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RL Manjunatha

Soil Health and Analytical
Department, DSCiGN BIOSYS
Pvt. Ltd., #91/2, Near Isha
Cashew Factory, Kumbalagodu
Industrial Area 2nd Phase,
Dodda Aladamara Road,
Gerupalya, Bangalore,
Karnataka, India

Dhananjay Naik

Soil Health and Analytical
Department, DSCiGN BIOSYS
Pvt. Ltd., #91/2, Near Isha
Cashew Factory, Kumbalagodu
Industrial Area 2nd Phase,
Dodda Aladamara Road,
Gerupalya, Bangalore,
Karnataka, India

KV Usharani

Soil Health and Analytical
Department, DSCiGN BIOSYS
Pvt. Ltd., #91/2, Near Isha
Cashew Factory, Kumbalagodu
Industrial Area 2nd Phase,
Dodda Aladamara Road,
Gerupalya, Bangalore,
Karnataka, India

Correspondence**RL Manjunatha**

Soil Health and Analytical
Department, DSCiGN BIOSYS
Pvt. Ltd., #91/2, Near Isha
Cashew Factory, Kumbalagodu
Industrial Area 2nd Phase,
Dodda Aladamara Road,
Gerupalya, Bangalore,
Karnataka, India

Nanotechnology application in agriculture: A review

RL Manjunatha, Dhananjay Naik and KV Usharani

Abstract

Nanotechnology is science of manipulating materials at nano-scale. It is working with the smallest possible particles which raise hopes for improving agricultural productivity through encountering problems unsolved conventionally. In the management aspects, efforts are made to increase the efficiency of applied fertilizer with the help of nano clays and zeolites and restoration of soil fertility by releasing fixed nutrients. In the controlled environment agriculture and precision farming input requirement of crops are diagnosed based on needs and required quantities are delivered in right time at right place with the help of nano biosensor and satellite system. Nanoherbicides are being developed to address the problems in perennial weed management and exhausting weed seed bank. Nano structured formulation through mechanisms such as targeted delivery or slow/controlled release mechanisms and conditional release, could release their active ingredients in response to environmental triggers and biological demands more precisely. Studies show that the use of nanofertilizers causes an increase in nutrients use efficiency, reduces soil toxicity, minimizes the potential negative effects associated with over dosage and reduces the frequency of the application. Hence, nanotechnology has a high potential for achieving sustainable agriculture, especially in developing countries.

Keywords: Nanotechnology, sustainable agriculture, nanofertilizer, nanoherbicide

Introduction

Agriculture is the backbone of most of the developing countries in which a major part of their income comes from agriculture sector and more than half of the population depends on it for their livelihood. The current global population is nearly 6 billion with 50% living in Asia. A large proportion of those livings in developing countries face daily food shortages as a result of environmental impacts or political instability, while in the developed world there is a food surplus. For developing countries, the drive is to develop drought and pest resistant crops which also maximize yield. In developed countries, the food industry is driven by consumer demand which is currently for fresher and healthier foodstuffs (Anonymous, 2009) [2]. Nanotechnology helps agricultural sciences and reduce environmental pollution by production of pesticides and chemical fertilizers by using the nano particles and nanocapsules with the ability to control or delayed delivery, absorption and more effective and environmentally friendly and production of nano-crystals to increase the efficiency of pesticides for application of pesticides with lower dose.

Nano means one-billionth, thus nanotechnology deals with materials measured in a billionth of a meter. A nanometer is 1/80,000 the diameter of a human hair or approximately ten hydrogen atoms wide. Nanotechnology is the science of very small things. But nanotechnology is not just involved with small things. Nanotechnology is a multi-disciplinary science. It includes knowledge from biology, chemistry, physics and other disciplines. Joseph and Morrison (2006) [23] defined Nano technology as the manipulation or self assembly of individual atoms, molecules or molecular clusters into structures to create materials devices with new or vastly different properties.

Agriculture has always been the backbone of most of the developing countries. It does not only fill the people abdomenbut also fuel the economy. According to 2014-2015 censuses, India's population is 1.27. With the concern of providing food to such a big population there has to be a new technology giving more yield in short period. In that manner, nature is complex which will have imbalances which directly affects plants and crops, and indirectly animals and human. In according to this, other factors which affect agriculture are deficiencies in macro and micro nutrient content, population explosion, industrialization, depletion of water source, difference in soil condition, and erosion of top soil. In agriculture the main reason to use fertilizer is to give full-fledged macro and micro nutrients which usually soil lacks. 35-40 per cent of the crop productivity depends upon fertilizer, but some of the fertilizer affects the plant growth directly. To overcome all these drawbacks a smarter way *i.e.*, nanotechnology can be one of the source. Since fertilizers are the main concern, developing nano based

fertilizer would be a new technology in this field. Fertilizers are sprayed in many ways either to soil or through leaves, even to aquatic environments. These inorganic fertilizers are supplied in order to provide three main components, Nitrogen, Phosphorous and Potassium in equal ratios (Corradini *et al.*, 2010) [8]. Nanofertilizers increases the Nutrient Use Efficiency (NUE) by 3 times and it also provides stress tolerating ability. Irrespective of the type of crop nono technology can be used, nanotechnology increase bio source use and eco friendly in nature, builds carbon uptake and improves soil aggregation. Since these nano fertilizers contain nutrients, growth promoters encapsulated in nano scale polymers, they will also have aslow and a targeted efficient release. Nanotechnology is gathering information of atom in nano scale range, with consideration to physical, catalytic, magnetic and optical properties (Sadik *et al.*, 2009) [45]. However, the concentration of usage chronically exposes soil microbes and micro fauna, as well as the plants themselves, to level of chemical reactivity that may be toxic. When comparing to chemical fertilizers requirement and cost, nano fertilizers are economically cheaper and are required in lesser amount. For years farmers have found that nitrogen uptake is the main reason for improper yield. In the past days development of sensing devices are in boom. When it comes to test a particular analyte from the soil causing disturbance in the filed there are assays which give accurate result but it has a drawback of consumption of time and also the high cost for performing. Sensors are those give better results with the live

pictures and conditions of the field (Ibtisam, 2001) [19]. Sensors do monitor changes or the effects caused by various pesticides, fertilizers, and herbicide, also the physical conditions of soil like pH, moisture level, and growth conditions of crop, stem, fruit or even root, toxicity studies, it can constantly monitor the toxicity produced in the field. Since it is a human friendly sensor it starts detecting and alarms farmer so as to indicate any correct measures to be taken before rather than acting for a consequence later. When it comes to wireless technology certain node installation is carried out which makes the person to monitor the happenings in the field all the nodes can be controlled at the same time through cloud computing or even through air programming. Therefore, various types of new sensors and types of fertilizers are reviewed at glance to place nanotechnology at the highest level.

Properties of the nanoparticles

Two principal factors cause the properties of nanomaterials to differ significantly from other materials increased relative surface area and quantum effects. Morphology-aspect ratio/size, hydrophobicity, solubility-release of toxic species, surface area/roughness, Surface species contaminations/adsorption, during synthesis/history, Reactive Oxygen Species (ROS) O_2 / H_2O , capacity to produce ROS, structure/composition, competitive binding sites with receptor and dispersion/ aggregation are the important properties of nanoparticles (Somasundaran *et al.*, 2010) [53].

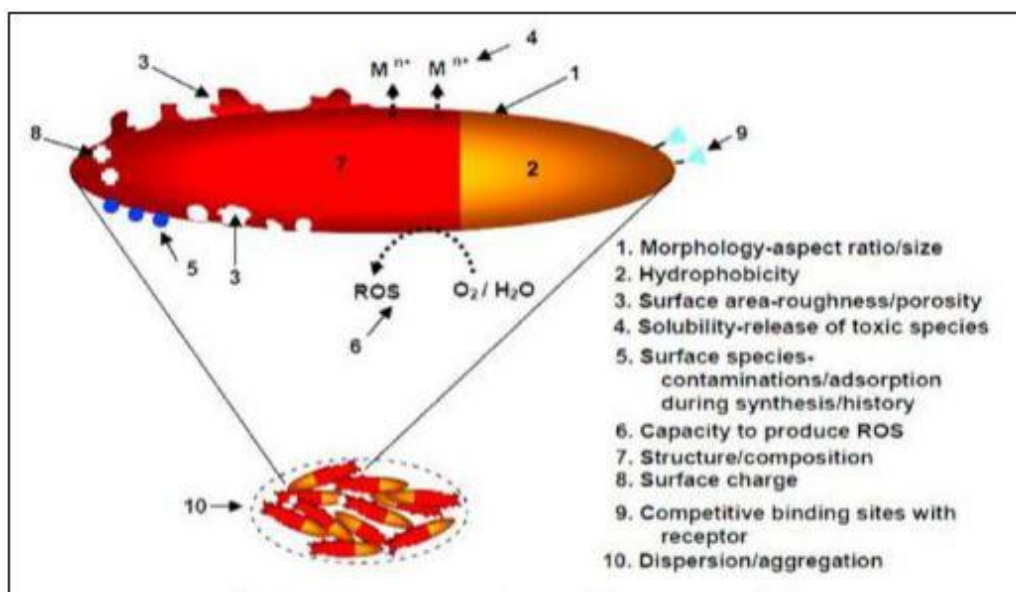


Fig 1: Properties of nanoparticles

Salamanca *et al.* (2005) has categorically grouped the top ten applications of the nanotechnologies and the detailed examples of the applications (Table 1).

Table 1: Top ten applications of nanotechnologies in the developing countries

Rank	Applications	Examples
1	Energy storage, production and conversion	CNT storage of H
2	Agricultural productivity Enhancement	Herbicide delivery
3	Water treatment and remediation	Nano-membranes
4	Disease diagnosis and screening	Lab-on-Chip
5	Drug delivery systems	Nano-capsules
6	Food processing and storage	Coating/packaging
7	Air pollution and remediation	Nano-catalysts
8	Construction	Durability
9	Health monitoring	Sensors
10	Vector and pest detection/control	Sensors and pesticides

Nanotechnology applications in agriculture and food production

Nanotechnology will transform the entire food industry changing the way food is produced, processed, packaged, transported and consumed. The key aspects of these transformations, highlighting current research in the agrifood industry and what future impacts these may have.

1. Nano-Agriculture

Nano biotechnology will increase agriculture's potential to harvest feed stocks for industrial processes. Mean while tropical agricultural commodities such as rubber, cocoa, coffee and cotton and the small-scale farmers who grow them, will find themselves quaint and irrelevant in a new nano economy of "flexible matter" in which the properties of industrial nanoparticles can be adjusted to create cheaper, "smarter" replacements. Just as Genetically Modified (GM) agriculture led to new levels of corporate concentration all along the food chain, so proprietary nano technology, deployed from seed to stomach, genome to gullet, will strengthen the grasp of agribusiness over global food and farming at every stage – all, ostensibly, to feed the hungry, safeguard the environment and provide consumers with more choice. For two generations, scientists have manipulated food and agriculture at the molecular level. Agro-nano connects the dots in the industrial food chain and goes one step further down. With new nano-scale techniques of mixing and harnessing genes, GM plants become atomically modified plants. Pesticides can be more precisely packaged to knock-out unwanted pests and add artificial flavourings and natural nutrients engineered to please the palate. Visions of an automated, centrally-controlled industrial agriculture can now be implemented using molecular sensors, molecular delivery systems and low-cost labour.

The European Union's (EU) vision is of a "knowledge-based economy" and as part of this; it plans to maximize the potential of biotechnology for the benefit of EU economy, society and the environment. There are new challenges in this sector including a growing demand for healthy, safe food, an increasing risk of disease and threats to agricultural and fishery production from changing weather patterns. However, creating a bioeconomy is a challenging and complex process involving the convergence of different branches of science. Nano technology has the potential to revolutionize the agricultural and food industry with new tools for the molecular treatment of diseases, rapid disease detection, enhancing the ability of plants to absorb nutrients *etc.*

2. Precision farming

Precision farming has been a long-desired goal to maximise output (*i.e.* crop yields) while minimising input (*i.e.* fertilisers, pesticides, herbicides, etc) through monitoring environmental variables and applying targeted action. Precision farming makes use of computers, global satellite positioning systems, and remote sensing devices to measure highly localised environmental conditions thus determining whether crops are growing at maximum efficiency or precisely identifying the nature and location of problems. By using centralised data to determine soil conditions and plant development, seeding, fertilizer, chemical and water use can be fine-tuned to lower production costs and potentially increase production all benefiting the farmer. In the Erosion, Technology and Concentration (ETC) group down to farm it is described that precision farming can also help to reduce agricultural waste and thus keep environmental pollution to a

minimum. Although not fully implemented yet, tiny sensors and monitoring systems enabled by nanotechnology will have a large impact on future precision farming methodologies. One of the major roles of nanotechnology-enabled devices will be increased use of autonomous sensors linked into a GPS system for real-time monitoring. These nanosensors could be distributed throughout the field where they can monitor soil conditions and crop growth. The union of biotechnology and nanotechnology in sensors will create equipment of increased sensitivity, allowing an earlier response to environmental changes.

For example:

- Nanosensors utilising carbon nanotubes¹² or nanocantilevers¹³ are small enough to trap and measure individual proteins or even small molecules.
- Nanoparticles or nanosurfaces can be engineered to trigger an electrical or chemical. Signal in the presence of a contaminant such as bacteria.
- Other nanosensors work by triggering an enzymatic reaction or by using nanoengineered branching molecules called dendrimers as probes to bind to target chemicals and proteins. Ultimately, precision farming, with the help of smart sensors, will allow enhanced productivity in agriculture by providing accurate information, thus helping farmers to make better decisions.

3. Encapsulating control

Nanotechnology enables companies to manipulate the properties of the outer shell of a capsule in order to control the release of the substance to be delivered. 'Controlled release' strategies are highly prized in medicine since they can allow drugs to be absorbed more slowly, at a specific location in the body or at the say-so of an external trigger. Pesticides encapsulated in nanomaterials for controlled release, stabilization of biopesticides with nanomaterials, slow release of nanomaterial assisted fertilizers, biofertilizers and micronutrients for efficient use and field applications of agrochemicals, nanomaterials assisted delivery of genetic material for crop improvement. With potential applications across the food chain (in pesticides, vaccines, veterinary medicine and nutritionally-enhanced food).

Examples of nano and microcapsule designs are:

1. **Slow release:** The capsule releases its payload slowly over a longer period of time (*e.g.*, for slow delivery of a substance in the body) (Garrard, 2004)^[13].
2. **Quick release:** The capsule shell breaks upon contact with a surface (*e.g.*, when pesticide hits a leaf)
3. **Specific release:** The shell is designed to break open when a molecular receptor binds to a specific chemical (*e.g.*, upon encountering a tumour or protein in the body)
4. **Moisture release:** The shell breaks down and releases contents in the presence of water (*e.g.*, in soil)
5. **Heat release:** The shell releases ingredients only when the environment warms above a certain temperature
6. **pH release:** Nanocapsule breaks up only in specific acidic or alkaline environment (*e.g.*, in the stomach or inside a cell)
7. **Ultrasound release:** The capsule is ruptured by an external ultrasound frequency
8. **Magnetic release:** A magnetic particle in the capsule ruptures the shell when exposed to a magnetic field
9. **DNA nanocapsule:** The capsule smuggles a short strand of foreign DNA into a living cell which, once released, hijacks cell machinery to express a specific protein (used for DNA vaccines)

4. Nano Sensors

Nanotechnology applications are also being developed to improve soil fertility and crop production. Nano sensors could also monitor crop and animal health and magnetic nanoparticles could remove soil contaminants. "Lab on a chip" technology also could have significant impacts on developing nations. Nanosensors for plant pathogen and pesticide detection, and Nanoparticles for soil conservation or remediation are other areas in agriculture that can benefit from nanotechnology. Enzyme immobilization for nanobiosensor using nanomaterials involves the high value low volume application of enzymes (Kim *et al.*, 2006) [27].

5. Nanotechnology and food systems

Since food systems encompass food availability, access and utilization, the scope of applications of nanotechnology for enhancing food security must encompass entire agricultural production - consumption systems. Further, in a rapidly globalizing economy, increasing access to food and its utilization in rural areas will be determined primarily by increase in rural incomes. The primary source of increasing rural incomes has been recognized as value addition across the different links in the agricultural production consumption chain. These links include farm inputs, farm production systems, post harvest management and processing and finally markets and consumers. From the food security perspective, it is therefore necessary that application of nanotechnology be not limited to the farm production level, but be extended across all the links of the agricultural value chain to increase agricultural productivities, product quality, consumer acceptance and resource use efficiencies. This will help to reduce farm costs, raise the value of production, increase rural incomes and enhance the quality of the natural resource base of agricultural production systems (Sastry *et al.*, 2007) [50]. In doing so, it is important to view nanotechnology as an enabling technology that can complement conventional technologies and biotechnology (Salerno *et al.*, 2008) [47]. Considering the concerns on biosafety and consumer acceptance emerging after agribiotechnology based products have entered the market place during last two decades, it is also essential that integrating and deploying new technologies like nanotechnology in agricultural and food systems be made after understanding the various societal and environmental implications (Sastry *et al.*, 2010) [51].

Assessing nanotechnology for enhanced food security in India

Assessment of emerging technologies like nanotechnology is difficult because historical data is not available for impact assessment and much of the work is at basic research stage with future promise of a range of applications. In such situations, bibliometrics and patent analysis can be used to both assess current status and trends in technology development and classify and map them to relevant application areas for strategic planning (Kostoff *et al.*, 2007; Hullmann and Meyer, 2003) [28, 18]. A general premise is that basic research is found largely in journals; where as potential commercial applications are found in patents. Patent documents are also well structured to provide standardized information about citation, issue date, inventors, institutions and their locations technology field classification *etc.* Such structured documentation makes them suitable for assessing technology developments in various areas. Bibliometric data on the other hand is less precisely structured but amenable to formal key word searches and more intensive text mining

approaches for technology assessment. A holistic systems framework was developed for patent and bibliometric analysis for assessment of the potential of nanotechnology for enhancing food systems security in India.

The framework was developed in two stages:

- i. Mapping nanotechnology to agri-food thematic areas across all the links of the agricultural value chain (farm inputs, production systems, postharvest management including storing and processing, markets and consumption).
- ii. Mapping nanotechnology to the determinants of food security (productivity, soil health, water security and food quality).

6. Nanoparticles based smart delivery systems

Nanoscale devices have the capability to detect and treat an infection, nutrient deficiency, or other health problem, long before symptoms were evident at the macro-scale. Smart delivery systems have the capacity to monitor the effects of the delivery of pharmaceuticals, nutraceutical, nutrients, food supplements, bioactive compounds, probiotics, chemicals, insecticides, fungicides, vaccinations.

Delivery systems in agriculture are important for application of pesticides and fertilizers as well as during genetic material mediated plant improvement. Application systems for pesticides need to focus on efficacy enhancement and spray drift management while fertilizers face problems of bioavailability due to soil chelation, over-application and run-offs. A viable alternative for these problems is provided by controlled delivery systems for the pesticide and fertilizer application. Controlled delivery technique aims towards measured release of necessary and sufficient amounts of agrochemicals over a period of time, to obtain the fullest biological efficacy and to minimize the harmful effects (Tsuji, 2001) [62]. For this purpose micronic and sub-micronic particles were explored as agrochemical delivery vehicles. In comparison to micronic particles ($\square 1000$ nm), nano particles (100 nm) offered the advantage of effective loading due to the larger surface area, easy attachment and fast mass transfer. Controlled release of the active ingredient is achieved due to the slow release characteristics of the nanomaterial, bonding of the ingredients to the material and the environmental conditions. In case of genetic material, delivery systems face challenges such as limited host range, transportation across cell membrane and trafficking to the nucleus. Nevertheless, the use of NPs assisted delivery for genetic material to develop insect resistant plant varieties is being studied. For instance, DNA-coated gold NPs are used as bullets in 'gene gun' system, for bombardment of plant cells and tissues to achieve gene transfer (Vijayakumar *et al.*, 2010) [65].

a. Delivery of pesticides/biopesticides

Nanotechnology has the potential for efficient delivery of chemical and biological pesticides using nanosized preparations or nanomaterial based agrochemical formulations. The benefits of nano material based formulations are the improvement of efficacy due to higher surface area, higher solubility, induction of systemic activity due to smaller particle size and higher mobility and lower toxicity due to elimination of organic solvents in comparison to conventionally used pesticides and their formulations (Sasson *et al.*, 2007) [49].

Infield, application of NPs for the delivery of pesticides and biopesticides face several challenges such as multiple environmental perturbations, large areas under spray coverage

and finally cost effectiveness. In the usual spraying regime the whole crop is sprayed with the chemical for the ease of application involving a high volume, low value preparation. Whereas nanomaterial based preparations are expected to involve a low volume, high value applications. Such controlled nanoparticulate delivery systems will require a targeted delivery approach focused using the knowledge of the life-cycle and the behaviour of the pathogen or pest.

b. Delivery of fertilizers

Wilson *et al.* (2008) [67] reported that application of large amounts of fertilizer, in the form of ammonium salts, urea, and nitrate or phosphate compounds are harmful. Besides much of the fertilizers are unavailable to plants as they are lost as run-off leaching causing pollution. Nanomaterials have potential contributions in slow release of fertilizers. Nanocoatings or surface coatings of nanomaterials, on fertilizer particles hold the material more strongly from the plant due to higher surface tension than conventional surfaces. Moreover, nanocoatings provide surface protection for larger particles (Brady and Weil, 1999; Santoso *et al.*, 1995) [5, 48]. Fertilizers with sulfur nanocoating (□□100 nm layer) are useful slow release fertilizers as the sulfur contents are beneficial especially for sulfur deficient soils. The stability of the coating reduced the rate of dissolution of the fertilizer and allowed slow sustained release of sulphur coated fertilizer. In addition to sulphur nanocoatings or encapsulation of urea and phosphate and their release will be beneficial to meet the soil and crop demands. Other nanomaterials with potential application include kaolin and polymeric biocompatible nanoparticles used biodegradable, polymeric chitosan nanoparticles (~ 78 nm) for controlled release of the NPK fertilizer sources such as urea, calcium phosphate and potassium chloride (Wilson *et al.*, 2008; Corradini *et al.*, 2010) [67, 8].

c. Field application of nano pesticides and fertilizers

The mode of pesticide and fertilizer application influences their efficiency and environmental impact (Ihsan *et al.*, 2007;

Matthews, 2008; Matthews and Thomas, 2000) [20, 34-35]. Currently spraying of pesticides involves either knapsacks that deliver large droplets (9-66 µm) associated with splash loss or ultra light volume sprayers for controlled droplet application with smaller droplets (3-28 µm) causing spray drift. Constraints due to droplet size may be overcome by using NP encapsulated or nanosized pesticides that will contribute to efficient spraying and reduction of spray drift and splash losses (Hoffmann *et al.*, 2007) [17]. Another practical problem faced during pesticide application in the field is settlement of formulation components in the spray tank and clogging of spray nozzles. The recent nano-sized fungicide (~100 nm, Banner MAXX, Syngent) prevented spray tank filters from clogging, did not required mixing and did not settle down in the spray tank due to the smaller sized particles (Robinson and Zadrazilova, 2010) [43]. Further, more this fungicide did not separate from water for up to one year due to nano-size, whereas fungicides that contained larger particle size ingredients typically required agitation every two hours to prevent clogging in the tank.

Proper application method of optimum quantities of fertilizer maximized nutrient uptake and reduced pollution. The choice of fertilizer application method mainly depends on: soil, crop, irrigation type and the nutrient applied. Current practices involving broadcasting, banding, side dressing and dusting face problems of run-off due to dissolution in soil moisture and leaching. Placement of large amounts of fertilizer near the seeds and reduction in soil moisture caused salt damage. The effect of different methods of nitrogen fertilizer application on the algal flora and biological nitrogen fixation in wetland rice soil was studied in pot and field experiments. In the broadcast method of urea application, nitrogen fixation was inhibited while growth of green algae was favored. In contrast, deep placement of urea granules (1- 2 g) did not suppress the growth of nitrogen fixing blue green algae (Roger *et al.*, 1980) [44]. NP coated fertilizers may contribute to slow release of the fertilizer preventing the rapid dissolution and therefore harm to the environment.

Table 2: Applications of nanotechnology in agriculture (Vandana *et al.*, 2011) [63]

Application	Nano particles	Reference
A. Pesticide delivery		
Chemical		
Avermectin	Porous hollow silica (15 nm)	Li <i>et al.</i> , 2007 [30]
Ethiprole or phenylpyrazole	Poly-caprolactone (135 nm)	Boehm <i>et al.</i> , 2003 [4]
Gamma cyhalothrin	Solid lipid (300 nm)	Frederiksen <i>et al.</i> , 2003 [11]
Tebucanazole/chlorothalonil	Poly vinyl pyridine and poly vinyl pyridine-co-styrene (100 nm)	Liu <i>et al.</i> , 2001 [33]
Biopesticides		
Plant origin: nanosilica for insect control <i>Artemisia arborescens</i>	Nanosilica (3-5 nm)	Barik <i>et al.</i> , 2008 [3]
Essential oil encapsulation	Solid lipid (200-294 nm)	Lai <i>et al.</i> , 2006 [29]
Microorganisms: <i>Lagenidium giganteum</i> cells in emulsion	Silica (7-14 nm)	Vandergheynst <i>et al.</i> , 2007 [64]
Microbial product: absorption of <i>Myrothecium verrucaria</i> enzyme	Chitosan/kaolin (250-350 nm)	Ghormade <i>et al.</i> , 2011 [14]
B. Fertilizer delivery		
NPK controlled delivery	Nano-coating of sulfur (100 nm layer)	Wilson <i>et al.</i> , 2008 [67]
	Chitosan (78 nm)	Corradini <i>et al.</i> , 2010 [8]
Genetic material delivery DNA	Gold (10-15 nm) Gold (5-25 nm)	Torney <i>et al.</i> , 2007 [60]
	Starch (50-100 nm)	Vijayakumar <i>et al.</i> , 2010 [65]
Double stranded RNA	Chitosan (100-200 nm)	Zhang <i>et al.</i> , 2010 [68]
C. Pesticide sensor		
Carbofuran /triazophos	Gold (40 nm)	Guo <i>et al.</i> , 2009 [16]
DDT	Gold (30 nm)	Lisa <i>et al.</i> , 2009 [31]

Dimethoate	Iron oxide (30 nm), zirconium oxide (31.5 nm)	Gan <i>et al.</i> , 2010 ^[12]
Organophosphate	Zirconium oxide (50 nm)	Wang <i>et al.</i> , 2009 ^[66]
Paraoxon	Silica (100-500 nm) Carbon nanotubes	Ramanathan <i>et al.</i> , 2009 ^[42]
Pyrethroid	Iron oxide (22 nm)	Kaushik <i>et al.</i> , 2009 ^[25]
Pesticide degradation Lindane	Iron sulfide (200 nm)	Paknikar <i>et al.</i> , 2005 ^[40]
Imidacloprid	Titanium oxide (30 nm)	Guan <i>et al.</i> , 2008 ^[15]

d. Conventional fertilizers v/s Nano-fertilizers

Conventional fertilizers are generally applied on the crops by either spraying or broadcasting. However, one of the major factors that decide the mode of application is the final concentration of the fertilizers reaching to the plant. In practical scenario, very less concentration to the targeted site due to leaching of chemicals, drift, runoff, evaporation, hydrolysis by soil moisture and photolytic and microbial degradation. It has been estimated that around 40-70% of nitrogen, 80-90% of phosphorus, and 50-90% of potassium content of applied fertilizers are lost in the environment and could not reach the plant which causes sustainable and economic losses (Trenkel, 1997; Ombodi and Saigusa, 2000) ^[61, 39]. These problems have initiated repeated use of fertilizer and pesticide which adversely affects the inherent nutrient balance of the soil.

The large-scale use of chemicals as fertilizers and pesticides has resulted in environmental pollution affecting normal flora and fauna. Tilman *et al.* (2002) ^[59] reported that excess use of fertilizers and pesticide increases pathogen and pest resistance, reduces soil microflora, diminishes nitrogen fixation, contributes to bioaccumulation of pesticides, and destroys habitat for birds. Hence, it is very important to optimize the use of chemical fertilization to fulfill the crop

nutrient requirements and to minimize the risk of environmental pollution. Accordingly, it can be favorable that other methods of fertilization be also tested and used to provide necessary nutrients for plant growth and yield production, while keeping the soil structure in good shape and the environment clean (Miransari, 2011) ^[36]. Nanotechnology has provided the feasibility of exploring nanoscale or nanostructured materials as fertilizer carrier or controlled-release vectors for building of the so-called smart fertilizers as new facilities to enhance the nutrient use efficiency and reduce the cost of environmental pollution (Chinnamuthu and Boopati, 2009) ^[6]. Derosa *et al.* (2010) ^[10] reported that nano-fertilizer refers to a product in nanometer regime that delivers nutrients to crops. For example, encapsulation inside nanomaterials coated with a thin protective polymer film or in the form of particles or emulsions of nanoscale dimensions. Surface coatings of nanomaterials on fertilizer particles hold the material more strongly due to higher surface tension than the conventional surfaces and thus help in controlled release. Delivery of agrochemical substance such as fertilizer supplying macro and micronutrients to the plants is an important aspect of application of nanotechnology in agriculture.

Table 3: Comparison of nanotechnology based formulations and conventional fertilizers applications (Cui *et al.*, 2010)

Properties	Nano-fertilizers-enabled technologies	Conventional technology
Solubility and dispersion of mineral micronutrients	Nano-sized formulation of mineral micronutrients may improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation, and increase the bioavailability	Less bioavailability to plants due to large particle size and less solubility
Nutrient uptake efficiency	Nano structured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer	Bulk composite is not available for roots resource and decrease efficiency
Controlled release modes	Both release rate and release pattern of nutrients for watersoluble fertilizers might be precisely controlled through encapsulation in envelope forms of semipermeable membranes coated by resin-polymer, waxes and sulfur	Excess release of fertilizers may produce toxicity and destroy ecological balance of soil
Effective duration of nutrient release	Nanostructured formulation can extend effective duration of nutrient supply of fertilizers into soil	Used by the plants at the time of delivery, the rest is converted into insoluble salts in the soil
Loss rate of fertilizer nutrients	Nanostructured formulation can reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking	High loss rate by leaching, run off, and drift

7. Nanotechnology in crop nutrition

Fertilizers have played a pivotal role in enhancing the food grain production in India especially after the introduction of high yielding and fertilizer responsive crop varieties during the green revolution era. Despite the resounding success in grain yield, it has been observed that yields of many crops have begun to stagnate as a consequence of imbalanced fertilization and decline in organic matter content of soils. Excessive use of nitrogenous fertilizer affects the groundwater and also causes eutrophication in aquatic ecosystems. A disturbing fact is that the fertilizer use efficiency is 20-50 per cent for nitrogen and 10-25 per cent for phosphorus. With nano-fertilizers emerging as alternatives to conventional fertilizers, build-up of nutrients in soils and thereby eutrophication and drinking water contamination may be eliminated. In fact, nano-technology has opened up new opportunities to improve nutrient use efficiency and minimize costs of environmental protection.

It has helped to divulge to recent findings that, plant roots and microorganisms can directly lift nutrient ions from solid phase of minerals. Slow-release of nano-fertilizers and nanocomposites are excellent alternatives to soluble fertilizers. Nutrients are released at a slower rate throughout the crop growth; plants are able to take up most of the nutrients without any waste. Slow release of nutrients in the environments could be achieved by using zeolites that are a group of naturally occurring minerals having a honeycomb-like layered crystal structure. Its network of interconnected tunnels and cages can be loaded with nitrogen and potassium, combined with other slowly dissolving ingredients containing phosphorous, calcium and a complete suite of minor and trace nutrients. Zeolite acts as a reservoir for nutrients that are slowly released on demand. Fertilizer particles can be coated with nanomembranes that facilitate slow and steady release of nutrients.

Tarafdar *et al.* (2012a) [56] reported that nano-fertilizer technology is very innovative and vast scope for the formulation of nano-fertilizers. Significant increase in yields has been observed due to foliar application of nano particles as fertilizer. It was shown that 640 mg ha⁻¹ foliar application (40 ppm concentration) of nanophosphorus gave 80 kg ha⁻¹ phosphorus equivalent yield of cluster bean and pearl millet under arid environment. Currently, research is underway to develop nano-composites to supply all the required essential nutrients in suitable proportion through smart delivery system. Balanced fertilization may be achieved through nanotechnology (Tarafdar *et al.*, 2012b) [57]. Nano-composites being contemplated to supply all the nutrients in right proportions through the “Smart” delivery systems also needs to be examined closely. The nutrient use efficiency is low due to the loss of 50-70% of the nitrogen supplied in conventional fertilizers. New nutrient delivery systems that exploit the porous nanoscale parts of plants could reduce nitrogen loss by increasing plant uptake. Fertilizers encapsulated in nanoparticles will increase the uptake of nutrients (Tarafdar *et al.*, 2012c) [58]. The release of nutrients can be triggered by an environmental condition or simply released at desired specific time. Coating and cementing of nano and subnano-composites are capable of regulating the release of nutrients from the fertilizer capsule (Liu *et al.*, 2006) [32]. A patented nano-composite consists of N, P, K, micronutrients, mannose and amino acids that increase the uptake and utilization of nutrients by grain crops has been reported (Jinghua, 2004) [21]. Adhikari *et al.* (2010) [1] reported that nanofertilizers for slow release and efficient use of water and fertilizers by plants are the prime potential application of the technology. Encapsulation of fertilizers within a nanoparticle is one of these new facilities which are done in three ways a) the nutrient can be encapsulated inside nanoporous materials, b) coated with thin polymer film, or c) delivered as particle or emulsions of nanoscales dimensions (Rai *et al.*, 2012) [41]. In addition, Nano fertilizers will combine Nano devices in order to synchronize the release of fertilizer-N and -P with their uptake by crops, so preventing undesirable nutrient losses to soil, water and air via direct internalization by crops, and avoiding the interaction of nutrients with soil, microorganisms, water, and air (Derosa *et al.*, 2010) [10].

8. Nanostructured formulation reduce nutrients loss into soil by leaching

The solubility and dispersion of insoluble mineral micronutrients, phosphate fertilizers have been significantly improved by nanosized or nanostructured processing. Slow release of nutrients in the environments could be achieved by using zeolites that are a group of naturally occurring minerals having a honeycomb-like layered crystal structure. Its network of interconnected tunnels and cages can be loaded with nitrogen and potassium, combined with other slowly dissolving ingredients containing phosphorous, calcium and a complete suite of minor and trace nutrients. Zeolite acts as a reservoir for nutrients that are slowly released “on demand”. Fertilizer particles can be coated with nanomembranes that facilitate slow and steady release of nutrients (Chinnamuthu and Boopathi, 2009) [6]. Kannan (2011) [24] reported that intake of the nutrients by the crop to an extent of 72 per cent with nanofertilizer and only 42 per cent urea and release of nano-fertilizer where zeolite was used went on for almost 50 days while that of the urea stopped after 12 days where zeolite was used as carrier. One of the advantages of nanoscale delivery vehicles in agronomic applications is its improved

stability of the payloads against degradation in the environment, thereby increasing its effectiveness while reducing the amount applied (Johnston, 2010) [22]. Chinnamuthu and Boopathi (2009) [6] reported that nano-clay particles like substances used will reduce the porosity of the polymer, or otherwise obstructs the diffusion of the active material being released, thereby increasing the length of the path of the diffusion through the host polymer.

9. Application of nanotechnology in seed science

Seed is self perpetuating biological entity that is able to survive in harsh environment on its own. Nanotechnology can be used to harness the full potential of seed. Seed production is a tedious process especially in wind pollinated crops. Detecting pollen load that will cause contamination is a sure method to ensure genetic purity. Pollen flight is determined by air temperature, humidity, wind velocity and pollen production of the crop. Use of bionanosensors specific to contaminating pollen can help alert the possible contamination and thus reduces contamination. The same method can also be used to prevent pollen from genetically modified crop from contaminating field crops. Novel genes are being incorporated into seeds and sold in the market. Tracking of sold seeds could be done with the help of nanobarcodes that are encodable, machine - readable, durable and sub-micron sized taggants (Nicewarner *et al.*, 2001) [38]. Disease spread through seeds and many times stored seeds are killed by pathogens. Nano-coating of seeds using elemental forms of Zn, Mn, Pt, Au, Ag will not only protect seeds but used in far less quantities. Su and Li (2004) [54] developed a technique known as quantum dots (QDs) as a fluorescence marker coupled with immuno-magnetic separation for *E coli* 0157:H7, which will be useful to separate unviable and infected seeds.

Natarajan and Sivasubramanian (2007) [37] reported that technologies such as encapsulation and controlled release methods have revolutionized the use of pesticides and herbicides. Seeds can also be imbibed with nano - encapsulations with specific bacterial strain termed as Smart seed. It will thus reduce seed rate, ensure right field stand and improved crop performance. A smart seed can be programmed to germinate when adequate moisture is available that can be dispersed over a mountain range for reforestation. Coating seeds with nano membrane, which senses the availability of water and allow seeds to imbibe only when time is right for germination, aerial broadcasting of seeds embedded with magnetic particle, detecting the moisture content during storage to take appropriate measure to reduce the damage and use of bioanalytical nanosensors to determine ageing of seeds.

Khodakovskaya *et al.* (2009) [26] have reported the use of carbon nanotube for improving the germination of tomato seeds through better permeation of moisture. Carbon nanotubes (CNTs) serve as new pores for water permeation by penetration of seed coat and act as a passage to channelize the water from the substrate into the seeds. These processes facilitate germination which can be exploited in rainfed agricultural system.

10. Nano-herbicide for effective weed control

Chinnamuthu and Kokiladevi (2007) [7] reported that multi-species approach with single herbicide in the cropped environment resulted in poor control and herbicide resistance. Continuous exposure of plant community having mild susceptibility to herbicide in one season and different

herbicide in other season develops resistance in due course and become uncontrollable through chemicals. Developing a target specific herbicide molecule encapsulated with nanoparticle is aimed at specific receptor in the roots of target weeds, which enter into roots system and translocated to parts that inhibit glycolysis of food reserve in the root system. This will make the specific weed plant to starve for food and gets killed. In rainfed areas, application of herbicides with insufficient soil moisture may lead to loss as vapour. Still we

are unable to predict the rainfall very precisely, herbicides cannot be applied in advance anticipating rainfall. The controlled release of encapsulated herbicides is expected to take care of the competing weeds with crops. Adjuvants for herbicide application are currently available that claim to include nanomaterials. One nanosurfactant based on soybean micelles has been reported to make glyphosate-resistant crops susceptible to glyphosate when it is applied with the 'nanotechnology-derived surfactant'.

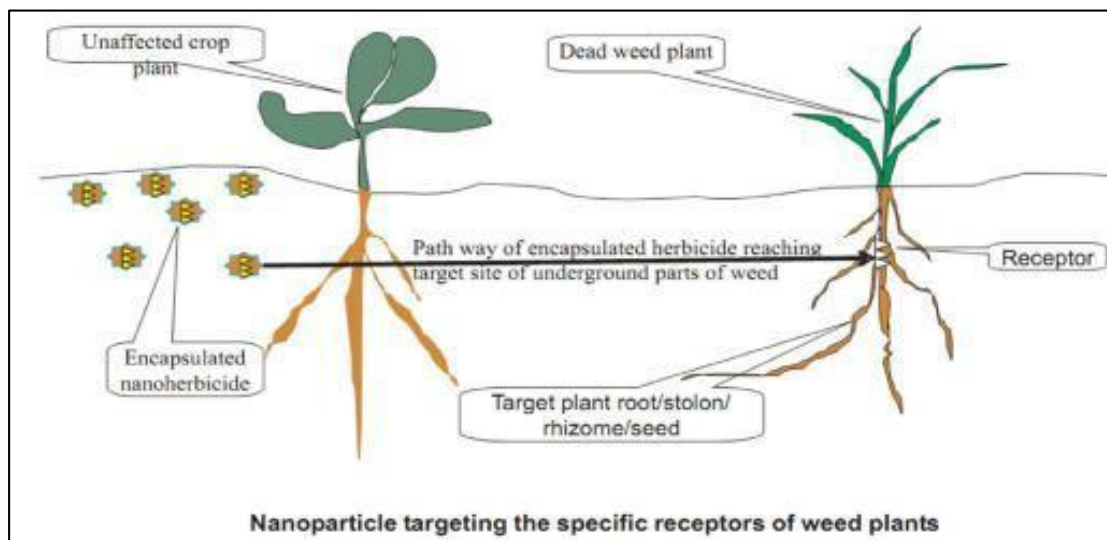


Fig 2: Smart delivery of nanoencapsulated herbicide in the crop-weed environment

Alginate/chitosan nanoparticles as a carrier system for the herbicide paraquat. The preparation and physico-chemical characterization of the nanoparticles was followed by evaluation of zeta potential, pH, size, and polydispersion. The techniques employed includes transmission electron microscopy; differential scanning calorimetry and fourier transform infrared spectroscopy. Significant differences between the release profiles of free paraquat and the herbicide associated with the alginate/chitosan nanoparticles were observed. The results showed that association of paraquat with alginate/chitosan nanoparticles alters the release profile of the herbicide, as well as its interaction with the soil (Silva *et al.*, 2011) [52].

a. Detoxification of herbicide residues

Excessive use of herbicides leave residue in the soil and cause damage to the succeeding crops. Continuous use of single herbicide leads to evolution of herbicide resistant weed species and shift in weed flora. Atrazine, an s-triazine-ring herbicide, is used globally for the control of pre and post-emergence broadleaf and grassy weeds, which has high persistence (half life-125 days) and mobility in some types of soils. Residual problems due to the application of atrazine herbicide pose a threat towards widespread use of herbicide and limit the choice of crops in rotation. Susha *et al.* (2009) [55] reported that application of silver modified with nanoparticles of magnetite stabilized with Carboxy Methyl Cellulose (CMC) nanoparticles recorded 88% degradation of herbicide atrazine residue under controlled environment.

11. Nano pesticide

Persistence of pesticides in the initial stage of crop growth helps in bringing down the pest population below the economic threshold level and to have an effective control for a longer period. Hence, the use of active ingredients in the

applied surface remains one of the most cost-effective and versatile means of controlling insect pests. In order to protect the active ingredient from the adverse environmental conditions and to promote persistence, a nanotechnology approach, namely "nano-encapsulation" can be used to improve the insecticidal value. Nano encapsulation comprises nano-sized particles of the active ingredients being sealed by a thin-walled sac or shell (protective coating). Nano-encapsulation of insecticides, fungicides or nematicides will help in producing a formulation which offers effective control of pests while preventing accumulation of residues in soil. In order to protect the active ingredient from degradation and to increase persistence, a nanotechnology approach of "controlled release of the active ingredient" may be used to improve effectiveness of the formulation that may greatly decrease amount of pesticide input and associated environmental hazards. Nano-pesticides will reduce the rate of application because the quantity of product actually being effective is at least 10-15 times smaller than that applied with classical formulations, hence a much smaller than the normal amount could be required to have much better and prolonged management. Several pesticide manufacturers are developing pesticides encapsulated in nanoparticles. These pesticides may be time released or released upon the occurrence of an environmental trigger (for example, temperature, humidity, light). Clay nanotubes (halloysite) have been developed as carriers of pesticides at low cost, for extended release and better contact with plants, and they will reduce the amount of pesticides by 70-80%, thereby reducing the cost of pesticide with minimum impact on water streams.

Future Prospects

Nanotechnology applications have the huge potential to change agricultural production by allowing better scientific management and conservation efforts to plant production.

Scientists in nanotechnology can do countless contributions for the betterment of society by applying this technology in agriculture and food production systems. Nanotechnology provides a much better effective way of environment detection, sensing and bioremediation. It can enhance agricultural productivity by using:

- i. Nanoporous zeolites for controlled release and efficient amount of water, fertilizer etc.
- ii. Nanocapsules for delivering of herbicide, vector and management of pests.
- iii. Nanosensors for detecting aquatic toxins and pests.
- iv. Nanoscale biopolymers (proteins and carbohydrates) based nanoparticles with few properties such as low impact on human health and the environment may be used in disinfection and recycling of heavy metals.
- v. Nanostructured metals can be explored in decomposition of harmful organics at room temperature.
- vi. Smart particles can be useful in effective environmental monitoring and purification processes.
- vii. Nanoparticles as a novel photocatalyst.

Thus, nanotechnology will transform agricultural practices including advanced pest management in future. Over the next 20 years, green revolution would be hastened by means of nanosciences. Nanomaterials would be beneficial in the development and formulation of next generation pesticides, insecticides and insect repellents. Thus, nanotechnology is considered as one of the best possible solution of the problems present in food and agriculture sector.

Conclusion

In the current agricultural scenario, the extensive use of agrochemicals to boost agricultural production has polluted not only the top soil, groundwater and food. Increasing agricultural productivity is necessary, but keeping the in mind the damage to the ecosystem new approaches need to be considered. Nanotechnology is becoming increasingly important for the agricultural sector. Promising results and applications are already being developed in the areas of delivery of pesticides, biopesticides, fertilizers and genetic material for plant transformation. The use of nanomaterials for delivery of pesticides and fertilizers is expected to reduce the dosage and ensure controlled slow delivery. A main contribution anticipated, is the application of nanoparticles to stabilize biocontrol preparations that will go a long way in reducing the environmental hazard. Nanotechnology, by exploiting the unique properties of nanomaterials, has developed nanosensors capable of detecting pathogens at levels as low as parts per billion. Apart from detection, nanotechnology also has solutions for degrading persistent chemicals into harmless and sometimes useful components. The tools of nanotechnology can be employed to address the urgent issues of environmental protection and pollution. Nanotechnology can endeavor to provide and fundamentally streamline the technologies currently used in environmental detection, sensing and remediation.

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