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Nanotechnology and its applications in agriculture: A review

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Abstract: With the growing limitation in arable land and water resources, the development of agriculture sector is only possible by increasing resources use efficiency with the minimum damage to agro ecology through effective use of modern technologies. Among these, nano technology has the potential to revolutionize agricultural systems, biomedicine, environmental engineering, safety and security, water resources, energy conversion, and numerous other areas. Nanotechnology 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. Research on smart seeds programmed to germinate under favourable conditions with nano polymer coating are encouraging. 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.

Key words: Nanofertlizer, Nanoherbicide, Nanotechnology, Smart delivary

Introduction

Annually of 4 per cent growth in agriculture is earmarked by the Indian national policy makers to ensure national food security with the limited availability of land and water resources. Avenue for achieving the demand is possible only by increasing productivity and income per unit of the scarce natural resources through effective use of improved technologies. This necessitates the continuous flow of new technologies into this sector (Mitchell, 2001; Anon., 2010; Chena and Yada, 2011). Industrial, information, biotechnological and recently the nanotechnology has taken the course in the developmental era. The agriculture is not an exception, thus it is also under constant developmental transformation to meet the changing needs and domains. Opara (2004) and Anon. (2010) has opined that among several advancements in science, the nanotechnology (NT) is a rapidly evolving field that has the potential to revolutionize food production systems. Chena and Yada, (2011) have demonstrated the Nanoscale science and nanotechnology potentialities in providing novel and improved solutions to many grand challenges facing agriculture and the society today and in the future.

“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) 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 abdomen but 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 draw backs 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). Nano fertilizers 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, nano technology 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 a slow 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). 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). 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).

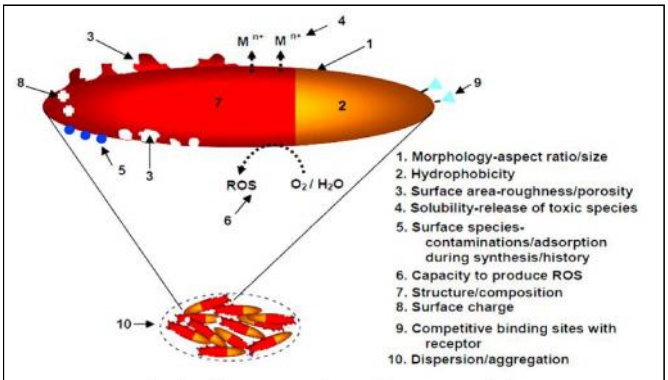

Fig1. The properties of nanoparticles

Top ten applications of nanotechnologies in the developing countries

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

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

Nanotechnology applications in agriculture and food production

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

Nano-Agriculture

In December 2002, the United States Department of Agriculture (USDA) drafted the world's first "roadmap" for applying nanotechnology to agriculture and food. A large group of policy makers, land grant university representatives and corporate scientists met at Cornell University (New York, USA) to share their vision on how to remake agriculture using nano-scale technologies.

Agriculture, according to the new nano-vision, needs to be more uniform, further automated, industrialized and reduced to simple functions. In our molecular future, the farm will be a wide area biofactory that can be monitored and managed from a laptop and food will be crafted from designed substances delivering nutrients and calories efficiently to the body.

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*.

Controlled environment agriculture (CEA)

Smart sensors and smart delivery systems will help the agricultural industry combat viruses and other crop pathogens. In the near future nanostructured catalysts will be available which will increase the efficiency of pesticides and herbicides, allowing lower doses to be used. Nanotechnology will also protect the environment indirectly through the use of alternative (renewable) energy supplies and filters or catalysts to reduce pollution and clean-up existing pollutants. An agricultural methodology widely used in the USA, Europe and Japan, which efficiently utilises modern technology for crop management, is called Controlled environment agriculture (CEA). CEA is an advanced and intensive form of hydroponically-based agriculture. Plants are grown within a controlled environment so that production practices can be optimized. The computerized system monitors and regulates localised environments for crops. CEA technology, as it exists today, provides an excellent platform for the introduction of nanotechnology to agriculture. With many of the monitoring and control systems already in place, nanotechnological devices for CEA that provide "scouting" capabilities could tremendously improve the grower's ability to determine the best time of harvest for the crop, the vitality of the crop, and food security issues, such as microbial or chemical contamination.

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. Wireless sensors are already being used in certain parts of the USA and Australia. For example, one of the Californian vineyards, Pickberry, in Sonoma county has installed wifi systems with the help of the IT company, Accenture. The initial cost of setting up such a system is justified by the fact that it enables the best grapes to be grown which in turn produce finer wines, which command a premium price. The use of such wireless networks is of course not restricted to vineyards, for example, Forbes Magazine has reported that small nanosensors are being used by Honeywell (a technology R&D company with global branches) to monitor grocery stores in Minnesota. This technology enables shop keepers to identify food items which have passed their expiry date and also reminds them to issue a new purchase order. The global market for wireless sensors is predicted to be Seven billion USD by 2010. 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 nano-cantilevers 13 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.

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. With potential applications across the food chain (in pesticides, vaccines, veterinary medicine and nutritionally-enhanced food), these nano- and micro-formulations are being developed and patented by agribusiness and food corporations such as Monsanto, Syngenta and Kraft.

Examples of nano and microcapsule designs are:

- **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 *et al.*, 2004)
- **Quick-release** – the capsule shell breaks upon contact with a surface (*e.g.,* when pesticide hits a leaf)
- **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)
- **Moisture release** – the shell breaks down and releases contents in the presence of water *(e.g.,* in soil)
- **Heat-release** – the shell releases ingredients only when the environment warms above a certain temperature
- **pH release** – nanocapsule breaks up only in specific acid or alkaline environment (*e.g.,* in the stomach or inside a cell)
- **Ultrasound release** – the capsule is ruptured by an external ultrasound frequency
- **Magnetic release** – a magnetic particle in the capsule ruptures the shell when exposed to a magnetic field
- **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)

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 nano-particles could remove soil contaminants. “Lab on a chip” technology also could have significant impacts on developing nations.

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 (Anon., 2007a &b). These links include farm inputs, farm production systems, post harvest management and processing and ûnally 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 (Kalpana Sastry *et al.*, 2007). In doing so, it is important to view nanotechnology as an enabling technology that can complement conventional technologies and biotechnology (Salerno *et al.,* 2008). 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 (Kalpana Sastry *et al.,* 2009, 2010b)

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; Kalpana Sastry *et al.*, 2010a). 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 ûeld classiûcation *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 frame-work was developed in two stages:

i. Mapping nanotechnology to agri-food thematic areas across all the links of the agricultural value chain (that is, farm inputs, production systems, post harvest 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).

Vandana *et al.* (2011) reviewed that potential applications of nanotechnology in agriculture are: delivery of nanocides–

Table 1. Applications of nanotechnology in agriculture

Application	Nano particles	Reference
A). Pesticide delivery		
Chemical		
Avermectin	Porous hollow silica(15 nm)	Li *et al.,* 2007
Ethiprole or phenylpyrazole	Poly-caprola ctone(135 nm)	Boehm *et al.,* 2003
Gamma cyhalothrin	Solid lipid (300 nm)	Frederiksen *et al.,* 2003
Tebucanazole/chlorothalonil	Polyvi nylpyridine andpolyvinylp yridine-co-styrene(100 nm)	Liu *et al.,* 2001
Biopesticides		
Plant origin: nanosilica for insectcontrol Artemisia arborescens	Nanosilic a (3-5 nm)	Barik *et al.,* 2008
Essential oil encapsulation	Solid lipid (200-294 nm)	Lai *et al.,* 2006
Microganisms: Lagenidiumgiganteum cells in emulsion	Silica (7-14 nm)	Vandergheynst *et al.,* 2007
Microbial product: absorption of Myrothrecium verrucaria enzyme	Chitos an/kaolin (250-350 nm)	Ghormade *et al.,* 2011
B). Fertilizer delivery		
NPK controlled delivery	Nano-coating of sulfur (100 nm layer) Chitos an (78 nm)	Wilson *et al.,* 2008, Corradini *et al.,* 2010
Genetic materia l deliveryDNA	Gold (10-15 nm) Gold (5-25 nm) Starch (50-100 nm)	Torney *et al.,* 2007, Vijayakumar *et al.,*2010, Liu *et al.,* 2008,
Double stranded RNA	hitosan (100-200 nm)	Zhang *et al.,* 2010
C). Pesticide sensor		
Carbofuran /triazophos	Gold (40 nm)	Guo *et al.,* 2009
DDT	Gold (30 nm)	Lisa *et al.,* 2009
Dimethoate	Iron oxide (30 nm),zirconium oxide (31.5 nm)	Gan *et al.,* 2010
Organophosphate	Zirconium oxide (50 nm)	Wang *et al.,* 2009
Paraoxon	Silica (100-500 nm) Carbon nanotubes	Ramanathan *et al.,* 2009, Joshi *et al.,* 2005
Pyrethroid	Iron oxide (22 nm)	Kaushik *et al.,* 2009
Pesticide degradation Lindane	Iron sulûde (200 nm)	Paknikar *et al.,* 2005
Imidacloprid	Titanium oxide (30 nm)	Guan *et al.,* 2008

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 ûeld applications of agrochemicals, nanomaterials assisted delivery of genetic material for crop improvement. Nanosensors for plant pathogen and pesticide detection, and NPs for soil conservation or remediation are other areas in agriculture that can beneût from nanotechnology. Enzyme immobilization for nanobiosensor using nanomaterials involves the high value low volume application of enzymes (Kim *et al.,* 2006). Usually, costly, large enzyme volumes are required for biocontrol in agricultural ûelds that would be practical if spray applications combined high volume with low value. Cost-effectiveness of such biocontrol preparations can be achieved by immobilization of enzyme/ inhibitors on nanostructures, providing large surface areas, to increase the effective concentration of the preparation.

Nanoparticles based smart delivery systems: Applications and advantages

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). For this purpose micronic and sub-micronic particles were explored as agrochemical delivery vehicles. In comparison to micronic particles (≥1000 nm), nano particles (b 1000 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)

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 beneûts 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).

In case of biopesticides, NPs can play a major role in enhancing the efficacy and stability of whole cells, enzyme and other natural products used. However, in the ûeld, application of NPs for the delivery of pesticides and biopesticides face several challenges such as multiple environmental perturbations, large areas under spray coverage and ûnally 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 deli very systems will require a targeted delivery approach focused using the knowledge of the life-cycle and the behaviour of the pathogen or pest.

Delivery of fertilizers

Localized 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 (Wilson *et al.,* 2008). 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).

Fertilizers with sulfur nanocoating ($\leq$ 100 nm layer) are useful slow release fertilizers as the sulfur contents are beneûcial especially for sulfur deûcient 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 beneûcial to meet the soil and crop demands. Other nanomaterials with potential application include kaolin and polymeric biocompatible NPs used biodegradable, polymeric chitosan NPs (~ 78 nm) for controlled release of the NPK fertilizer sources such as urea, calcium phosphate and potassium chloride (Wilson *et al.,* 2008 and Corradini *et al.,* 2010).

Field application of nano pesticides and fertilizers

The mode of pesticide and fertilizer application inûuences their efficiency and environmental impact (Ihsan *et al.,* 2007; Matthews, 2008; Matthews and Thomas, 2000). 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).

Another practical problem faced during pesticide application in the ûeld is settlement of formulation components in the spray tank and clogging of spray nozzles. The recent nano-sized fungicide (~ 100 nm, BannerM AXX, Syngent) prevented spray tank ûlters 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). 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 ûora and biological nitrogen ûxation in wetland rice soil was studied in pot and ûeld experiments. In the broadcast method of urea application, nitrogen ûxation 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 ûxing blue green algae (Roger *et al.,* 1980). Placement NP coated fertilizers may contribute to slow release of the fertilizer preventing the rapid dissolution and therefore harm to the environment.

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). These problems have initiated repeated use of fertilizer and pesticide which adversely affects the inherent nutrient balance of the soil. According to an estimate by International Fertilizer Industry Association, world fertilizer consumption sharply rebounded in 2009-2010 and 2010-2011 with growth rates of 5-6% in both campaigns. World demand is projected to reach 192.8 Mt by 2016-2017 (Heffer and Prud'homme 2012). But the large-scale use of chemicals as fertilizers and pesticides has resulted in environmental pollution affecting normal flora and fauna. Tilman *et al.* (2002) 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). 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). A 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 (De Rosa *et al.*, 2010). 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.

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. Nano-fertilizer technology is very innovative but scantily reported in the literature.

Nano-fertilizer technology is very innovative but scantily reported in the literature. However, some of the reports and patents strongly suggest that there is a vast scope for the formulation of nano-fertilizers. Significant increase in yields have been observed due to foliar application of nano particles as fertilizer (Tarafdar *et al.*, 2012a; Tarafdar *et al.*, 2012b). It was shown that 640 mg ha^{-1} foliar application (40 ppm concentration) of nanophosphorus gave 80 kg ha^{-1} P equivalent yield of clusterbean and pearl millet under arid environment. Currently, research is underway to develop nano-composites to supply all the required essential nutrients in suitable proportion

Table 2. Comparison of nanotechnologybased 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 absorptionand 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 ofsemipermeable membranes coated by resin-polymer, waxes, and sulfur	Excess release of fertilizers may produce toxicity and destroy ecological balance of soil
Effective duration of nutrientrelease	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, rain off, and drift

through smart delivery system. Preliminary results suggest that balanced fertilization may be achieved through nanotechnology (Tarafdar *et al.,* 2012b).

Indeed the metabolic assimilation within the plant biomass of the metals, *e.g.,* micronutrients, applied as Nano-formulations through soil-borne and foliar application or otherwise needs to be ascertained. Further, the Nano-composites being contemplated to supply all the nutrients in right proportions through the "Smart" delivery systems also needs to be examined closely. Currently, 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). In the next generation of nanofertilizers, the release of the 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 fertlizer capsule (Liu *et al.,* 2006). 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). Research on the controlled release pattern of nutrients using clay nanoparticle is on the go at Tamil Nadu Agricultural University (TNAU) India. Adhikari *et al.* (2010) has opined 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). In addition, nanofertilizers will combine nanodevices 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).

Nanostructured formulation reduce nutrients loss into soil by leaching and/or leaking

In China, the development of nanobased slow or controlled-release fertilizers have been actively implemented since the beginning of this century and supported by the National High-Tech R&D Program. Significant progress has been made especially on film-coating urea and granular compound fertilizers. Some nanobased agrochemicals have been commercialized. The solubility and dispersion of insoluble mineral micronutrients; phosphate fertilizers have been significantly improved by nanosized or nanostructured processing. Kalpana Shastry *et al.* (2011) have reviewed the patents and confirm that china is having the maximum number of the patents registered globally. The patented products include the nanoencapsulated products, nanofertilizers.

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).

Rahale working on "Nutrient Release Pattern of Nano-Fertilizer Formulations" for her thesis at TNAU, India has observed 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 (Kannan, 2011). 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). Nano-clay particles like substances used will reduces 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. Research on the controlled release pattern of nutrients using clay nanoparticle is on the go at Tamil Nadu Agricultural University, Coimbatore (Chinnamuthu and Boopathi, 2009).

Application of nanotechnology in seed science

Seed is nature's nano-gift to man. It 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 (Nicewarner Pena *et al.,* 2001) that are encodable, machine - readable, durable and sub-micron sized taggants. Disease spread through seeds and many times stored seeds are killed by pathogens. Nano-coating of seeds using elemental forms of Zn, Mn, Pa, Pt, Au, Ag will not only protect seeds but used in far less quantities than done today. Su and Li (2004) developed a technique known as quantum dots (QDs) as a flourescence marker coupled with immuno-magnetic separation for *E coli* 0157:H7, which will be useful to separate unviable and infected seeds.

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 (Natarajan and Sivasubramanian, 2007). Coating seeds with nano membrane, which senses the availability of water and allow seeds to imbibe only when time is right for germination, aerial broadcating 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 are some possible thrust areas of research.

A group of research workers is currently working on metal oxide nano-particles and carbon nanotube to improve the germination of rainfed crops. Khodakovskaya *et al.* (2009) have reported the use of carbon nanotube for improving the germination of tomato seeds through better permeation of moisture. Their data show that 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.

Nano-herbicide for effective weed control

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 (Chinnamuthu and Kokiladevi, 2007). 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 preciously; 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'.

Silva *et al.* (2011) in a study prepared 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 included transmission electron microscopy; differential scanning calorimetry and Fourier transform infrared spectroscopy. Significant differences between the release profiles of free

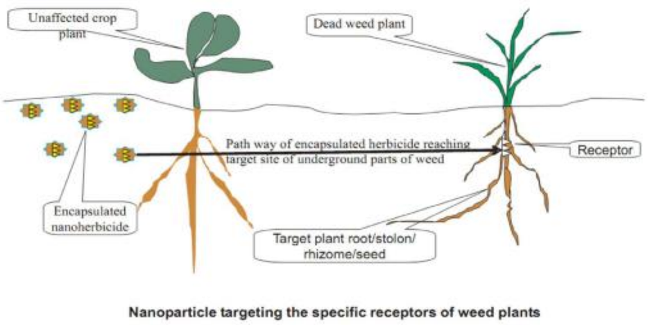

Fig. 2. Smart delivery of nanoencapsulated herbicide in the crop-weed environment

paraquat and the herbicide associated with the alginate/chitosan nanoparticles were observed in the study. 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, indicating that this system could be an effective means of reducing negative impacts caused by paraquat. Tests showed that soil sorption of paraquat, either free or associated with the nanoparticles, was dependent on the quantity of organic matter present.

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. Recent finding from TNAU, India raises hope to remediate the atrazine residue from soil within a short span of time. 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 (Susha *et al.*, 2009).

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. Nanoencapsulation 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 (OECD and Allianz, 2008). These pesticides may be time released or released upon the occurrence of an environmental trigger (for example, temperature, humidity, light). It is unclear whether these pesticide products will be commercially available in the short-term. 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.

Post harvest food processing

Food poisoning outbreaks take lives of a large number of people and also cause losses to economy in terms of lost man days and health care expenditure. Nano-materials help to keep products fresh for a longer period of time by using nano-sensors placed in food production and distribution facilities, food packaging or the food itself which can detect all kinds of food pathogens like *E.coli*, Campylobactor and Salmonella by attaching themselves to the pathogens. A single nano-sensor can have thousands of nano-particles that can detect the presence of any number and kind of bacteria and pathogens rapidly and accurately. Nano-sensors can work by different methods e.g. nano-sensors can be tailor-made to fluoresce into different colours or can be made out of magnetic materials.

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 cocohleates delivery system protects these substances from degradation. Polyphenols and resveratrol are the substances present in most foods and wine, respectively. They get degraded and oxidized when exposed to air. Nanocochleates solve early oxidation by individually capturing and wrapping them in a phospholipids wrap and maintaining the internal nutrients secure from water and oxygen. Bio delivery Sciences International have developed nanocochleates, which are 50 nm coiled nanoparticles 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.

Food packaging

Consumers' demand food to be fresh for long time, and the packaging materials should be ease for handling, safe and healthy. A major problem in food science is determining and developing an effective packaging material. Using nanoparticle technology, Bayer has developed an even more airtight plastic packaging that will keep food fresher and longer than plastics, which is "hybrid system" as it is enriched with an enormous number of silicate nanoparticles (Bayer, 2005). Researchers at Leeds University have demonstrated that nanoparticles with antimicrobial properties can be employed for safer food packaging. Nanoparticles such as titanium dioxide, zinc oxide and magnesium oxide, as well as a combination of them, once functionalized can be efficient in killing micro-organisms and are cheaper and safer instead of metal based nanoparticles.

The most problematic element for food packaging engineers is oxygen because it spoils the fat in meat and cheese and turns them pale. Nanoparticles in Durethan®, Bayer's new plastic material, cannot permit air to penetrate like in other conventional plastics. Incorporation of nanoparticles of clay into an ethylene-vinyl alcohol copolymer and into a poly (lactic acid) biopolymer was found to increase barrier properties to oxygen. Polymer-silicate nanocomposites have also been reported to have improved gas barrier properties, mechanical strength, and thermal stability. Nanoclay-nylon coatings and silicon oxide barriers for glass bottles are used to impede gas diffusion.

Future of farming: nanobio-farming?

It is important to note that nanomaterials, owing to their increased contact surface area , might have toxic effects that are not apparent in the bulk materials especially in open agricultural ecosystems (Nel *et al.,* 2006). The selection of nanomaterial for application in the field may be critical as materials which are non -toxic, biocompatible and biodegradable are desirable. Few food and nutrition products that contain nanoscale additives already in the market , such as iron in nutritional drink mixes, micelles that carry vitamins, minerals and phyto chemicals in oil and zinc oxide in breakfast cereals (Hoyt and Mason, 2008).

The future if foreseen would allow the advancements in agricultural nanotechnology to promote 'precision farming' allowing optimum use o f the natural resources with judicious farming practices. Different sensor and controlled delivery technologies would change the face of farming. The use of a net work of sensors, global positioning system, global information system and actuators throughout an agricultural area could measure (data and statistics) and report on a number of different environmental, crop and pest variables. These reports would support the experience of the farmer an d permit choices for intervention during irrigation, fertilization, pest control and even harvesting. Although costly, this would be largely offset by the rising cost of food, the need for higher quality and increasing legislation. The technology already exists to measure each of these variables. However, measurement requires technical expertise is labor-intensive and can take days, by which time the opportunity for optimal intervention could be missed. By providing robust, portable or remote in situ nanotechnology based sensing and monitoring, backed up with analytical software, farmers can begin to maket heir own informed choices, in real-time, and apply agrochemicals or engage expert help only when necessary.

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. A major hurdle in the removal of harmful ûeld, which was costly with conventional methods. 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. Agricultural technology should take advantage of the powerful tools of nanotechnology for the contaminants from soil was its detection in the beneût of mankind. 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.

Finally a quote

“We have to launch vertical missions under an umbrella organization with the public-private investment in atleast 10 nanotechnology products in water, energy, agriculture, healthcare, space, defense sectors. Encourage the youth to take up the challenge in these missions with international collaborations.” (President Dr. A.P.J.Abdul Kalam address to scientist and technologists during April 2005 at Delhi).

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