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Latest Developments and Applications of Nanotechnology in Agriculture Sector: A Review

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ABSTRACT

Nanotechnology, a term coined by Norio Taniguchi first time in 1974, pertains to controlling, building, designing, restructuring materials and devices on the scale of atoms and molecules. Till today nanotechnology is used in the entire spectrum of the agriculture sector, such as agriculture production, single-molecule detection for the determination of enzyme-substrate interactions, nanocapsules for efficient and timely delivery of agrochemicals and growth hormones in a controlled fashion, nanosensors for monitoring soil conditions, crop growth and quality and for detection of animals and plant pathogens, nanochips for the preservation of identity and tracking, nanocapsules for vaccine delivery and nanoparticles to deliver DNA (Deoxyribonucleic Acid) to plants, a process known as "targeted genetic engineering." Especially in the agriculture sector, research and technical innovation are important, addressing the crucial global challenges like population growth, drastic climate change and the limited availability of prime plant elemental nutrients such as phosphorus and potassium. Despite these tremendous advantages, uses of nanotechnology are still comparably marginal in the agricultural sector and research has not been commercialized and reached to market to any larger extent in comparision to the other sectors of nanotechnology application. Major safety concerns and stringent laws related to human health and the environment were raised towords industrial-scale manufacturing and use of nanomaterials hinders its use in the agriculture sector as well.

Key words: Agriculture, Agri-nanotechnology, Nanotechnology.

Agriculture is an essential and a substantial sector as it yields raw components for food and feed industries. According to the Ministry of Finance Report, Govt. of India, the substantial increase in agriculture growth was 3.59% between 2004-2014. It was proposed that the above-stated growth was lesser than the targeted 4% annual growth (Dasgupta *et al*., 2015). In the current scenario, intense efforts are being made to attain sufficient growth in the agriculture sector. One of the major concerns in agriculture is food grain production (Dasgupta *et al*., 2015). Due to the depletion of natural resources such as producible land, soil and water, there has been a great obligation in promoting development in the agriculture sector, which must be economically viable and eco-friendly (Duhan *et al*., 2017). Advanced technologies and their judicial use would undoubtedly promote agricultural growth by enhancing natural resources per unit productivity (Duhan *et al*., 2017). Despite numerous scientific advancements, nanotechnology has emerged as one of the most promising fields in the food and agriculture industry (Abbas *et al*., 2016). Nanotechnology has been identified as one of the six "Key Enabling Technologies" by the European Commission. Nanotechnology is the branch of science that deals with the technology of molecules measuring one of their dimensions in the nanoscale (1-100 nm) (Cheng *et al*., 2016). It involves thorough understanding of molecules, individual atoms and clusters of molecules and physical, chemical and mechanical properties associated with them. It also deals with fabricating devices at the nanoscale level (Ditta, 2012). Due to the rapid increase in the population in the underdeveloped and developing countries, their increasing demand for food supply triggers the need for agricultural advancements (Grillo *et al*., 2016).

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The development of agriculture is a compulsory phenomenon for the purge of poverty and hunger, which must be removed from the present situation (Kumari and Yadav, 2014). Many potential techniques have been established to increase the farm yield and simultaneously reduce the environmental hazards associated with them (Pramanik *et al*., 2020). Nanotechnology has emerged as a promising field to handle critical issues related to health, energy, agriculture and water (Abobatta, 2018). Efforts have been made to leverage nanotechnology applications in the agricultural sector, emphasizing sustainable production (Abobatta, 2018). Novel and new agrochemical agents have been developed through nanotechnology to enhance crop productivity and the new delivery mechanisms (Chen and Yada, 2011). Some of the major applications of nanotechnology in the agricultural sector include: nanoformulations used in crop improvement as fertilizers and pesticides, nanodevices developed for genetic improvements of stocks in plants, nanosensors for determination of diseases and other

techniques to enhance animal breeding, health and post-harvest management (Peralta *et al*., 2020). A humongous amount of agricultural wastes are generated every year due to their perishable nature and persistence of insects and pests (Sekhon, 2014). Thus, nanotechnology has made it possible to comprehend insecticide resistance mechanisms in real time and reduced the need for plant protection products. Nanocapsules have been developed to eradicate the occurrence of diseases and to help in the early detection of diseases (Sekhon, 2014). In the current scenario, there have need to develop reliable, cheap and fast systems to detect and monitor biological host molecules in agricultural sectors. In the modern world, there have been a great advancements in agriculture. Thus, there is a need for agrochemicals such as fertilizers and pesticides to be produced efficiently and sustainably (Servin and White, 2016). Nanobiosensors have been developed for biochemical analysis and detection of mycotoxins in food products. They have high sensitivity, stability and are compact to use.

Types of nanotechnology systems and their applications in agriculture

The nanotechnology systems that have been effectively and efficiently used in various agriculture fields are nanoparticles, nanoemulsions, nanosuspensions, nanocapsules, agri-based materials in nanocomposites, nanosensors, *etc*. Table 1 enlists the different nanosystems and their uses in the agriculture sector (Zaytseva and Neumann, 2016).

Nanoparticles

Nanoparticles are the solid colloidal particles ranging from 1-100 nm in size. They are classified into nanospheres [in which the material to be delivered is evenly dispersed], nanocapsules (in which the material to be delivered is encapsulated in a polymer membrane and confined to a cavity), solid lipid nanoparticles, polymeric nanoparticles, magnetic nanoparticles, polymeric micelles, ceramic nanoparticles, metallic nanoparticles, semiconductor nanoparticles, *etc*. (Chhipa, 2019). Nanoparticles can further be classified as metallic and non-metallic nanoparticles. Metal oxides nanoparticles such as TiO_2, Fe_2O_3, CuO show photocatalytic characteristics. They have the property of interacting with photons and when the incident energy is greater than the energy bandgap, an electron is excited to the conduction band (Fraceto *et al*., 2016). This creates a positive hole for hydroxyl radicles in the valance bond, thus leading to degradation reactions. Nanoparticles exhibiting such properties can be exploited to treat wastewater, agricultural waste and to remove persistent pollutants such as pharmaceutical compounds, dyes and recalcitrant (Fraceto *et al*., 2016). Plant diseases caused by bacteria, insects, fungi, nematodes and viruses are responsible for major devastations of agricultural products (Rizwan *et al*., 2014). Most of the inorganic nanoparticles like silver, Zinc oxide, TiO_2, Magnesium and Silicon have been utilized to act on the fungal diseases (Rizwan *et al*., 2014).

Table 1: Nanotechnology systems and their potential uses in agriculture.

Nanotechnology systems	Uses	References
Nanoparticles	Carbon nanotubes in agrochemicals, Silver nanoparticles in antimicrobial, Gold nanoparticles in nanomedicines, nanodiagnostics, Nanoclay in antimicrobial, filler for composites, Metal oxides [*e.g.*, TiO_2, ZrO] in disease control, fertilizer, agrochemical applications, Biochar in sorption, filtration media, soil amendment	Zaytseva and Neumann (2016)
Nanocapsules	Improved delivery, increased stability, controlled release of agrochemicals	Walz *et al*. (2017)
Nanogels	Encapsulation of active ingredient	Abd Elrahman and Mostafa (2015)
Nanoemulsions and suspensions	Increased solubility, potency, accessibility and controlled release of the active ingredient	Mousavi and Rezaei (2011)
Nanosensors	Detection of agrochemicals, pathogens, moisture, pH, *etc*., detection of environmental pollutants	El Beyrouthya and El Azzi (2014)
Nanocomposites	Nanoclay as fillers for food packaging film, Metal oxide fillers as antimicrobials	Ashfaq *et al*. (2020)
Agri-based materials in nanocomposites	Starch and cellulosic derivatives as polymeric matrix, Nanocellulose as filler, Agri-based materials as compatibilizing agents	Gupta (2018)
Nanobarcodes: Smart cards for plants and animals for identification and tracking	In information technology	Pramanik *et al*. (2020)

Ag nanoparticles can cause suppression of anthracnose pathogen *Colletotrichum* spp. in field trials. Ag nanoparticles combined with the fungicide fluconazole had the greatest anti-fungal activity against *Pleospora herbarum*, *Trichoderma* sp., *Candida albicans, Phoma glomerata* and *Fusarium* (Rizwan *et al*., 2014). ZnO nanoparticles have proven to be a more appropriate choice for fungal pathogen control than Ag. ZnO nanoparticles demonstrated higher inhibition (26%) against *Fusarium graminearum* in comparison to bulk ZnO because of the high surface area exposure to the fungi (Singh *et al*., 2015). Nanotechnology has proved to be a compelling approach to control the ever-increasing viral strains affecting the plants (Prasad *et al*., 2017). Green synthesis of silver nanoparticles using the spore crystal mixture of *Bacillus thuringiensis* was effective in complete suppression of sun hemp rosette virus on cluster bean leaves (Prasad *et al*., 2017). Many different nanoparticles *i.e*., silver nanoparticles, aluminum oxide nanoparticles, zinc oxide nanoparticles, titanium oxide nanoparticles are used to control the *B. mori* nuclear polyhedrosis virus (Prasad *et al*., 2017). For nutrient release, biodegradable, polymeric chitosan nanoparticles (78 nm) have been used for controlled discharge of NPK (Nitrogen, Phosphorous, Potassium) fertilizer sources equivalent to urea, calcium phosphate and potassium chloride (Manjunatha *et al*., 2016). Soil amended with metallic CuNPs significantly increased 15-day lettuce seedling growth. They had the potential to reduce the toxicity of the soil and decrease the frequency with which the fertilizers are applied in the fields (Manjunatha *et al*., 2016).

Carbon nanotubes (CNTs)

CNTs are hexagonal networks of carbon atoms present as a layer of graphite rolled into a cylinder (Kizilbash *et al*., 2020) with a diameter of 1 nm and a length ranging from 1-100 nm. Two types of CNTs are: Multi walled CNTs (MWCNTs) and Single walled CNTs (SWCNTs). They have a distinct size, shape and have remarkable physical and physicochemical properties. These have an ordered structure, high electrical and thermal conductivity, a high aspect ratio, high mechanical strength, metallic or semi-metallic behavior and high surface area. A number of CNT-based nanomaterials have been developed due to their potential applications in regulating plant growth (Patel *et al*., 2020). CNTs have shown to enhance the biomass productivity and yield by inducing changes in metabolic functions of plants. It has been reported that MWCNTs bolstered plant growth and seed germination in lettuce, radish, rye, maize, cucumber, rapeseed, *Phaseolus mungo* L. and *Brassica juncea* L (Patel *et al*., 2020). Similarly, it has been reported that SWCNTs induced seed germination in tomato, carrot, onion cucumber and lettuce. They have also shown a significant increase in the root length of ryegrass. Most of the CNTs are generally absorbed by plants (Patel *et al*., 2020). The factors affecting the absorption include the types of CNTs used and plant species (Patel *et al*., 2020). Depending upon the properties of the CNTs such as concentration, size, structure and chemical properties, their effect on plants can be neutral, positive or negative. Several cases have been reported that interaction with CNTs has led to change in gene expression and biological pathways. MWCNTs are used to enhance the fruit production in plants, however over absorption could lead to shrinkage of cytoplasm, generation of vacuoles and disappearance of nuclei (Peralta *et al*., 2020).

When citric acid molecules were mixed with MWCNT-designated pesticides such as Zineb and Mancozeb and entrapped in aqueous solution, it led to the encapsulation of the pesticides, which damaged the fungi *Alternaria alternate* (Mukherjee *et al*., 2016). Multi-walled Carbon nanotubes in conjugation with iron coated nanoparticles have been used to remove Chromium [III] (Rudakiya *et al*., 2019). MWCNTs have been used to adsorb Procion Red MX-5B dye from various industrial effluents. There has been an increment in seed germination rate and vegetative biomass of tomato seeds with the aid of MWCNTs (Rudakiya *et al*., 2019). Here, penetration of cell wall by nanoparticles led to an increase in uptake of water by seeds, which caused the enhancement in germination percentage (Rudakiya *et al*., 2019). Multiwalled carbon nanotubes have been used to enhance water and nutrient (Ca, Fe) uptake to facilitate the germination of seeds and growth of plants. It has been reported that there is a great enhancement in root elongation in rape, ryegrass and corn by MWCNTs. SWCNTs exposure to cucumber seedlings and onion enhanced their root growth (Rudakiya *et al*., 2019).

Quantum dots (QDs)

Quantum dots are semiconducting materials made up of a core, shell (to improve optical properties) and a cap (to enhance solubility in aqueous buffers). They are neither atomic, nor bulk material. Their size ranges from 10-100 Å (Mukhopadhyay, 2014). These have a bright fluorescence, narrow emission, broad UV excitation and high photo stability. ZnCdSe/ZnS core shell QDs, InP/ZnS core shell QDs, Mn/ZnSe QDs, gold nanorods, core shell QDs, *etc*. have been used in controlled release of trace elements (Mukhopadhyay, 2014). QDs exhibit several properties such as narrow and symmetric broad absorption spectra, high cell permeability, high hydrophobicity which are relevantly applicable in agricultural sector (Walz *et al*., 2017). It has been reported that Carbon QDs integrated with thionin increased the disease resistance ability of rice plant. There is a correlation between the structures of plant hormones and metabolic fate of CQDs. Thus, it leads to the promotion of plant growth (Walz *et al*., 2017). Nowadays, researches are being carried out to synthesize green engineered CQDs (Prasad *et al*., 2017). Semiconductors are used for the synthesis of QDs because of narrow and symmetric fluorescence spectra, high resistance to photobleaching, high quantum yield and large effective excitation, high molar extinction coefficients and exceptional resistance to photochemical degradation. QDs are widely used in the bioimaging field and fabricating nano biosensors. It has been shown that low concentration of QDs exhibit no detectable

cytotoxicity for growth and seed germination. Thus, it has also been used as a delivery systems and live imaging of plant root systems to thoroughly understand the physiological processes (Prasad *et al*., 2017).

Nanocomposites

These are the composite materials with at least one dimension equal to 1nm. They are the materials with atoms arranged in nanosized clusters, which become the constituent grains or building blocks of the material. They have excellent mechanical strength, toughness and electrical or thermal conductivity. Nanocomposites are categorized according to their matrix material such as ceramic, metal or polymer nanocomposites. Some of the examples of nanocomposites used in agriculture are- ceramic matrix nanocomposites, elastomeric nanocomposites, bio nanocomposites, polymer-matrix nanocomposites and polymer- silicate nanocomposites *etc*. (Ashfaq *et al*., 2020). Some nanocomposites have shown to be 1000 times tougher than the bulk component materials. They have been used for controlled and timely release of nutrients from the fertilizer granules, which considerably reduces the loss of nutrients and simultaneously enhances the crop yield (Ashfaq *et al*., 2020).

Nanocomposites have been widely used as pesticides. Although the mechanism of nanocomposite is still elusive, it has been widely used to eradicate various pests such as fungal, bacteria and microorganisms (Gupta, 2018). Metal nanocomposites tend to bind with different cellular organelles such as lysosomes, endoplasmic reticulum, mitochondria, Golgi bodies and ribosomes after entering into the microbial cell. Nanocomposites disrupt the metabolic processes occurring in a metabolic cell affecting the biochemical processes after penetrating into specific cell organelles. They exhibit toxic behavior against mitochondria and induce oxidative stress by generating reactive oxygen species (Gupta, 2018). They further disrupt all other necessary processes such as ATP production, inhibition of protein synthesis and DNA replication, disrupt the permeability of the membrane by inhibiting the process of microbial respiration. Moreover, they also react with the H-bonding of DNA and disrupts mRNA synthesis leading to cell death (Gupta, 2018). It has been reported that nanocomposites have a profound effect on plant growth. Silver nanocomposites have a positive effect on enriching soil bacterial diversity and help to grow root and shoot parameters of wheat, *Brassica* and cowpea (Ashfaq *et al*., 2020). Gold nanocomposites have shown to enhance nutrient efficiency by promoting soil enzyme and microbial community. A report has shown that combination of silver, zinc, carbon and titanium nanocomposites help the growth of *Piriformospora indica*. Silver nanocomposites have shown to impart antifungal activity against *Bipolaris sorokiniana* in wheat plants along with *Serrati sp*. Copper nanocomposites showed antibacterial activity against *E. coli* and *Micrococcus luteus* (Ashfaq *et al*., 2020).

Zeolite

Zeolites are crystalline, microporous aluminosilicates which are found on earth's surface and in soils, seafloor deposits, hydrothermal alteration products, altered volcanic deposits, sediments, *etc*. (Nakhli *et al*., 2017). Their structure resembles a sponge but with a difference of being rigid, unlike the flexible sponge. Zeolites are classified on the basis of their pore diameter and ring size. Zeolites have been widely used in agriculture due to their exceptional properties such as desorption, special cation exchange and molecular sieving. They are widely used as fertilizers, chelators, stabilizers and as organic and inorganic fertilizers. Due to their large porosity, they have high affinity for potassium and ammonium cations. They can be exploited as carriers of nutrients and they have been widely employed in agriculture for storage, capture and slow release of nitrogen (Mahesh *et al*., 2018). They help to reduce the loss of nitrogen in agricultural field by trapping most of the ammonium in the fields. Zeolites with charged ammonium charged have shown to enhance the solubilization of phosphate minerals. They showed an increase uptake of phosphorous by sudangrass. They are also used as nitrogen fertilizer by increasing the uptake of nitrogen uptake in crop production systems (Mahesh *et al*., 2018). Zeolites have been successfully modified as a potting media in horticulture and used for the subsequent release of nutrients and substrates for growth of plants (Sangeetha and Baskar, 2016). However, some of the inorganic zeolites such as erionite have proved to be harmful for humans and cattle. Some of the zeolites are used to improve the availability of P from N-NH4+ *etc*. and increase the efficiency of water holding capacity of the plants. Zeolites have caused increased efficiency of nitrogen uptake in rice plants. Surfactant modified zeolites are widely used as an excellent sorbent for nitrate uptake which helps in the process of nitrification. Moreover, they have the capacity to enhance water retention and absorption of NPK fertilizers. They are used to control overuse of herbicides. Humic acid zeolites have proved to remove extra atrazine from soil and absorb phenylurea herbicides. Due to the crystalline nature of zeolites, they have high porous structure which holds more than half of their weight of water and improves soil physical properties. They can act as permanent water reservoir to the roots and promote rapid rewetting and keep the soil aerated and moist (Sangeetha and Baskar, 2016).

Nanobarcodes

Nanobarcodes are used as identification tags in agricultural biotechnology as they are small in size and can make a large number of combinations. The materials to be used to make a nano barcode should be easily encodable, machine-readable, durable, sub-micron sized taggant particles (Sertova, 2015). Nanobarcodes have been employed in various aspects of agriculture biotechnology, such as improvement in the plant resistance against various environmental stresses like drought, salinity, diseases, cost-effective detection of pathogens from food products, *etc*. (Sertova, 2015). In current scenario, it has become a practice to apply identification tags in livestock products and wholescale agriculture. Because of their miniature size, they have been widely used in multiplexed bioassays. An ideal nanobarcode should be- durable, easily encodable and