial activity increases with increasing incorporation of SWCNTs 18% with 0.1 weight % of SWNTs and 76% for 1.0 weight % of SWNTs into electrospun polysulfone mat [73]. The charge on the functional group of the carbon nanotubes does not contributes in the antibacterial activity rather it depends on the buffer and concentration of CNTs. Strong antibacterial activity achieved by the modification of surface group of SWCNT with –OH &-COOH with ~7 log against all targeted bacterial cell, This activity is also dependent on concentration and time of interaction with pathogens as reported in previous reports [74].

The antibacterial and antifouling properties of silver nanoparticles (Ag NPs) and carboxylated MWCNTs are due to excellent chemical, thermal, and mechanical stability and hydrophilicity may be used as an additive to increase polymer membrane performance. Silver nano-particles are doped on MWCNT/poly-phenyl sulfone (PPSU) membranes of nanocomposite which have strong activity against *Escherichia coli* and *Staphylococcus aureus* bacteria. MWCNT/PPSU nanocomposite membrane may be used for the removal of ions as well as bacteria. Ag-MWCNT/PPSU membrane plate count analysis shows that pristine PPSU membranes have more colonies while Ag-MWCNT/PPSU nanocomposite membranes lower number of colonies [75]. The *E. coli* cells rigorously spoiled, and some were abnormal and irregular in shapes, due to direct interaction with the Ag-MWCNTs, the cell wall and cell membrane were widely broken. ROS reactive oxygen species (superoxide anion, hydroxyl radical, and singlet oxygen) are produced by Ag NPs which increases the antibacterial activity of Ag-MWCNT/PPSU membranes and breaks the cell membrane, Biomolecules such proteins, DNA, and intracellular systems such as the respiratory system. Electrostatic adsorption of bacteria membrane due to positive charges of the functional groups on MWCNTs surface increases the antibacterial activity of MWCNTs against *E. coli, S. Typhimurium and S. aureus* [76]. The MWCNTs coated Ag NPs combined with polyethersulfone (PES) have strong antibacterial activity against disease-causing bacteria and non-disease-causing bacteria like *Lactobacillus acidophilus*, *Bifidobacterium adolescentis, E. coli, Enterococcus faecalis, S. aureus, Salmonella typhimurium* [77]. *Aspergillus fumigatus* is type of a fungus which is responsible for lung diseases, leading to life-threatening pulmonary infections tuberculosis while *Aspergillus ochraceus* produces a mycotoxin (Ochratoxin A (OTA)) in the food mostly in grain. The silver and zinc oxide nanoparticles, with pristine MWCNTs) by mild acid treatment, using nitric acid shows high antifungal activity on dry weight estimation and inhibiting the growth of both *Aspergillus* species [78]. MWCNTs with different surface groups (OH-, COOH-, and NH2-) displayed strong antifungal activities against fungi *Fusarium graminearum* with inhibition of spore elongation and germinations compared to pristine MWCNTs. After interaction of 500 µg mL^{-1} MWCNTs-COOH, MWCNTs-OH, and MWCNTs-NH2 separately with the fungi, its spore length reduces almost a half from 54.5 µm to 28.3, 27.4, and 29.5 µm showing that surface-modified MWCNTs, decreases the spore germination and the germination rate was only about 18.2%, three times lower than pristine MWCNTs [79, 80].

11. Role of MWCNTs in plants

Different studies have been conducted to evaluate the effect of the MWCNTs on the plants' seed germination, MWCNTs enhance the germination rate of the seeds of a variety of crops like tomato, corn, soybean, barley, wheat, maize, peanut, and garlic [81]. The application of MWCNTs with 100 *µg*/mL concentration on the crops of *Hordeum vulgare*, Glycine max,*Zea* mays has a positive effect on the germination and seedling of the plants. Similarly, *Allium sativum, Triticum aestivum, Arachis hypogaea, Zea mays* crops also show enhanced germination, accumulation, and increased potential of water absorption of seed after treatment with MWCNTs with 50µg/mL concentration [82].

In a study by McGehee et al., It was found that MWCNTs can increase fruit production in *L. esculentum* (tomato) plants. A considerable effect on the metabolome content by absorption of MWCNTs on the tomato fruits was confirmed by the results of HPLC-MS (high-performance liquid chromatogrpahy) [83]. A positive growth effect on broccoli was observed when MWCNTs were given at a low concentration [84].

MWCNTs also affect the germination and growth of plants due to the delivery system of chemicals and DNA to the cells of plants. Ca and Fe nutrients and water uptake efficiency are stimulated by MWCTs, improving development, seed germination, and plant growth. The imperative crops of barley, soybean, and corn seed germination are improved by the application of MWCNTs added to sterile agar medium after penetration of MWCNTs into the seed coats as the nanotube agglomerates were found inside the seed coats using TEM (Transmission Electron Microscopy) and Raman Spectroscopy [85]. Gene expression encrypting numerous kinds of water channel proteins in soybean, corn, and barley seed coats is controlled by MWCNTs. The plants of tomato, *Brassica juncea*, hybrid Bt-cotton, rice, and *Phaseolus mungo* showed extreme germination frequency with MWCNTs. MWCNTs increase the marker genes for water transport (aquaporin, *NNtPIP1*), cell divisions (*CycB*), and cell wall formation (*NtLRX1*) and enhance the growth of tobacco cell culture [86]. The water-retaining volume and biomass, flowering, and fruit of crop are increased by the application of MWCNTs [87]. The concentration of MWCNTs, heavy metal type, and plant species are decisive factors for the effect of MWCNTs on heavy metal buildup in plant seedlings and growth parameters [88].

Table 4: Effects of MWCNTs on plant

Plant	**Effects**	**Reference**
L. esculentum	Fruit production	[89]
Onion (Allium cepa L.)	Increase levels of plant height, chlorophyll rate, and leaf area.	[90]
Onion (Allium cepa L.)	Enhanced seedling growth. ZnO/MWCNTs	[91]
Maize and soybean	MWCNTs accumulated in the xylem and phloem, stimulation of growth in maize and growth inhibition in soybean was observed, and dry biomass of treated maize was higher than control.	[87]

O.sativa	Plant seedlings improved	[92]
Amaranthus dubius	Membrane disruption and cell death	[93]
Lactuca sativa	Reduces the use of pesticide	[94, 95]
Cucumis sativus	Seed germination & root Growth. Sludge & sewage stress resistance	[96]
Brassica napus	The moisture content of seeds & water absorption	[97]
Cucurbita cylindrica	Root length increases	[98]
Zea mays	Plant growth increases leaf, root, stem length, and biomass	[99]
Phoenix dactylifera	Callus growth promoted	[95]
Momordica charantia	Increases fruit yield and water content	[100]
Brassica oleracea	Controls ionic stress in plants	[101]
Hordeum vulgare L., *Glycine max*, *Zea mays*	Germination	[85]
Triticum aestivum, Zea mays, Arachis hypogaea, Allium sativum	Germination & water absorption	[95]
Lycopersicon esculentum Mill	Plant height and number of flowers	[102]
Nicotiana tabacum	Growth	[103]
Lycopersicon esculentum Mill	Uptake nutrients (Ca, Fe, K, Zn and Mn)	[102]
Rose periwinkle (Catharanthus roseus)	Increase in plant growth, biomass, and root length, a slight increase in chlorophyll and carotenoids, increase in proteins, CAT, and POX enzymes	[104]
Satureja khuzestanica	Enhanced flavonoids and phenols content in callus culture at 100	[105]
Thymus daenensis	Increased seedling biomass and height, highest total phenolic content, total flavonoid content, and antioxidant activity achieved	[106]

The application of MWCNTs on the plant of *Lactuca sativa* has a positive effect and no pesticide is applied for controlling the pests but it does not play a role in the germination of plant [107]. *Cucumis sativus* showed improvement in the root, seed germination, and sludge & sewage stress resistance Oleszczuk et al. [108]. Due to the increase in the amount of moisture, the seed germination is increased as well and water absorption through the root is also enhanced by the interaction of MWCNTs with *Brassica napus* Lin and Xing [109].

12. Role of SWNTs in plants

An appropriate delivery system of chemicals to cells by penetration into cell walls and membranes is provided by CNTs due to having unique properties. The transport of dye molecules and DNA to plants is carried out by SWCNTs which act as nano-transporters. Liu and his colleagues [110] assessed the ability of SWNTs to pass cell membranes and cell walls of intact plant cells and revealed the uptake of SWCNTs/fluorescein isothiocyanate and SWCNTs/ DNA conjugates by plant cells indicating the potential of SWCNTs as nano-transporters for plant cells having an intact cell wall. Moreover, it also can transport various cargos in different organelles of cells. SWNT phytotoxic effect was also observed in *O. sativa and Arabidopsis* which caused death overtime [111]. In *A.thaliana,* toxic effects of SWNTs were observed which resulted in cell aggregation, H_2O_2 accumulation, activity of superoxide dismutase, chromatin condensation, reduction in dry weight of cell, cell viability, and chlorophyll content [112]. Impact of SWCNTs on germination of plants has been studied in salvia (*Salvia macrosiphon*), pepper (*Capsicum annuum*), and tall fescue (*Festuca arundinacea*), the results revealed that SWCNTs treatment can induce seed germination. A concentration of 10mg/L and 30mg/L were considered ideal for achieving highest germination rate in pepper (*C.annuum*), salvia (*S. macrosiphon*)and tall fescue (*F. arundinacea*), respectively. A dosage dependent effect of SWCNTs on plants is observed in which it was seen that a higher dosage (100mg/L) of SWCNTs caused deleterious effects and induced ROS while a lower dosage (10-50mg/L) had a positive effect on cell growth [51, 105].

Table 5: Effects of SWCNTs on plants

Plant	Effects	References
O. sativa and Arabidopsis	Phytotoxic effect	[113]
A.thaliana	Toxic effects on plant	[114]
Salvia macrosiphon, Capsicum annuum, Festuca arundinacea	Seed germination	[115]
Plant organelles	Cargo for several molecules	[116]
Rice plant	Improved water uptake	[117]
Blackberry, Maize	Root elongation	[98]
Fig plant, Maize	Plant germination	[118]
Tomato	Plant germination	[95]
Salvia, pepper and tall fescue	Plant germination	[51]

CONCLUSION

Nanotechnology has been utilized to elevate the yield with quality improvement by improving cultivating frameworks in the field of agriculture. The rise of nanomaterials and their activities inside the edge of the agriculture field have altered world farming practice drastically by curiosity, quick development, and hugeness to meet the projection of worldwide nourishment request. The revolutions in science and technology have been developed by application of the carbon nanotubes provide fruitful results in the area of agriculture field. The CNT's small amount of absorbance produces physiological responses, and valuable effects produced by lower concentration while high revolution concentration produces harmful effects on plants, induces oxidative stress by formation of ROS, establishment of stress defense systems, and improved seed and fruit germination. The low concentration of CNTs (SWNCTs & MWCNTs) translocated into the whole part including the upper part (fruit, shoot, leaves) and lower parts (seed and root), and results in the growth of all parts, in turn, plant growth. It is necessary to assess the behavior and contact with the environment of high-concentration CNTs

(SWNCTs & MWCNTs), further studies should be conducted to evaluate the mechanism, and its distribution into plants, microorganisms, and the environment. More studies should be conducted to check the toxicity of CNTs (SWNCTs & MWCNTs) as smaller CNTs (SWNCTs & MWCNTs) are more easily translocated into the plant and less toxic and provide fruitful results in the development of the plant. It appears that MWCNT has assumed a positive effect in plants under salt pressure utilizing improving the ability to adapt to changes in the water slope through the forced symplastic pathway; nonetheless, this is just the beginning stage of a chain of biochemical changes which is to be explored as alongside the development of MWCNTs to parts of the plants (e.g., leaves and organic products) in various ecological conditions while SWNCTs showed strong antimicrobial activities as compared to MWCNTs. Long-term studies would be essential to survey the maturing impact and its association with soil microorganism environment and nanoparticles. Further studies are needed to focus on the positive impact of CNTs (SWNCTs & MWCNTs) in plant systems.

Conflicts of Interest

The authors declared no conflict of interest.

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