

CARBON NANOTUBES: THEIR ROLE IN THE MODIFICATION OF SOIL ENVIRONMENT TO FACILITATE SUSTAINABLE CROP PRODUCTION

Abstract

Carbon nanotubes (CNTs) are allotropes of carbon (C) with a round and hollow nanostructure, framed by the movement of hexagonally shaped C molecule planes (graphene sheets) into tubes. There could be both single-walled and multi-walled nanotubes. They are renowned for their extremely high thermal (greater than $3000 \text{ W m}^{-1} \text{ K}^{-1}$) and electrical conductivities ($10^6\text{-}10^7 \text{ dS m}^{-1}$). The application of CNTs to boost crop productivity is a relatively new field that requires investigation. Due to endo-osmotic root pressure, water-soluble carbon nanotubes in the vascular bundle of plants form a "head-to-tail configuration". In response to CNT treatment, plant water absorption increases considerably. Natural organic matter (NOM) is absorbed by carbon nanotubes, and the isotherm experiment results are consistent with a modified Freundlich isotherm model. At high quantities, carbon nanotubes inhibit the activity of C degrading and phosphorus (P) mineralizing enzymes (500 ppm or beyond that). It is also capable of altering the microbial community structure in certain crop rhizospheres. According to reports, carbon nanotubes have a priming effect on C mineralization in various soils. The mineral nutrient delivery (Calcium, Iron, and Chlorine) to plants is similarly affected by multi-walled CNTs. Carbon nanotubes have been credited with increasing the growth and productivity of various crops, such as tomato (*Solanum lycopersicum*), gram (*Cicer arietinum*), and others. But CNTs are not always a win-win strategy, as greater concentrations have a negative impact on soil microbes, notably the fungal community. Despite the potential of CNTs, it is evident that society is currently evaluating potential results.

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Keywords: carbon nanotubes, sustainable agriculture, water uptake, soil environment

I. CONCEPT OF CARBON NANOTUBE

Carbon nanotubes, also known as CNTs, are a type of carbon allotrope that have a nanostructure in the form of a tube. It has been demonstrated that nanotubes can be produced with a length-to-diameter ratio that is up to 132,000,000:1. These spherical and hollow carbon atoms have irregular qualities that are essential for nanotechnology, electronics, optics, and other areas of materials science and innovation. These irregular characteristics include: CNTs are increasingly being used as additions in a variety of fundamental materials, particularly due to the remarkable thermal conductivity, mechanical, and electrical properties that they possess. For example, a small fraction of the material(s) in certain (mainly carbon fibre) baseball bats, golf clubs, and vehicle components made of Damascus steel are encased in nanotubes. Individual members of the fullerene auxiliary group are known as nanotubes. Their name comes from their structure, which resembles a continuous void and is split into individual voids by sheets of graphene that are only one molecule thick. The qualities of the nanotube, such as whether or not the nanotube shell is metallic or semiconducting, are determined by a combination of the moving point and the span of the nanotube. Single-walled nanotubes (sometimes abbreviated as SWNTs) and multi-walled nanotubes (often abbreviated as MWNTs) are the two primary categories of nanotubes. Self-organization of nanotubes typically results in "ropes" that are held together by van der Waals forces, namely pi-stacking. Quantum physics, namely orbital hybridization, provides the most accurate representation of mixtures as they occur in nanotubes. In the same way that graphite is made up solely of sp^2 bonds, the synthetic holding of nanotubes is the same way. Nanotubes have exceptional properties as a result of these bonds, which are far more reliable than the sp^3 bonds that are present in alkanes and diamonds.

II. CHRONOLOGICAL EVENTS IN THE DEVELOPMENT OF CARBON NANOTUBES

1952: L.V. Radushkevich published tubes made up of carbon from the Soviet Union.

1976: Koyama showed carbon fibers with nanoscale dia.

1979: John Abrahamson presented evidence for CNT.

1981: Soviet scientists: chemical structural characterization of CNTs.

Finally, CNTs were discovered in 1991 by the Japanese scientist Sumio Iijima using transmission electron microscopy (TEM).

III. TYPES OF CARBON NANOTUBES

- 1. Single-Walled Nanotube (SWNT):** It is formed by rolling a sheet of graphene into a cylinder along an (n, m) lattice vector in the graphene plane. The (n, m) indices determine the diameter (d) and chirality (Θ). $d = \{(n^2 + m^2 + nm)^{0.5}\}^{0.0783}$ nanometer
- 2. Multi -Walled Nanotube (MWNT):** It consists of multiple rolled layers (concentric tubes) of graphene. Russian Doll model: sheets of graphite are arranged in concentric cylinders. Parchment model: a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper.

IV. METHODS OF SYNTHESIS OF THE CNTs

Carbon nanotubes can be synthesized by different methods

1. **Arc discharge method:** In 1991, nanotubes were discovered in the carbon soot of graphite electrodes during an arc discharge with 100 amps of current intended to produce fullerenes. As a result of the high discharge temperatures, the carbon in the negative electrode sublimates during this process. This approach can produce single- and multi-walled nanotubes with lengths of up to 50 micrometers and minimal structural flaws at a maximum yield of 30 percent by weight. The arc-discharge approach utilizes higher temperatures (over 1700 °C) for CNT synthesis, which frequently results in the expansion of CNTs with fewer structural defects than other methods.
2. **Laser ablation:** In a reactor operating at a high temperature, a graphite target is vapourized by a pulsed laser during the process of laser ablation, which also involves the introduction of an inert gas into the chamber. On the cooler surfaces of the reactor, nanotubes begin to form as the vapourized carbon begins to condense. It is possible for the system to incorporate a surface that is cooled by water in order to collect nanotubes. During the time that Dr. Richard Smalley and his colleagues at Rice University were working on the discovery of carbon nanotubes, they were blasting metals with a laser in order to make a variety of different metal complexes. As soon as they realized that nanotubes existed, they began replacing the metals in the process with graphite in order to produce MWCNTs. In the latter half of that year, the scientists created SWCNTs by mixing graphite and particles of metal catalysts (cobalt and nickel produced the highest yield). The yield of the laser ablation method is around 70%, and the majority of the nanotubes that are produced are SWCNTs with a diameter that is determined by the temperature at which the reaction takes place. In spite of this, the cost is significantly higher than that of arc discharge and chemical vapour deposition.
3. **Chemical vapour deposition:** The thermal or plasma-enhanced (PE) catalytic chemical vapour deposition (CCVD) process is currently considered to be the gold standard for the production of CNTs. This trend is expected to continue in the near future. The CCVD is seen as a more economically viable process for generating large amounts of highly pure CNTs compared to laser ablation, which is the traditional method. The key advantages of using CVD are the ease with which the reaction course may be controlled and the great purity of the material that is produced, amongst other advantages. The CNT growth model is currently the topic of ongoing discussion. For the production of SWNTs, the nanoparticle catalyst needs to be smaller than about 3 nanometers in size. In the chemical vapour deposition (CVD) process, the role of the catalyst is to facilitate the breakdown of carbon sources by plasma irradiation (PE-CVD) or heat (thermal CVD), followed by the nucleation of CNTs. Transition metals, notably iron, cobalt, and nickel, are the most prevalent types of catalysts. Normal catalysts are sometimes "doped" with extra metals, such as gold, on rare occasions. With regard to the supply of carbon, CVD favours the use of various types of hydrocarbons, such as short chain alkanes, alkenes, alkynes, and/or ethanol etc.

V. EFFECT OF CNTs ON SOIL pH

Typically, the principal sorption mechanism involves metal ions and CNT surface functional groups. In the aqueous phase, CNT's carboxylic and phenolic protons exchanges with metal ions. After equilibrium in metal ion sorption onto CNTs, the solution pH lowers due to the release of H⁺ from the CNT surface, lowering the pH. The pH decreased in proportion to the initial concentration of metal ions, demonstrating that the sorption of more metal ions onto CNTs releases more H⁺ ions from the surface. Researchers found that surface-oxidized CNTs adsorb metal ions via sorption-precipitation and electrostatic attraction. Surface-oxidized CNT protons interact with metal ions in the aqueous phase. After metal ions are sorbed onto CNTs in neutral soil, the solution pH decreases due to the release of H⁺ from the CNT surface. In acidic soil, excess H⁺ ions react with CNT's surface hydroxyl ions, neutralizing some H⁺ ions and raising soil pH [1].

VI. EFFECT OF CNTs ON WATER UPTAKE BY PLANTS

Water follows the Fickian mechanism even in microscopic tubes. Reference [2] was the first to measure water's movement in SWNTs with 1.1 to 2.1 nm diameters. The axial diffusion coefficient was lower than bulk water and decreased with pore diameter. When water molecules are restricted in a one-dimensional channel, they cannot pass one other; hence, the diffusion could be single-file, where the mean square displacement (msqd) scales with the square root of time. When water molecules in confinement travel in a highly coordinated manner, ballistic diffusion occurs, and msqd scales with the square of time [2]. Because of the endo-osmotic root pressure caused by the xylem, initially-disorderly water-soluble carbon nanotubes become structured in the vascular bundle of plants. Then, within the treacherous parts of the xylem, a "large capillary" is generated by the "head-to-tail arrangement" of one carbon nanotube to the next. Thus, carbon nanotubes serve as conduits via which water is transported within a plant at considerably faster velocities. In response to CNT treatment, gram plants (*Cicer arietinum*) absorbed considerably more water as the dose of CNT gradually rose [3].

VII. EFFECT OF CNTs ON ADSORPTION OF SOIL ORGANIC MATTER

Natural organic matter (NOM) is a mixture of chemically varied polyelectrolytes with different molecular weights generated by the decomposing plant and animal wastes. NOM's carboxylic and phenolic groups give it a negative charge in nature. Physical and chemical aspects of NOM may affect NOM-CNT interaction. Hyuang and Kim (2008) studied natural organic matter (NOM) adsorption MWCNTs. CNTs absorb NOM, and isotherm experiment results best fitted a modified Freundlich isotherm model that accounts for NOM's heterogeneity. Researchers found a linear relationship between aromatic carbon content and adsorption capacity (K_F). Due to the π-π interaction, which encouraged preferential adsorption of higher molecular weight NOM on CNTs, less soluble, higher molecular weight humic acids have a better adsorption capacity than fulvic acids. Ionic strength and pH also affect NOM adsorption on CNT. The K_F increases with an increase in ionic strength, perhaps due to a change in NOM's molecular structure. As ionic strength increases, humic compounds become more coiled and compressed. As more molecules occupy the same surface, absorption capacity rises. As the NOM molecule shrinks, the area for NOM-MWNT

interaction decreases, as does the NOM's attractive force on the MWNT surface. Ionic strength enhances adsorption strength. Increasing ionic strength increases double layer compression in NOM-MWNT agglomerates, boosting NOM adsorption onto MWNT. As pH rises, NOM molecules uncoil and loosen. Increasing pH negatively charges carboxylic and phenolic groups. At a higher pH, NOM and the NOM-coated CNT surface repel each other, blocking adsorption [4].

VIII. IMPACT OF CNTs ON NUTRIENT UPTAKE BY PLANTS

1. Delivery of fertilizer to plants by CNTs: Nanoparticles and other things from the outside can't easily get into plant cells because of the cell wall. The size of the pores in a cell wall, which ranges from 5 to 20 nm, shows how well it can filter things. So, only nanoparticles or groups of nanoparticles with a diameter smaller than the size of the pores in the cell wall can easily get to the plasma membrane. When designed nanoparticles interact with cells, pores may get bigger or new pores may be made in the cell wall, which makes it easier for cells to take in nanoparticles. When nanoparticles are put on the surface of a leaf, they enter through the stomatal openings or the trichome bases and then move to other parts of the plant. Research into the mechanism of nanoparticle uptake and production within plants has inspired investigations into the use of plants as sources for nanoparticle synthesis. Fertilizers may benefit from the use of nanomaterials. Surface coatings of nanomaterials on fertilizer particles are more effective in retaining the fertilizer from the plant than regular surfaces because of their higher surface tension. Furthermore, nano-coatings shield larger particles from contact with the environment. Fertilizer degradation was slowed by the longevity of the coating, which meant that nutrients were released over a longer period of time. Biofertilizers are live microorganism compositions. Biofertilizer formulations are coated with polymeric nanoparticles to provide desiccation-resistant formulations. Micronutrients in nano-formulations can also be used as crop sprays to enhance foliar absorption. A slow release of micronutrients encased in nanomaterials would improve plant growth and soil health [5,6].

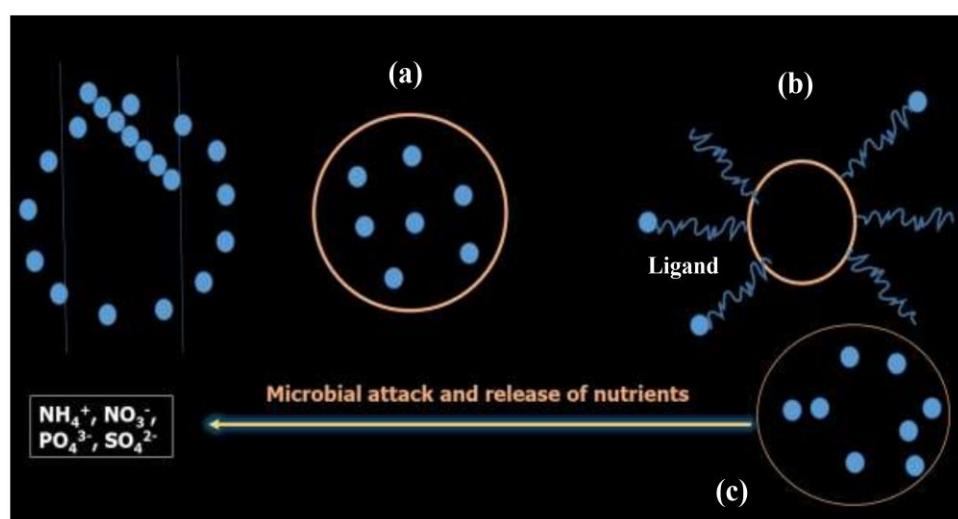


Figure1: Schematic Diagram Showing that the Active Ingredient is Attached to Nanotubes Either by (A) Adsorption on Nanoparticles; or (B) Attachment on Nanoparticle-Mediated by Different Ligands, Where CNT Acts as a Core; or by (C) Encapsulation in the Nanoparticulate Polymeric Shell.

- 2. Case study:** Maize (*Zea mays*) seedlings were grown in a nutrient agar gel with varying concentrations of pristine MWCNTs non-ultrasonically distributed inside it [7]. They discovered that CNTs affected the mineral nutrient supply to maize seedlings and, as a result, their growth parameters. At low concentrations of MWCNTs, they observed an increase in the germination rate of maize seedlings, but a decrease at higher concentrations. The MWCNTs increased water delivery was primarily responsible for the enhanced growth. The MWCNTs altered mineral nutrient availability to the seedling via water input and ion-CNT transient-dipole interaction. By large, low doses of MWCNTs improved water absorption, plant biomass, and Ca and Fe nutrient concentrations in the normal medium. This opens the door for future commercial agricultural uses of MWCNTs.

IX. EFFECT OF CNTs ON MICROBIAL COMMUNITY STRUCTURE

In an experiment conducted by [8], the relative abundances of bacterial groups in untreated and CNT-treated soils were determined using pyrosequencing data. According to the taxonomic assessment of pyrosequencing data, there was no substantial impact on bacterial diversity. The majority of species found in all samples were uncultured bacteria. In an acidic sandy loam soil, the Acidobacter population decreased after 8 weeks of incubation at the greatest application rate of multi-walled CNTs (5000 micrograms/g). This may be related to a rise in soil pH from 4 to 5.5 after 8 months of CNT application at the maximum rate. Lower CNT concentrations had no measurable impact [9].

X. ROLE OF CNTs IN REMEDIATION OF POLLUTED SOIL

Soil pollution is the presence of one or more chemical substances in amounts that are harmful to soil organisms and those that depend on soil. There are two primary categories of soil pollutants: organic pollutants, such as polychlorinated biphenyls and pesticides, and heavy metal and inorganic pollutants, such as arsenic, manganese, mercury, lead, etc. There are numerous strategies for remediating damaged soil, with nanotechnology being an emerging one. Inorganic and carbon-based nanoparticles are the most common forms of nanoparticles utilized for soil remediation [10]. Due to their higher electronegativity and adsorption affinity for organic matter, [11] reported that the application of CNTs to polluted soil had a greater immobilization effect for lead and copper than nickel and zinc. The combined use of graphene oxide nanoparticles and *Bacillus subtilis* resulted in greater heavy metal immobilization than other treatments [12]. Reference [13] discovered that carbon nanotubes were more successful than nano-clay and nano-alumina at adsorbing dichloro diphenyl trichloroethane (DDT) and polychlorinated biphenyls (PCBs) because of π - π electron interaction between the benzene rings of the contaminants and CNT. So, it is obvious that nanoparticle application efficiently lowers or immobilizes soil pollution. To completely comprehend the beneficial or adverse influence that nanoparticles have on the soil, plant, human, and animal, however, a thorough examination of the potential environmental impacts associated with their use is required.

XI. TOXIC EFFECT OF CNTs ON SOIL ENZYMES' ACTIVITIES

Reference [14] investigated the impact of CNTs on soil microbial activity in an incubation experiment. Enzyme activities were unaffected by the addition of 50 micrograms of multi-walled CNT per g of soil. However, the addition of CNTs at high concentrations (500 micrograms per g of soil and above) strongly inhibited the activity of both carbon degrading and P oxidizing enzymes at both sites. Direct interaction with highly pure CNTs and bacterial cells resulted in membrane breakdown, physical penetration, and oxidative stress. In addition, the tubes typically include a high concentration of metal contaminants due to the use of metal nanoparticles as catalysts for CNT growth, which can also have hazardous effects on microbial organisms.

XII. FUTURE AREAS OF RESEARCH

To combat the monster of population expansion, we must cultivate the application and adaptability of CNTs. This exposure risk could be reduced by the use of efficient nanomaterial application technologies in agriculture. It would be ideal for their effective use in agricultural production if nanomaterials could be produced that have good dispersion and hydrophilicity, that are biodegradable in soil and environment, that are less hazardous and more photo-generative, that have well-understood toxico-kinetics and toxico-dynamics, that are perceptive and stable, and that are easy to fabricate and apply in agriculture.

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