



Nanotechnology in Agriculture: A Review

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ABSTRACT

To satisfy the food demands of alarmingly increasing world population, it has become mandatory to shift our focus towards improvement in agriculture sector with the aim to increase crop production. The establishment of mankind area under production is very limited, hence the only option for increasing production per unit capita can be taken under consideration. Although, there are many other factors that decreased crop production including abiotic and biotic stress, environment pollution and soil fertility and productivity. But, among all these soil fertility and productivity are the most important constrains to be maintained for achieving the desired goal of increased production. Also, continuous use of various agrochemicals in the form of fertilizer, pesticides and insecticides degrade the physical structure of soil, change chemical equilibrium and also destroy the soil microbial population, hence resulting in decreasing in soil fertility and productivity which in turn affects the crop production. But with the fast moving world or the world of technologies, a new technique of nanotechnology is adopted to overcome this problem. Different materials when reduced to nanoscale, shows some properties which are different from what they exhibited earlier, enabling unique and much wider range of application. Nanotechnology introduces a variety of agricultural practices in various agricultural field like nanoform zeolites for slow release and efficient dosage of water and fertilizers, nanosensors for soil quality and pest detection, nanomagnets for removal of soil contaminants, nano-filtration and desalination, diagnosis of nutrient disorders in plants, shelf life of food products, seed and weed management etc. Nanotechnology is emerging as a new science, which raise hope for new innovation in agriculture sector.

Key word: Nanotechnology, Nanofertilizer, Agriculture and Production.

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INTRODUCTION

Agriculture is the key food providing sector for humans, directly and indirectly. In order to cope up with the ever increasing demands of world population, it is necessary to use the modern technologies such as nanotechnology in agricultural sciences. Nanomaterials are at the leading edge of rapidly developing field of nanotechnology. According to the National Nanotechnology Initiative (NNI), "Nanotechnology research and development is directed towards understanding and creating improved materials, devices and systems that exploit nanoscale properties" [1].

The term "nano" is derived from the Greek word meaning "dwarf." Also it means 10^{-9} or one billionth part of a meter. Particles with at least one dimension less than 100 nm are considered as "nanoparticles" [2]. These particles have wide applicability range as these have high surface area to volume ratio, nanometer regime, and unique properties, which makes them highly applicable. Nanotechnology is emerging as a promising tool in the field of interdisciplinary research. It owns enormous potential uses and benefits. In developing countries, a large proportion of population faces daily food shortages because of various environmental impacts. For developing countries, the drive is to develop drought and pest resistant crops, which also maximize yield. The application of nanotechnology to agriculture and food industries is also a eye catching topic now a day. Agriculture investments have high range of benefits range from improved food quality and safety to reduced agricultural inputs and improved processing and nutrition. Nanoparticles also have a number of other applications in agriculture system, viz., detection of pollutants, plant diseases, pests, and pathogens, controlled delivery of pesticide, fertilizers, nutrients, and genetic material; and can act as nanoarchitects in formation and binding of soil structure [3]. Nanoparticles can

result in modification of plant gene expression and associated biological pathways which ultimately affect plant growth and development [4].

NANO-AGROCHEMICALS

Nowadays the use of agrochemicals in agriculture has reached a peak. There are various agriculture chemicals including pesticides fertilizers and many more. Pesticides share a wide range among them, having a total consumption of about 400 million tonnes in world. Their use is generally associated with a number of problems like high persistence, low degradability, non-targeted effects etc. Nanopesticides are one of the new strategies being used to address the problems of pesticides. Nanopesticides cover a wide variety of products, some of which are already on the market. In general, these are not considered as a single entity; rather such nanoformulations combine several surfactants, polymers (organic), and metal nanoparticles (inorganic) in the nanometer size range. A versatile tool among this is microencapsulation used for hydrophobic pesticides, which enhances their dispersion in aqueous media and allowing a controlled release of the active compound. Nanomaterials serve equally as additives (mostly for controlled release) and active constituents. A well known example of microencapsulation is the Controlled-release (CR) formulations of imidacloprid (1-(6-chloro-3-pyridinyl methyl)-N-nitroimidazolidin-2-ylideneamine), synthesized from polyethylene glycol and various aliphatic diacids. These have been used for efficient pest management in different crops. In another study the bioefficacy of the prepared CR formulations and a commercial formulation were evaluated against major pests of soybean [5]. Most of the CR formulations of imidacloprid performed better as compared to its commercial formulations in controlling of the pests. However, of the CR formulations, poly (oxyethylene-1000)-oxy-suberoyl amphiphilic polymer-based formulation performed better than others for controlling of both stem fly incidence and Yellow Mosaic Virus infestation transmitted by white fly. In addition, some of the developed CR formulations recorded higher yield over commercial formulation and control.

Halloysite

Halloysite, a naturally found clay nanotube with diameters typically smaller than 100 nanometers and length ranging from 500 nm to over 1.2 μm was found by a start-up company in Rochester, New York. They used it for a low cost delivery for pesticides in order to achieve an extended release and better contact with plants. An estimated reduction of about 70 or 80 percent was observed in pesticides applied with a significant reduction in quantity and cost of pesticides as well as less impact on water streams [6].

Nano-Fertilizers

Fertilizers play an axial role in enhancing the food production in developing countries especially after the introduction of high yielding and fertilizer responsive crop varieties. In spite of this, it is known that yields of many crops have begun to depression as a result of imbalanced fertilization and decrease in soil organic matter. Moreover, excessive applications of nitrogen and phosphorus fertilizers affect the groundwater and also lead to eutrophication in aquatic ecosystems. Such cases along with the fact that the fertilizer use efficiency is about 20-50 percent for nitrogen and 10-25 percent for phosphorus fertilizers implies that food production will have to be much more efficient than ever before. Indeed, nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as fertilizer carriers or controlled-release vectors for building of so-called "smart fertilizer" as new facilities to enhance nutrient use efficiency and reduce costs of environmental protection.

Phosphate-Based Nano-particles as Fertilisers:

Phosphorus is an important nutrient and phosphate based nano-particles have capacity to be used as P-nano-fertilizer for agriculture use. These are applicable for heavy metal remediation by forming highly insoluble and stable phosphate compounds [7]. Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) particles (~10nm) and apatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) particles (<200nm) are phosphate based nano-particles. Vivianite nano-particles synthesized with sodium carboxymethyl cellulose (CMC) as a stabilizer for in situ immobilization of lead in soils. Vivianite can effectively reduce the TCLP (toxicity characteristic leaching procedure) leach-ability and PBET (physiologically-based extraction test) bio-accessibility of Pb^{2+} in calcareous, neutral, and acidic soils. Compared to soluble phosphate used for in situ metal immobilization, use of the vivianite result in 50% decline in phosphate leaching into the environment [8].

Nitrogen Based Nano-particles as Fertilisers:

Nitrogen is a primary essential nutrient responsible for greater biomass production in agriculture. Conventional Nitrogen fertilizers with particle size dimensions greater than 100nm are used at a large scale. A huge amount of applied Nitrogen fertilizer lost from soil via leaching, emission as ammonia and nitrogen oxides, and soil microorganism-mediated incorporation into soil organic matter over time. To overcome these losses the nano-strategies emerging out in which, nano-fertilizers are expected to be far more effective to reduce these losses even than polymer-coated conventional slow-release fertilisers due

to their high surface area to volume ratio. A nano-strategy involving a slow-release fertilizer combination based on urea-modified hydroxyl-apatite (HA) nano-particles encapsulated into the cavities exist in soft wood. HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) nano-particles are rated as one of the outstanding candidates in agricultural applications, which can supply phosphorus nutrient [9].

Iron Based Nano-particles as Fertilizers:

Iron is the metal used at the active site of many essential redox enzymes dealing with cellular respiration and oxidation reduction in plants and animals [10]. Although, Iron is abundant in soil even than its shortage is common for plants as it is present in insoluble form. Only a small amount of iron is soluble ($\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})^{+2}$, Fe^{+3} , Fe^{+2}). Iron is a crucial element for growth of plants, lack of iron causes chlorosis and significantly reduction in photosynthesis activity and consequently biomass produced [11]. Iron chelate nano-fertilizer can be recognized as a rich and decisive source of bivalent iron for plant because of its high stability and slow release of iron in a broad pH range (3-11). Absence of ethylene compounds in its structure is a benefit of this nano-fertilizer. Ethylene enhances growth progress and restricts chlorosis leaves. Second advantage of these nano-fertilizers is increasing ratio of ferrous iron to ferric iron in chelate surface which results in increasing synthesis of chlorophyll in plant [12].

Zinc Based Nano-particles as Fertilizers:

The deficiency of zinc has been identified as one of the main problem limiting agricultural productivity in alkaline calcareous soils. Thus, zinc is often included in all macronutrient fertilizers to enhance crop production and quality. On addition of zinc fertilizers to soil, zinc transforms gradually from more active and available fractions into less available species such as precipitates (i.e., ZnCO_3) and adsorbs to oxide phases (e.g., Fe-, Al-oxides). However, the availability of zinc to plants in calcareous soils mainly depends on the diffusion of zinc from fertilizer granules to the plant root. Nano-material sciences can be applied in designing more soluble and diffusible sources of zinc fertilizer for there better efficiency. The smaller size, higher specific surface area and reactivity of nano-particulate ZnO compared to bulk ZnO may affect zinc solubility, diffusion and hence availability to plants [13].

Aluminium Based Nano-particles as Fertilizers:

Nano-aluminium is widely being used in various industries. Hence, there is great chance for the interaction of such nano-materials with higher plant that constitutes a major portion of the ecosystem. Pure alumina nano-particles reduced root elongation in various plants like, *Zea mays*, *Cucumis sativus*, *Glycine max*, *Daucus carota* and *Brassica oleracea* thus potentially retarding the growth of plants [14]. However, it was surprising, that when nano-particles were loaded with phenanthrene (polycyclic aromatic hydrocarbons) their toxicity significantly decreased showing no adverse effects on roots of plants. This showed the relevance of proper surface modifications which reduce the phyto-toxicity of nano-particles. The impact of aluminium oxide with carboxylate ligand coating particles (100nm) on plants shows no adverse effect on the growth [15]. An increase in concentration of aluminium by 2.5-fold above control tests was observed in rye grass whereas no uptake of aluminium was observed in kidney beans which inferred the difference in uptake and distribution efficiency of even the same kind of nano-particles by different plants.

Zeolites for water retention and also as nano fertilizer

Nano clays and zeolites that are a group of naturally occurring minerals with a honeycomb-like layered crystal structure are other strategies for increasing fertilizer use efficiency [16]. Zeolites are naturally occurring crystalline aluminium silicates that can significantly improve the water retention of sandy soils and increase porosity in clay soils. Its network can be filled with nitrogen, potassium, phosphorous, calcium and a complete set of minor and trace nutrients. So acts as a nutrients supply that are slowly released "on demand".

NANOMATERIALS AS SMART DELIVERY SYSTEMS FOR DISEASE AND PEST CONTROL

Nanocapsule and nanoparticle are the most relevant nanodevices for plant protection. In a nanocapsule, there is a shell containing an active compound against pests or diseases. Various constituents of the shell may be polymers, lipids, viral capsids or nanoclays. Main function of the shell is to protect the active compound until it is released, but it can also improve the solubility and the penetration of the compound into the plant tissues. The slow and gradual or complete release of active compound after the shell opening depending on the specific characteristics of the shell is triggered by certain circumstances (e.g. pH changes or enzymatic degradation). These nanoparticles have a solid core or a matrix that can be composed by different materials (such as metals or polymers) and is surrounded by linkers and biomolecules.

The use of nanodisks for delivering amphotericin B, an important antimicrobial, is a well known example of application of nanocapsules for plant protection is. The nanodisk is a matrix composed by a bilayer of

phospholipids containing the molecules of amphotericin inside. This structure protects amphotericin molecules against the degradation by external agents (e.g. pH or light) while improves its solubility. A nanogel prepared from a pheromone, methyl eugenol (ME) using a low-molecular mass gelator. It has a significant potential for crop protection, long lasting residual activity, excellent efficacy, favorable safety profiles and well-suited for pest management in a variety of crops[17]. Sulfur nano particles (SNPs) used as a green pesticide on *Fusarium solani* and *Venturia inaequalis* phytopathogens. It has been found that small sized particles of SNP (~35 nm) are very effective in preventing the fungal growth and can be useful for the protection of important crops such as tomato, potato, apple, grape *etc.*, from different diseases, mainly for organic farming[18].

While medical applications are intended to protect or cure one individual at a time, plant protection in agriculture is a massive treatment for thousands of plants. Therefore, it is important that the active compound is applied in relatively small doses to cover large plant surfaces. The characteristics of the product must thus be designed taking into account these wide treatments, and also if the mechanism of action is systemic or by contact. An important aspect concerning plant protection products involves the way in which they are absorbed by the plant and their translocation within the plant tissues and organs.

Starch-based nanoparticles in sustainable agriculture

Sustainable production methods also make use of agricultural nanotechnology such as organic agriculture. Indeed, the Department of Agriculture, Forest, Nature and Energy (DAFNE) at the University of Tuscia in Italy is carrying out a research project for the development of starch-based nanocontainers for the delivery of nutrients, biostimulants and crop protection molecules into the plants tissues. The clear advantage of this approach is that starch is biocompatible, biodegradable and non-toxic for plants, animals and the environment.

The first step to develop starch nanocontainers is to produce starch with improved content of amylose, which is the linear fraction composing starch and determines its functional properties, and therefore easily obtain starch particles with reduced size. This is possible through improved wheat varieties with higher amylose content obtained by molecular mutagenesis techniques. The next step is the sustainable preparation, functionalization and characterization of starch nanoparticles. The main approach adopted to produce nanoparticles from starch is based on the acid hydrolysis of starch granules. But these methods have several drawbacks also, like long duration, low yield and various environmental concerns about the production of toxic wastes. In order to overcome these problems, it is the successful application of ultrasounds. These act as an eco-friendly approach for the production of wheat starch nanoparticles, without the need of any additional chemical reagent. Once nanoparticles are produced, their surface has to be functionalized: their physical-chemical and biological properties must be chemically or enzymatically modulated to obtain the entrapment of molecules to be delivered and released in a controlled way. Starch nanocontainers can be employed to deliver nutrients into plants tissues at slow release rates for the long-term feeding of plants, and to protect phosphorus and micronutrients (e.g. iron, manganese, zinc) in alkaline soils. Biostimulant compounds can also be released slowly through nanocontainers according to the plant needs, while being protected from microbial degradation before plant uptake. Also, starch nanocontainers can be developed for the delivery of plant protection products, e.g. antibacterial active principles, which can also be suitable for organic agriculture (e.g. vegetal extracts, copper) and thereby used in smaller amounts. On horticultural as on stone fruit plants, recent successful experiences (in greenhouse as well as in open field) revealed the great potentiality of these nanocontainers to protect the plants along the time against harmful pathogens.

APPLICATIONS OF NANOTECHNOLOGY IN FOOD INDUSTRY

Oxygen is one of the major problematic factors in food packaging. It makes the packed food rancid, foul smelling and unfit for consumption. But, in order to prevent the situation of rancidity and food deterioration nanotechnology has become an indispensable tool in the food industry. It is developing new plastic for food packaging industry, using nano particles in the production of these plastics. Nano particles have been found to be in a zig-zag pattern in the new plastic, and hence prevent the penetration of oxygen by acting as a barrier. In other words, the oxygen for entry into package should during longer route, and hence with the long route for oxygen molecules, food can be spoiled later. Polymer-silicate nano composites have also been reported to have improved gas barrier properties, mechanical strength, and thermal stability. In glass bottles nanoclay-nylon coatings and silicon oxide barriers are used to impede gas diffusion.

Recently, various nano-coatings are produced for fruits that cover the fruits completely, preventing weight loss and shrinkage[19]. Developing smart packaging to optimize product shelf-life has been the goal of many companies. Such packaging systems would be able to repair small holes/tears, respond to

environmental conditions (e.g. temperature and moisture changes), and alert the customer if the food is contaminated. Nanotechnology can provide solutions for these, for example modifying the permeation behaviour of foils, increasing barrier properties (mechanical, thermal, chemical, and microbial), improving mechanical and heat-resistance properties, developing active antimicrobial and antifungal surfaces, and sensing as well as signaling microbiological and biochemical changes [20, 21]. In food and beverage industry, attempts have been made to add micronutrients and antioxidants to food substances. But these antioxidants degrade during manufacturing and food storage. Nano cochleae delivery system protects these substances from degradation. Bio Delivery Sciences International have developed nano cochleae, which are 50 nm coiled nano particles and can be used to deliver nutrients such as vitamins, lycopene and omega 3 fatty acids more efficiently to cells, without affecting the colour or taste of food. The delivery vehicle is made of soyphosphatidylserine which is 100% safe and provides a protective coat for range of nutrient additives [16].

NANOTECHNOLOGY AND AGRI-ENVIRONMENT

The use of various chemicals in the form of pesticides and fertilizers in agriculture in order to improve food production has led to an uncontrolled release of undesired substances into the environment. In addition to prevention of crop from various pest attacks and increasing the yield, these also result in various other associated problems like negative impact on non targeted flora and fauna, dissipation and residues, disturbance in soil microbial health and hence soil structure and Physico-chemical properties of soil. Today, nanotechnology represents a promising approach to improve and remediate all the above said ill effects. Researchers have reported the recent applications of nanotechnologies in agro-environmental studies, paying particular attention to the fate of nanomaterials once introduced in water and soil. They showed that the use of these materials improved the environmental balance and helped in the detection and remediation of polluted sites. Nanoparticulate zero-valent iron has been used for some time for the remediation of waters, sediments, and soils to remove nitrates via reduction and has most recently for detoxifying organochlorine pesticides and polychlorinated biphenyls [22]. However, very few nanomaterials demonstrated potential toxic effects. The impact of iron nanoparticles on terrestrial plants revealed that orange–brown complexes/plaques, formed by root systems of all plant species from distinct families tested, were constituted of nanoparticles containing iron. Further, the formation of iron nanocomplexes was reported as an ideal homeostasis mechanism evolved by plants to modulate uptake of desired levels of ionic iron [23].

Converting carbon dioxide to useful chemicals in a selective and efficient manner remains a major challenge in renewable and sustainable energy research. Silver electrocatalyst converts carbon dioxide to carbon monoxide at room temperature; however, the traditional polycrystalline silver electrocatalyst requires a large overpotential. A nanoporous silver electrocatalyst enables electrochemical reduction of carbon dioxide to carbon monoxide with approximately 92% selectivity at a rate (that is, current) over 3,000 times higher than its polycrystalline counterpart under moderate overpotentials of 0.50 V. The improved higher activity is a result of a large electrochemical surface area and intrinsically higher activity compared with polycrystalline silver.

One of the important steps in the development of plant-based nano-manufacturing is by growing and harvesting organic nanoparticles from plants. It is a significant improvement on the exploitation of plant systems for the formation of metallic nanoparticles. An enhanced system for the production of English ivy adventitious roots and their nanoparticles by modifying GA7 Magenta boxes and identifying the optimal concentration of indole-3-butyric acid for adventitious root growth was developed. It represents a pathway for the generation of bulk ivy nanoparticles for translation into biomedical applications. Recent research has demonstrated that the adventitious roots of English ivy are responsible for the production of an adhesive compound composed of polysaccharide and spherical nanoparticles 60–85 nm in diameter [24]. The recent advances brought into methodology for biological and eco-friendly synthesis and characterization of herbal and medicinal plant-mediated nanoparticles were reported.

NANOCOMPOSITES/NANOBIOCOMPOSITES

Many studies have concluded that composites made from particles of nanosize ceramics or metals smaller than 100 nm can suddenly become much stronger than predicted. For example, metals with a so-called grain size of around 10 nm are as much as seven times harder and tougher than their ordinary counterparts with grain sizes in the hundreds of nanometers. A nanocomposite is a multiphase solid material where one of the phases has one, two, or three dimensions of less than 100 nm, or structures having nanoscale repeat distances between the different phases that make up the material. Nanocomposites are polymers reinforced with small quantities (up to 5% by weight) of nanosized

particles, which have high aspect ratios which are able to improve the properties and performance of the polymer. Polymer composites with nanoclay restrict the permeation of gases. Nanozinc oxide and nanomagnesium oxide are the examples of polymer nanocomposites incorporating metal or metal oxide nanoparticles utilized mainly for their antimicrobial action. Cellulose nanocrystal is also an attractive material to incorporate into composites because they provide highly versatile chemical functionality [25].

CONCLUSIONS

This paper has intended to provide a brief overview of nanotechnology applications in agriculture in the context of an insight of the current situation around the world, and to form the basis of recommendations and future strategies based on some of current scientific knowledge. Some potential beneficial applications, implications for human and environmental health, challenges (including technical, financial and capacity-related challenges) as well as opportunities and strategies for developing countries have been identified. Finally, possible mechanisms for partnerships and collaborations (e.g., between developed and developing countries, public-private, between research institutions and international organizations etc) are also identified and suggested.

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