RECENT ADVANCEMENTS IN CARBON NANOPARTICLES AND ITS APPLICATION AS NANO FERTILIZER FOR ENHANCEMENT OF GROWTH TO VARIOUS CROPS IN THE FIELD OF AGRICULTURE.

Mr. Rakesh, Mrs. Babitha, Assistant Professor
Department of Chemistry, Garden City University.

Abstract

Agriculture is the key feature for sustained growth and development of any country. Food is the essential part of all living organisms. So, evolution in food industry is very important for developing country like India. With increase in population which may reach around 10 billion in near future results in scarcity of food. Thus, increase in production of various required raw materials which can be obtained from farming in limited time remains always hot topic. Hence, Fertilizers play a vital role to increase the yield of various essential crops in Agriculture. Particularly, nano fertilizer helps in reaching the above goal at faster rate. Organic nano fertilizers like carbon nano fertilizers have been found greater advantage compared to other chemical fertilizers in terms of increase in stem height, life span, yield of product, quality of soil, hybrid substances and many other aspects constrained to the growth of the plant

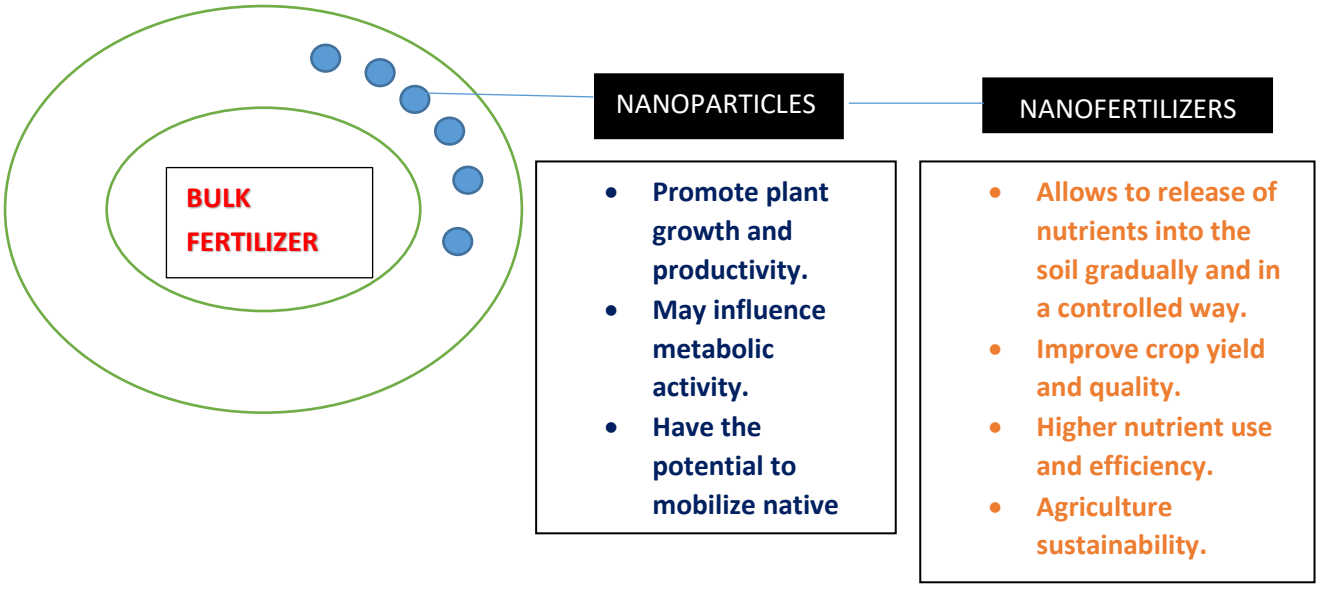
Keywords: *Agriculture, evolution, farming, population, nano fertilizer.*

1.1 Introduction

Nano fertilizers are those that contain components in nanoscale ranging from 1-100nm which have been found useful in agricultural fields. Though it has both positive and negative effect, but it has infinite amount of uses and effects towards development of plant growth, soil nourishment and climate changes. Nano fertilizers plays a promising role in supplying micronutrients that are required for plants growth and development. Nano-fertilizers are designed in such a way that it should release the nutrients in minimal amount required for plant growth over an extended period. It also ensures that a constant steady supply of micronutrients to plants is maintained. Nowadays, this system has become more efficient than traditional system of providing fertilizers to plants. There are various nanoparticles ranging from simple to complex like nitrogen-phosphorus-sulphur fertilizers commonly called as NPS nano fertilizers, Zinc fertilizer, copper fertilizer and many more. But carbon containing nanoparticles like nanotubes, quantum dots and graphene have found to be more advantageous compared to others.

These nano fertilizers made up of nanoparticles which have unique qualities that can act as plant growth enhancer like sorption capacity, they increase the surface to volume ration as well as controlled release of nutrients to targeted plants.

ADVANTAGES OF NANOFERTILIZERS



1.2 Synthesis of various carbon nanoparticles

There are various methods of synthesis of carbon nanoparticles which includes arc discharge, chemical vapor deposition, electrolysis, ball milling and many other as well.

1.2.1 Electric arc discharge:

This is one of the most typical methods of synthesis of carbon nanoparticles. It includes cathode and anode where anode contains powdered carbon precursors like polyacrylonitrile, Rayon, methane, ethanol, and coal which gets vaporized at high temperature and gets deposited at cathode which is usually filled with graphene. On passing current, there will be a discharge of arc which is in the form of loop and develops high temperature converting gas present in the system to a plasma state. The electrons which got ionized in the plasma state undergo collision with anode and aggregate the carbon cluster which grows slowly to form nanostructures.

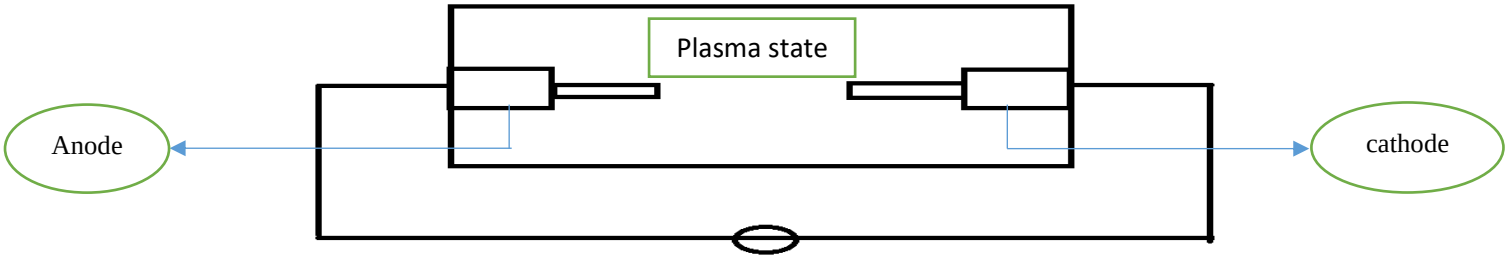


Fig 1: Diagrammatic representation of loop arc discharge

1.2.2 Microwave method:

Here carbon precursors are kept under microwave oven over 300W for 3-4 hour which undergoes pyrolysis in polyethylene glycol (PEG) commonly used as scale up process in the synthesis of carbon nanoparticles. The colour of the solution changes which is centrifugated and purified by washing several times. Thus, obtained nano particles were found to be less fluorescent and cannot be used for Photoluminescence activities. Nano particles obtained through microwave method contain PEG which cannot be separated very easily and cannot be applied for bulk synthesis.

1.2.3 Conventional methods of carbon dot synthesis

Carbon Dot can be prepared conventionally by two methods: Top down and bottom-up approaches. Top down includes breaking down the larger molecules to smaller ones whereas bottom up is other way round. Both have their own significance but bottom up is found to be easy, cost effective, less harmful compared to top down. There are various methods in both the approaches which is shown table 1.

Top down	Bottom up
Laser ablation	Laser irradiation
Electrochemical oxidation	Hydrothermal
nanolithography	Pyrolysis
Sonication	Carbonization
Chemical exfoliation	Plasma state

Tab 1: Table showing different methods of forming carbon dots.

1.2.4 Chemical Exfoliation

It is one of the top-down methods which includes breaking the carbon precursors using various concentrated acids like Nitric acid, sulfuric acid, citric acid, Phosphoric acid and oxidizing agents. Mild oxidizing agent such as Hydrogen peroxide (H_2O_2) is found to be better for cleavage compared to other as they require purification. We can synthesize quantum dot naturally from biological products like muskmelon, tomato etc. The obtained nanoparticles have high optical properties including photoluminescence.

Carbon polymers -----oxidizing agent----→ Carbon dots

1.2.5 Pyrolysis / carbonization

It is one of the powerful techniques which requires less time, solvent free, low cost with minimal production. In one of the experiment, Cl- doped graphene carbon dot(GCD) was prepared by adding HCl along with O and H groups of fructose were dehydrated and nucleus of GCD was prepared through hydrothermal method. It includes four stages which is shown in fig 2.

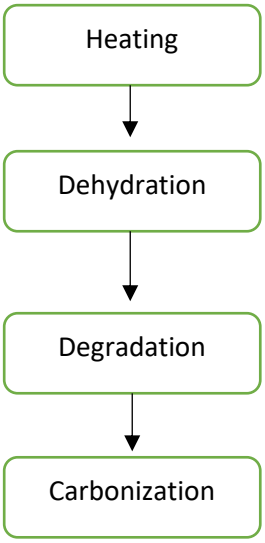


Fig 2: flowchart showing pyrolysis method of synthesis.

1.2.6 Synthesis of Carbon dot coated Metal organic framework (MOF) for usage of nano fertilizer.

Metal organic frameworks (MOF) are very good fertilizer as they supply efficient nutrients to crops such as nitrogen, phosphorus and metal micro-nutrients like iron, zinc etc. Most used MOF such as benzene-1,3,5-tricarboxylic acid, ethylene diamine tetra acetic acid, oxalate phosphate amine act as fertilizer. When it is coated with carbon dot using autoclave hydrothermal can be transferred to various pore through root, stem, leaves and other parts of the plant efficiently at the faster rate compared to other fertilizers.

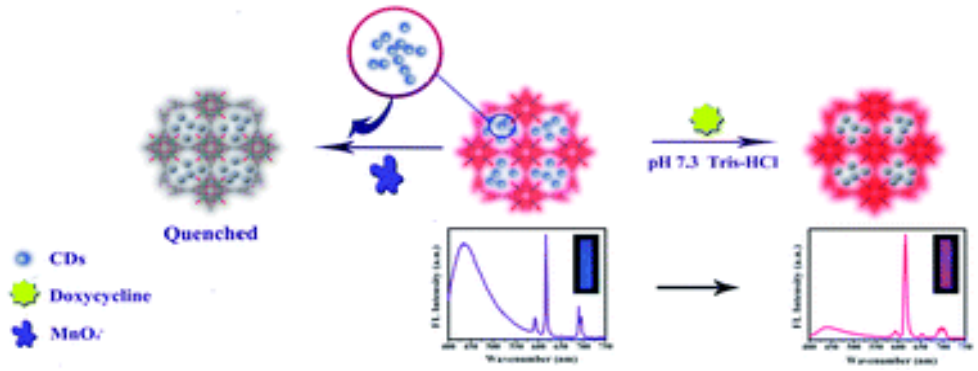


Fig 3: Carbon dot synthesis with MOF

1.3 Mechanistic action of nano fertilizer into the plant system

1.3.1 Entry to plants and effects on growth

Nano fertilizers effects depends on factors such as soil, environment, nanoscale properties and its mode to deliver micronutrients to plants. Till today foliar mode of entry was best as nutrients enter through pores of plasmodesmata of leaf, as nanomaterials make the way so that nutrients can enter from root hairs to reach the xylem then leaves and stem.

Based on their actions, Nano fertilizers are classified into 2 types:

1. Nutrient composition
2. Consistency

Under the classification, we can include various categories of Nano fertilizers like nano fertilizer targeted delivery, controlled release Nano fertilizers, nutrient loss controlling fertilizers, hybrid fertilizer, nutrient loaded fertilizer, and nano carrier-based fertilizers. Most significantly used Nano fertilizers for target delivery system is of nano aptamers. These are the tiny molecules made up of oligonucleotides or peptides that bind to enzymes or hormones of plant and target specific molecules to deliver nutrients.

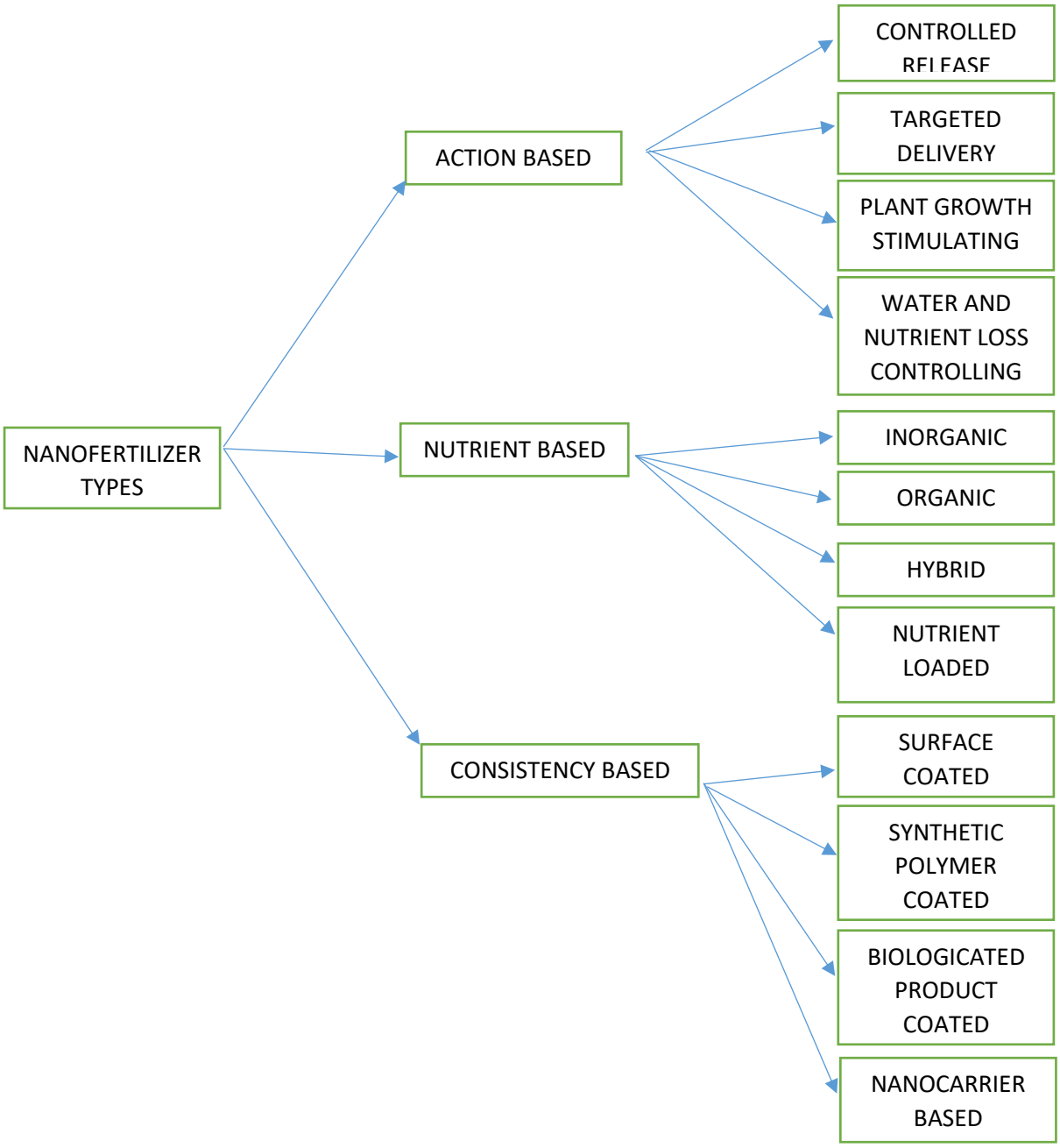


Fig 3: Flowchart showing different types of nano fertilizers having diverse effect on plant growth.

Controlled release fertilizers are more of like granular structure, designed to deliver nutrients over a period ranging from weeks to months depending on their requirements. As mentioned earlier, carbon nanotubes, graphene and quantum dots have exclusive properties that make them controlled release fertilizer. These are known to enhance crop productivity, nutrient use efficiency or to be more specific towards plant health. Nowadays, carbon based nanostructured particle is playing a vital role as nano fertilizers as biochar. This biochar contains innumerable carbon nanostructures which when exposed to air undergoes oxidation. Due to this oxidation, it creates a pore where micronutrients can enter through its way and it's beneficial for plant growth too. Nano capsule-based fertilizers are microscopic composed of organic and inorganic materials used to encapsulate it, due to this they form a critical shield where the micronutrients are supplied in a fullness of time. These capsules are made up of silica, lipids, biopolymers, and carbon nanotubes. Chitosan based Nano fertilizers are considered as bio polymer.

1.3.2 Types of nano fertilizers and its pathway into the various parts of Plant system

1) Chitosan being a cationic polymer it can easily react with negatively charged materials. Due to this property of forming complexes, it can effortlessly interact with micronutrients.

2) Plant growth stimulating nano fertilizers like carbon nanotubes which stimulate plant growth and boost the carbon nutrient contents in soil. This carbon nanotubes are considered as a best nano fertilizer due to diverse property. To list them a few, it can improve the soil structure, helps in water retention, helps in penetrate deep into to soil, nutrient storage capacity, they can increase the mechanical strength of plant stalk and stem.

3) Water and nutrient loss controlling fertilizers are type of fertilizer which are designed to control the water loss and nutrient loss in plants. These fertilizers have a pore which facilitate the rate of flow of nutrient to plants over a time. The surface of nano fertilizers like nanobeads or nano emulsion are encapsulated with hydrophilic materials because of this reason it controls water and nutrient loss as well as evaporation.

4) Inorganic nano fertilizers are made up of metal, non-metals, and metalloids. These fertilizers provide essential nutrient such as nitrogen, phosphorus, and potassium in a required amount to a targeted plant, thereby enhancing the yield of that plant. We can classify inorganic nano fertilizers as macronutrient and micronutrient based, macronutrient nano fertilizers are required to plants in maximum amount like nitrogen, phosphorus, potassium; micro-nutrient nano fertilizers are required to plants in minimum amount like copper, boron, iron.

5) Organic nano fertilizers are mostly carbon-based compounds which are eco-friendly, and these fertilizers are natural available from the environment and helps to maintain soil pH, moisture and intake enough nutrients required to growth. These fertilizers are synthesized from various organic compounds such as micelles, liposomes, capsules etc. We can also extract natural polymer from gum, tamarind seed polysaccharide, mucilage, chitosan, pectin is these can be used in preparation of organic nano fertilizers.

1.3.3 Hybrid Nano fertilizers

Hybrid Nano fertilizers are obtained by combining polymer matrix and nanofillers. Hybrid Nano fertilizers have nanoparticles which contain thin protective layer, this layer is porous making the nutrients available to plants for longer period. These fertilizers are injected into irrigation systems so, this process is called as nano fertigation. The concept of this fertilizer is to directly enter through roots so that the plant can directly intake the nutrients required.

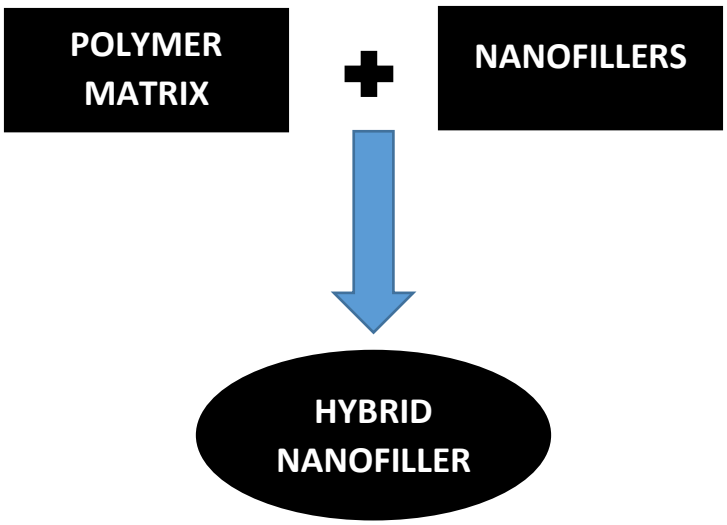


Fig 4: Diagram showing hybrid nanofiller formation.

Nutrient loaded nano fertilizers are nano-porous zeolites. This is formed by reaction of volcanic ash and alkaline lake water this results in honeycomb like structure due to this formation the porosity increases making them good nano fertilizers. So, this form of nano-porous zeolites is mixed in required ration along with nitrogen, phosphorus and potassium thereby increasing the absorption. Surface coated nano fertilizers are nano fertilizers made by coating nanoparticle with gold, carbon, or silver, due to this coating adherence to plant surface increases thereby facilitate the absorption of nutrients. Synthetic polymer coated nano fertilizers are coated with synthetic polymer, this helps them to protect from environmental degradation.

1.4 Importance of Carbon-based nano particles as Nano Fertilizers

Carbon quantum dots as cross investigated carbon-based nanomaterials, as they have rightness characters like optical activities and low toxic effects. These carbon quantum dots (CQD) have many applications in the field of sensing, solar cells, drug delivery. These CQD were studied and synthesized under water soluble or photoluminescent and these were acting as a link for various purposes. As a result, CQD was showing more positive result than expected for synthesis. By using the potential of this CQD, the physiological processing of plants were demonstrated together with photosynthesis and growth.

Carbon nanotubes as a part of major application which is seen in agriculture as nanotubes are encapsulated with smart delivery system that are automated, effective planning specifically

taunted for components like fertilizers and pesticides. These carbon nanotubes are synthesized from graphene oxide sheets into single cylindrical wall or multiple walls. As a result, uptake of nutrients will be improved, in turn boost up the quality of crops. Nanotubes have high efficiency of water holding capacity as nanotubes are coated with carbon which have capacity to release nutrients in slower phase which could orderly reduce water pollution. If CNTs concentration is low, this improves the seedling growth and seed germination. The effect of CNTs in plants have resulted directly or indirectly with plant metabolism. As compared to carbon nanotubes fullerenes exhibited no toxicity at its concentration as all these have nanoparticles that can inhibit infected pathogens.

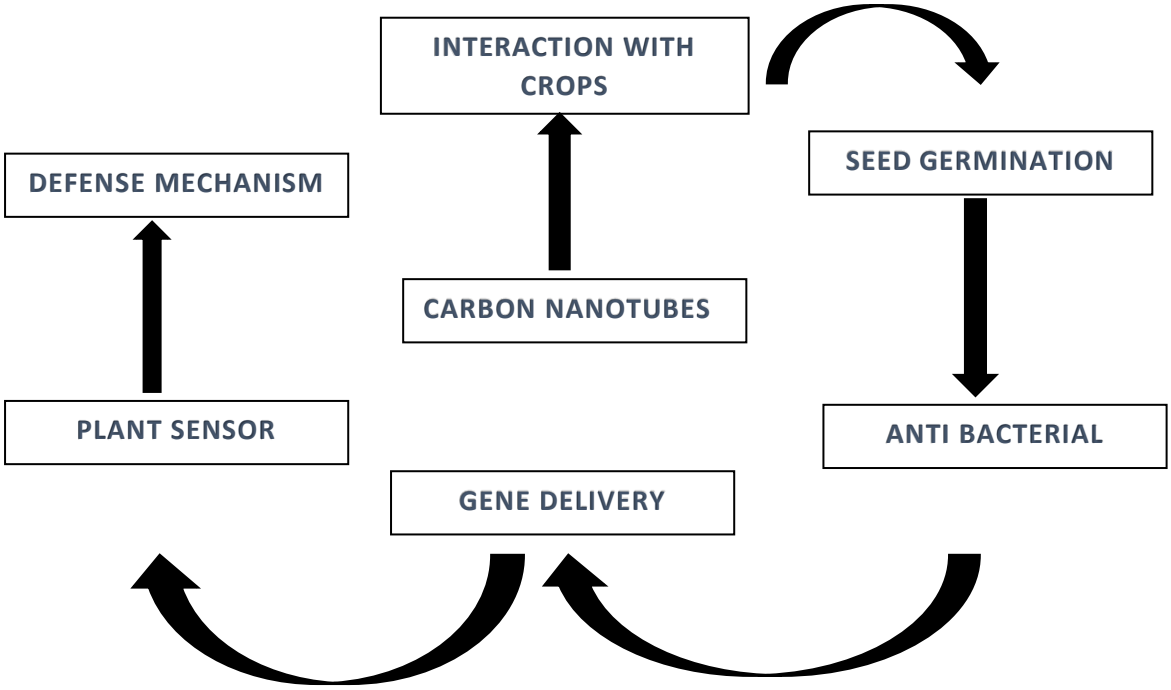


Fig 5: Illustration of uses of CNTs in various fields

As we all know that seed germination is first step in plant growth as it is a sensitive stage its cycle. Many experiments have demonstrated that CNTs can invade into seed coat and accelerating the seed germination in faster rate. As it increases the dry and fresh weight of plant root and shoot system.

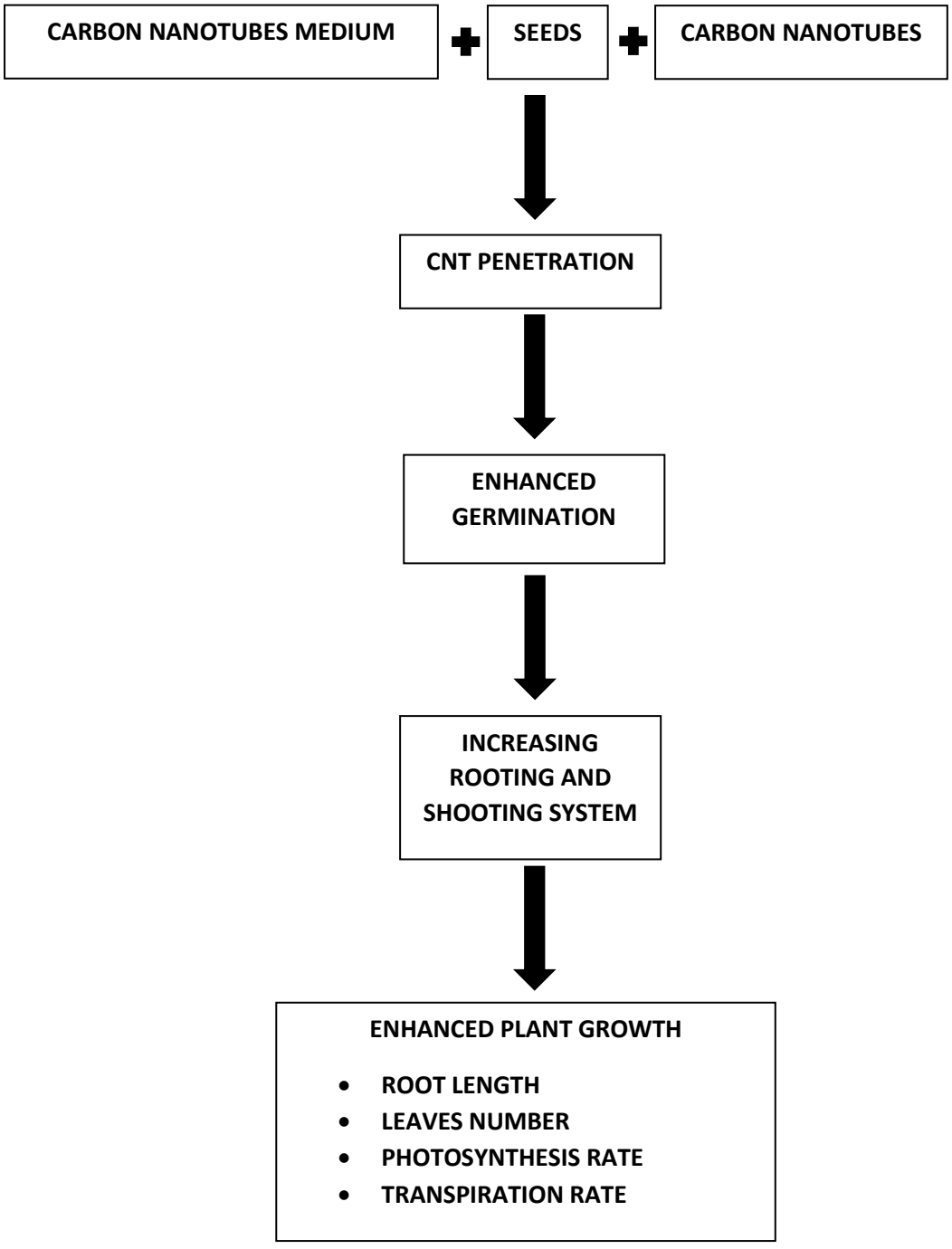


Fig 6: Flowchart showing CNTs entering into plant system

Conclusion

Nanoparticles based nano fertilizers have shown positive development in the field of Agriculture. Nano particles can be synthesised in various ways of which biological method of synthesis have lot of applications. By knowing the exact mechanism of interaction of nano fertilizers with crops and its various uses, carbon dot coated metal organic framework has been efficiently used as fertilizer for increase in growth of crops economically. However, slight modification in fertilizers after studying its composition have witnessed various changes in plant height, number of leaves, average fruit weight and other aspects as well. But still, fertility of soil, temperature conditions, conditions of terrestrial region also affect the growth of crops. Thus, modifications in nano fertilizers considering above aspects is still under research and lot of scope as well.

References

1. Safdar, M., Kim, W., Park, S., Gwon, Y., Kim, Y. O., & Kim, J. (2022). Engineering plants with carbon nanotubes: a sustainable agriculture approach. *Journal of Nanobiotechnology*, *20*(1), 1-30.

2. Swathi, S., Ravikumar, C., Naveenkumar, S., Senthilvalavan, P., & Manivannan, R. (2022). Consequences of Nano fertilizers usage in agriculture-A Little Review.

3. Bratovcic, A., Hikal, W. M., Said-Al Ahl, H. A., Tkachenko, K. G., Baeshen, R. S., Sabra, A. S., & Sany, H. (2021). Nanopesticides and nanofertilizers and agricultural development: Scopes, advances and applications. *Open Journal of Ecology*, *11*(4), 301-316.

4. Gaur, M., Misra, C., Yadav, A. B., Swaroop, S., Maolmhuaidh, F. Ó., Bechelany, M., & Barhoum, A. (2021). Biomedical applications of carbon nanomaterials: fullerenes, quantum dots, nanotubes, nanofibers, and graphene. *Materials*, *14*(20), 5978.

5. Kalwani, M., Chakdar, H., Srivastava, A., Pabbi, S., & Shukla, P. (2022). Effects of nanofertilizers on soil and plant-associated microbial communities: Emerging trends and perspectives. *Chemosphere*, *287*, 132107.

6. Verma, K. K., Song, X. P., Joshi, A., Rajput, V. D., Singh, M., Sharma, A., ... & Li, Y. R. (2022). Nanofertilizer possibilities for healthy soil, water, and food in future: An overview. *Frontiers in Plant Science*, *13*, 865048.

7. Elmer, W., & White, J. C. (2018). The future of nanotechnology in plant pathology. *Annual review of phytopathology*, *56*, 111-133.

8. Guleria, G., Thakur, S., Shandilya, M., Sharma, S., Thakur, S., & Kalia, S. (2022). Nanotechnology for sustainable agro-food systems: The need and role of nanoparticles in protecting plants and improving crop productivity. *Plant Physiology and Biochemistry*.

9. Ahmed, H. B., Mahmoud, N. E., Mahdi, A. A., Emam, H. E., & Abdelhameed, R. M. (2022). Affinity of carbon quantum dots anchored within metal organic framework matrix as enhancer of plant nourishment. *Heliyon*, *8*(12).

10. Arora, N., & Sharma, N. N. (2014). Arc discharge synthesis of carbon nanotubes: Comprehensive review. *Diamond and related materials*, *50*, 135-150.

11. Benzon, H. R. L., Rubenecia, M. R. U., Ultra Jr, V. U., & Lee, S. C. (2015). Nano-fertilizer affects the growth, development, and chemical properties of rice. *International Journal of Agronomy and Agricultural Research*, *7*(1), 105-117.

12. Raliya, R., Saharan, V., Dimkpa, C., & Biswas, P. (2017). Nanofertilizer for precision and sustainable agriculture: current state and future perspectives. *Journal of agricultural and food chemistry*, *66*(26), 6487-6503.

13. Hussein, H. S., Shaarawy, H. H., Hussien, N. H., & Hawash, S. I. (2019). Preparation of nano-fertilizer blend from banana peels. *Bulletin of the National Research Centre*, *43*, 1-9.

14. Tarafder, C., Daizy, M., Alam, M. M., Ali, M. R., Islam, M. J., Islam, R., ... & Khan, M. Z. H. (2020). Formulation of a hybrid nanofertilizer for slow and sustainable release of micronutrients. *ACS omega*, *5*(37), 23960-23966.

15. Chhipa, H., & Joshi, P. (2016). Nanofertilisers, nanopesticides and nanosensors in agriculture. *Nanoscience in food and agriculture 1*, 247-282.