

Nanotechnology in agriculture and food sciences

Historically, agriculture preceded the industrial revolution of about 90 centuries; the history of the technological innovation in agriculture and agri-food have produced profound changes in production, in the landscape and environment, and in significant socio economic relationships, revolutionizing farming operations with less dependence on farm workers to specific tasks. The latest series of technological innovations include the new genetics, biotechnology, intensive farming of animals and new techniques of cell reproduction. The products of these technological innovations have affected differently large segments of agriculture, new varieties of seeds and animals, new varieties of chemical products, more pesticides, fertilizers and veterinary drugs. Nanotechnology, as an emerging technology, presents an important opportunity for the scientific and business community. Industrial development-intensive chemical agriculture in recent decades has produced high environmental costs associated with the loss of biodiversity, toxic pollution of land and waterways, increased salinity, erosion and decreased soil fertility. Nanotechnology is now imposing, albeit with light and shade and not in the all areas, as an element of development in modern agriculture and in the food sector where it can be a driving economic force in the near future. Nanoscience and nanotechnology are new frontiers of this century (Raliya et al., 2013). Nanotechnology enables plants to use water, pesticides and fertilizers more efficiently; industrial development aims important role in the development of novel methods for the production of new products, to replace existing production plants and to

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reformulate new materials and chemicals with improved performance resulting in lower consumption of energy and materials, reduced damage to the environment, environmental remediation, sustainability and enhancement of nutritional food, including crops intended for human consumption and animal feed. Ultimately, nanotechnology could be described as the science of designing and building machines in which every atom and chemical bond is precisely specified (Ditta, 2012). According to another definition, “nanomaterial” means a natural, incidental, or manufactured material containing particles in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution one or more external dimension is in the range 1-100 nm. Nanoscale materials exhibit novel properties such as increased strength, enhanced optical features, antimicrobial properties, and superconductivity. Nanotechnology is unlike some other sectors of the chemical industry, where significant capital is already invested in the form of large plants and established supply chains in which production techniques are technologically and culturally embedded. It is not a set of special techniques, devices or products, but the set of capabilities that we have when technology is approaching the limits of the atomic physics. However, while research in nanotechnology began to grow for industrial applications almost half a century ago, the momentum for the use of nanotechnology in agriculture came only recently (Agrawal and Rathore, 2014) respect to their use in drug delivery and pharmaceutical products. Engineered nanoparticles (NPs) are now present in matrices that can interfere with food production (Sonkaria et al., 2012). In fact their industrial use for a wide range of potential applications led to the contamination of environmental media (water, air, soil) with nanomaterials so it may raise concerns related to environmental risk. Between 2006 and 2011, reports have shown that the number of nanotechnology-related products across the world grew by 521 percent. By 2015, the market for nano products was expected to hit \$ 2.4 trillion. Nanotechnology use may bring potential benefits to farmers through new agrochemical agents and new delivery mechanisms to improve crop productivity. Furthermore it promises to reduce pesticide use, increase food production and to improve the food industry through the development of innovative products for preservation and packaging uses. Applications include nanoparticle-mediated gene or DNA transfer in plants for the development of insect-resistant varieties, food processing and storage, nanofeed additives, increased product shelf life, nanosensors/ nanobiosensors for detecting pathogens, for soil quality and for plant health monitoring, nanoporous zeolites for slow-release and efficient dosage of water and fertilizers for plants and

release of nutrients and drugs for livestock, nanocapsules for agrochemical delivery in form of green slow-release fertilizer (Kottegoda et al., 2011), bio-fuels, nanocomposites for plastic film coatings used in food packaging, antimicrobial nanoemulsions for applications in decontamination of food, nanobiosensors for identification of pathogen contamination, and improving plant and animal breeding (Espitia et al., 2013). Nanomaterials can enter the water cycle in various ways: for example, domestic sewage may be affected by textiles, detergents, cosmetics, pharmaceuticals or building materials, while bathing waters by sun protection products, and groundwater by industrially manufactured or processed nanomaterials which are discharged into various water cycles, or by fertilizers and landfill leachates. Nanotechnology promises to accelerate the development of biomass-to-fuels production technologies. Experts feel that the potential benefits of nanotechnology for agriculture, food, fisheries, and aquaculture need to be balanced against concerns for the soil, water, and environment and the occupational health of workers. Raising awareness of nanotechnology in the agri-food sector is one of the keys to influencing consumer acceptance. While the successful implementation is important for the growth of the global economy, nanotechnology offers much promise, in fact these novel properties and behaviors may also pose new risks so there is also a need to consider the possible environmental health and safety impact. On the basis of only a handful of toxicological studies, concerns have arisen regarding the safety of nanomaterials, and researchers and companies will need to prove that these nanotechnologies do not have a negative impact on the environment. There is increasing concern of the toxicity of engineered nanomaterials and their effects on biological systems and environment, which remain largely unknown (Podila and Brown, 2013). Nanomaterials possess physical and chemical properties that can have an unpredictable impact on safety and human health; biological naturally occurring nanoparticles nanoclay, tomato carotenoid lycopene, many chemicals derived from soil organic matter, lipoproteins, exosomes, magnetosomes, viruses, ferritin, have diverse structures with wide-ranging biological roles; biological nanoparticles are often biocompatible and have reproducible structure (Giordani et al., 2012). The interaction of these nanomaterials with human organs and tissues initially aroused scientific interest for possible applications in biomedicine, later began a major concern in both scientific organizations and health-conscious environment. Population exposure to nanoparticles may occur directly or indirectly. Indirect exposure occurs both by nano particles produced by natural processes such as fires, earthquakes and volcanic eruptions, both from nano particles from air pollution caused by technological

advances that led to the accumulation of large amounts in the environment and can cause changes in the final products or changes of metabolites that may also lead to high risks (Cushen et al., 2012). A number of recent reports and reviews have identified the current and short-term projected applications of nanotechnologies in the food sector (Groves, 2008; Kuzma and VerHage, 2008; Kuzma, 2010; Mura et al., 2013; Bouwmeester et al., 2007). There are already identified potential uses of nanotechnology in virtually every segment of the food industry with four key focus areas:

(i) agriculture-pesticide, fertilizer or vaccine delivery; animal and plant pathogen detection; targeted genetic engineering; nanoagrochemicals and water pollution,

(ii) food processing-encapsulation of flavor or odor enhancers; food textural or quality improvement; new gelation or viscosifying agents in nanofood,

(iii) food packaging-pathogen, gas or abuse sensors; anticounterfeiting devices, UV-protection, and stronger, more impermeable polymer films, in agri-environment

(iv) nutrient supplements-nutraceuticals, cosmetic with higher stability and bioavailability.

Finally, the use of nanomaterials in the environment can cause changes in the final products or changes of metabolites that may also lead to high risks. On basis of these stresses a new discipline called “nanotoxicology” is born who is trying to study the interactions of these nanostructures with biological structures with the laying of a certain question about the gap: science and ethics in nanotechnology. Significant evidence indicates that manufactured nanomaterials and combustion-derived nanomaterials elicit toxicity in humans exposed to these nanomaterials. The toxicology studies worked on in vitro cytotoxicity studies of cells, lately also in vivo studies have increased. The number of studies that have been published on the topic of nanosafety speaks for itself. We have seen an almost exponential rise over the past 15 years or so in the number of articles on nanotoxicology. Although only a couple of hundred papers had appeared on the topic of “Nanomaterials: environmental and health effects” before 2000, this number has exploded to over 10 000 since 2001. Most of these studies, however, do not offer any kind of clear statement on the safety of nanomaterials. On the contrary, most of them are either self-contradictory or arrive at completely erroneous conclusions (Krug, 2014). The epidemiological studies are very complicated, for the interaction of multiple components and biological events that occur in vivo. The environmental effects require further research to determine whether the assessment methods currently used (organisms, cell cultures, exposure regimens, analytical me-

thods) are applicable to the testing of nanomaterials in standardized toxicity tests to determine the effects of nanomaterials in ecosystems (Stanley, 2014). Their absorption, distribution, metabolism and excretion (ADME) evaluates these parameters for different nanomaterials in order to examine the interaction of nanomaterials with model ecosystems (Fedeeel et al., 2015).

NANOAGROCHEMICALS

A doubling in global food demand projected for the next 50 years poses huge challenges for the sustainability both of food production and of terrestrial and aquatic ecosystems and the services they provide to society. Recent agricultural practices associated with the Green Revolution have greatly increased the global food supply (Brennan, 2012). They have also had an inadvertent, detrimental impact on the environment and on ecosystem services, highlighting the need for more sustainable agricultural methods (Gogos et al., 2012). It is well documented that excessive and inappropriate use of fertilizers and pesticides has increased nutrients and toxins in groundwater and surface waters, incurring health and water purification costs, recreational opportunities, and decreasing fishery in Developing Countries (Chaudhry and Castle, 2011). Agricultural practices that degrade soil quality contribute to eutrophication of aquatic habitats and may necessitate the expense of increased fertilization, irrigation, and energy to maintain productivity on degraded soils (Marchiol, 2012). Agriculturalists are the principal managers of global usable lands and will shape, perhaps irreversibly, the surface of the Earth in the coming decades. Degraded ecosystems have become a serious threat to human health and civilization. The benchmark for ecosystem degradation is linked to its failure to retain carbon and prevent escape of various forms of nitrogen from the soil to water bodies and the atmosphere. It leads to increased pests, reduced availability of clean water and biodiversity loss. Land degradation is often the result of land mismanagement, including: deforestation, overgrazing, monoculture, salinization, pollution of land and water sources by agriculture or industries, misuse of fertilizers and/or chemicals, poor farming practices, and soil erosion. Farmland is a fundamental resource for human survival and development, however, farmland fragmentation has become a serious problem, causing ecological damage and low crop production efficiency in many parts of the world (Cheng et al., 2015). Despite many adjustments to agricultural policy, intensification of production in some regions and concurrent abandonment in others remain the major threat to the

ecology of agro-ecosystems impairing the state of soil, water and air and reducing biological diversity in agricultural landscapes. The impacts also extend to surrounding terrestrial and aquatic systems through water and aerial contamination and development of agricultural infrastructures (e.g. dams and irrigation channels). Improvements are also documented regionally, such as successful support of farmland species, and improved condition of water-courses and landscapes. All of this increases food insecurity and makes the affected areas, their populations and business operations more vulnerable to climate change. Manufactured nanoparticles can be produced from nearly any chemical; however, most NPs that are currently in use have been made from transition metals, silicon, carbon (carbon black, carbon nanotubes; fullerenes), and metal oxides; few of these nanoparticles have been produced for several decades on an industrial scale, but various new materials such as carbon nanotubes, fullerenes or quantum dots have only been discovered within the last two decades. Agrochemical companies are reducing the existing chemical emulsions to the nanoscale and substituting active ingredients with their encapsulated nanosized equivalents in attempt to bring a number of benefits into potential applications of nanotechnology to pesticides, and other agrochemicals such as fertilizers and plant growth regulators (DeRosa et al., 2010). New incentives and policies for ensuring the sustainability of agriculture and ecosystem services will be crucial if we meet the demands of improving yields without compromising environmental integrity or public health (Garcia et al., 2010). Nanotechnology can improve crops yield, germination, nutritional values (Khodakovskaya et al., 2009), and can offer added value to crops or environmental remediation (El-Ramady, 2014). Particle farming is one such fields, which yields nanoparticles for industrial use by growing plants in gold rich soil. The gold nanoparticles can be mechanically separated from the plant tissue following harvest (Owolade et al., 2008). New applied research also aims to make plants use water, pesticides and fertilizers more efficiently, to reduce pollution and to make agriculture more environmentally friendly. Smaller companies are forming alliances with major players such as LG, BASF, Honeywell, Bayer, Mitsubishi, and DuPont to make complete plant health monitoring systems in the next 10 years using nanotechnologies. Opportunities for applying nanotechnology in agriculture lie in the areas of genetic improvement of plants, delivery of genes and drug molecules to specific sites at the cellular level in plants (Giraldo et al., 2014), plant nanobionics approach to augment photosynthesis and biochemical sensing, nanoarray-based technologies for gene expression in plants to overcome stress and development of sensors and protocols for its application in preci-

sion farming, management of natural resources, early detection of pathogens and contaminants in food products, smart delivery systems for agrochemicals like fertilizers and pesticides (Vidyalakshmi et al., 2009), and integration of smart systems for food processing, packaging, and monitoring of agricultural and food system security. 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. With nanofertilizers emerging as alternatives to conventional fertilizers, buildup of nutrients in soils by eutrophication and contamination of drinking water may be eliminated (Manimegalai et al., 2011). Pesticides are commonly used in agriculture to improve crop yield and efficiency, smart delivery system has a huge potential for improving efficiency of fungicides in agriculture systems. Development of these technologies in plant protection would allow their use in crop protection. The application of smart delivery systems for improving treatment of plant diseases with chemicals (fungicides, insecticides, herbicides) could be immediate (Rai et al., 2012). However, the more complex part is the translocation of the substances within the plant to reach the action point. Nanopesticides are one of a new strategy being used to address the problems of non-nanopesticides and 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. Nanopesticides cover a wide variety of products, some of which are already on the market, U.S. EPA statement, several manufacturers have been interested in releasing nanoscale pesticides. Nevertheless, almost no major agrochemical companies, except Syngenta, have announced that they are manufacturing products, which contain nanomaterials having a diameter less than 100nm. Syngenta has been selling its Primo MAXXR for several years. Primo MAXXR is by far the most widely used Plant Growth Regulator (PGR) by golf course superintendents and other professional turf managers since its introduction in 1993. Syngenta claims that the particle

size of this formulation is about 250 times smaller than typical pesticide particles. According to Syngenta, it is absorbed into the plant's system and cannot be washed off by rain or irrigation. In 1998 Monsanto entered an agreement with Flamel Nanotechnologies to develop "Agsome" nanocapsules of Roundup, which might have been more chemically efficient than the conventional formula. They cannot be considered as a single entity; rather such nanoformulations combine several surfactants, polymers (organic), and metal nanoparticles (inorganic) in the nanometer size range (Ray, 2013), it is marketed as a "micro-emulsion" concentrate. The lack of water solubility is one of the limiting factors in the development of crop-protecting agents. Micro-encapsulation has been used as a versatile tool for hydrophobic pesticides, enhancing their dispersion in aqueous media and allowing a controlled release of the active compound. Polymers often used in the nanoparticle production have been reported (Perlatti et al., 2013), 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. Researchers have reported various aspects of nanoparticle formulation, characterization, effect of their characteristics, and their applications in management of plant diseases. First of all, polycaprolactone and poly(lactic) acid nanospheres were used for encapsulation of the insecticide ethiprole, silica nanocapsules were prepared by a recently reported emulsion and biomimetic dual-templating approach under benign conditions and without using any toxic chemicals (Wibowo et al., 2014). Nanonization is an attractive solution to improve the bioavailability of the poorly soluble drugs, to improve therapies, in vivo imaging, in vitro diagnostics and for the production of biomaterials and active implants (Sheth et al., 2012). Nanoparticles in the pharmaceutical industry and the use of supercritical fluid technologies for nanoparticle production in drug delivery, application of nanotechnology is commonly referred to as Nano Drug Delivery Systems (NDDS). In this case, results indicated that nanospheres do not provide a controlled release of agrochemical active ingredients but, due to their small size, they enhanced the penetration in the plant compared to the classical suspension (Boehm et al., 2003). In vivo experiments carried out with Egyptian cotton leaf worm *Spodoptera littoralis* larvae indicated that the toxicity of nanoparticles of novaluron resembled that of the commercial formulation (Elek et al., 2010). Nanomaterials serve equally as additives (mostly for controlled release) and active constituents (Adak, 2012), controlled-release (CR) formulations of imidacloprid (1-(6-chloro-3-pyridinyl methyl)-N-nitroimidazolidin-2-ylideneami-

ne), synthesized from polyethylene glycol and various aliphatic diacids using encapsulation techniques, have been used for efficient pest management in different crops. The bioefficacy of the prepared CR formulations and a commercial formulation were evaluated against major pests of soybean, namely stem fly, *Melanagromyza sojae* Zehntmer and white fly, *Bemisia tabaci* Genadius. Most of the CR formulations of imidacloprid exhibited better control of the pests compared with its commercial formulations; however, of the CR formulations, poly(poly(oxyethylene-1000)-oxy suberoyl) amphiphilic polymer-based formulation performed better than others for controlling of both stem fly incidence and Yellow Mosaic Virus infestation transmitted by white fly. In addition, some of the developed CR formulations recorded higher yield over commercial formulation and control (Adak et al., 2012a; Adak et al., 2012b). CR formulations of carbofuran and imidacloprid provided better or equal control against the aphid, *Aphis gossypii* and leafhopper, *Amrasca biguttula* Ishida on potato crop, than commercial formulations (Kumar et al., 2011). Nanoparticles in insects and their potential for use in insect pest management have been reported (Elek et al., 2010; Al-Samarrai, 2012). The residue of carbofuran and imidacloprid in potato tuber and soils was not detectable at the time of harvesting in any one of the formulation (Jdyalakshmi et al., 2009). Nanomaterials including polymeric nanoparticles, iron oxide nanoparticles, gold nanoparticles, and silver ions have been exploited as pesticides. Nanoencapsulation helps slow release of a chemical to the particular host for insect pest control through release mechanisms that include dissolution, biodegradation, diffusion, and osmotic pressure with specific pH (Barik et al., 2008). Nanoparticles loaded with garlic essential oil proved effective against *Tribolium castaneum* Herbst. The use of amorphous nanosilica as biopesticide has been reported (Jayaseelan et al., 2011). Nanocopper particles suspended in water have been used since at least 1931, in a product known as Bouisol as fungicide in the growing of grapes and fruit trees (Hatschek, 1931). In the research and development stage, nanosized agrochemicals or nanoagrochemicals are mostly nano-reformulations of existing pesticides and fungicide. (Green et al., 2007; Kah et al., 2013). Nanoformulations are generally expected to increase the apparent solubility of poorly soluble active ingredients, to release the active ingredient in a slow/targeted manner, and/or to protect against premature degradation (Kumar et al., 2010). Nanopesticides offer a way to both control delivery of pesticide and achieve greater effects with lower chemical dose. Agrochemical companies are reducing the particle size of existing chemical emulsions to the nanoscale, or are encapsulating active ingredients in nanocapsules designed to split open,

for example, in response to sunlight, heat, or the alkaline conditions in an insect's stomach. The smaller size of nanoparticles and emulsions used in agrochemicals is intended to make them more potent. Many companies make formulations that contain nanoparticles within the 100-250 nm size range that are able to dissolve in water more effectively than existing ones, thus increasing their activity (Perez-de-Luque et al., 2009). Other companies employ suspensions of nanoscale particles (nanoemulsions), which can be either water-based or oil-based and contain uniform suspensions of pesticidal or herbicidal nanoparticles in the range of 200-400 nm. Potential advantages described by the research community are the solubilisation of hydrophobic pesticides (hence no need for toxic organic solvents). However, it should be noted that manufacturing opportunities are not developed, as the precise mechanisms by which nanoemulsions form and how their properties controlled are still the subject of intense basic research. The benefit of nano-emulsions over coarser systems is not so clear. Information from our interviews with industrial representatives suggests that the use of tailor made adjuvants together with micron particles is likely to override the nano-emulsions which are much more complicated with regard to preparation as well as stabilisation (Anton and Vandamme, 2011). Nanocapsules can enable effective penetration of herbicides through cuticles and tissues, allowing slow and constant release of the active substances. Viral capsids can be altered by mutagenesis to achieve different configurations and deliver specific nucleic acids, enzymes, or antimicrobial peptides acting against the parasites (Perez-de-Luque et Rubiales, 2009). The ultimate expression of this technology would be development of a vector that encapsulates, protects, penetrates, and releases DNA-based BW [biological warfare] agents into target cells but is not recognised by the immune system. Such a 'stealth' agent would significantly challenge current medical counter measure strategies (Defense Intelligence Agency analysts, US government, Washington, DC). Silver nanoparticles at 100 mg/kg inhibited mycelia growth and conidial germination on cucurbits and pumpkins against powdery mildew (Afrasiabi et al., 2012). Silver nanoparticles have received significant attention as a pesticide for agricultural applications. The potential of nanomaterials in insect pest management as modern approaches of nanotechnology, has been reported (Rai et Ingle, 2012). Nanoencapsulation is currently the most promising technology for protection of host plants against insect pests. With nanoencapsulation techniques it is possible to step down the chemical release under controlled situations, reducing the current application dosage and improving efficiency. Nanoparticles can be used in the preparation of new formulations like pesticides, insecticides, and insect repel-

lants (Peisker and Gorb, 2013). Treatment of *Bombyx mori* leaves with grasperie disease with ethanolic suspension of hydrophobic alumina–silicate nanoparticles significantly reduced the viral load (Goswami et al., 2010). DNA-tagged gold nanoparticles are effective against *Spodoptera litura* and would therefore be a useful component of an integrated pest-management strategy (Chakravarthy et al., 2012). Development of nanobased viral diagnostics including kits can help to detect the exact strain of virus and identify differential proteins in healthy and diseased states during the infectious cycle and the stage of application of therapeutics to stop disease, thus increasing speed as well as power of disease detection (Scrinis and Lyons, 2007). Nano-silica has been successfully employed to control a range of agricultural insect/pest and ectoparasites in animals. Such nanoparticles get absorbed into cuticular lipids (used by insects to prevent death from desiccation) by physisorption and cause insect death by physical means when applied on leaves and stem surfaces. Antifungal activities of polymer-based copper nanocomposites against pathogenic fungi, and silica–silver nanoparticles against *Botrytis cinerea*, *Rhizoctonia solani*, *Callectotrichum gloeosporioides* (Cioffi et al., 2004; Jo et al., 2009). *Bipolaris sorokiniana*, and *Magnaporthe grisea* have been reported. Copper nanoparticles in soda lime glass powder showed efficient antimicrobial activity against gram-positive and gram-negative bacteria and fungi (Esteban-Tejeda et al., 2009). A novel photodegradable insecticide involving nanoparticles has been reported (Guan et al., 2008). Specific nanoencapsulated pesticides will have the ability to kill targeted insects only, thereby reducing the effective dose when compared to traditional pesticides (Park et al., 2006). Further, these are absorbed on the surface of the plant, facilitating a prolonged release that lasts for a longer time compared to conventional pesticides that wash away in the rain. Significant mortality of two insect pests, *Sarocladium oryzae* and *Rhyzopertha dominica*, after 3 days' exposure to nanostructured alumina-treated wheat was reported (Dimkpa et al., 2013). Halloysite nanotube has potential to be applied as a nanocontainer for encapsulation of chemically and biologically active agents such as agromedicines and pesticides (Naderi and Danesh-Shahraki, 2013). It is essential to remove weeds for increasing the yield of any crop and weeding using nanoherbicides is seen as an economically viable alternative. Conventional herbicides have proved highly effective in controlling weeds without damage to crops or environment. However, chemical weed management under rain-fed areas depends on the moisture availability during the application of herbicides. Lack of moisture limits the use and efficiency of the application. The nano-silicon carrier comprising diatom frustules (pore size 1–100 nm) has been used for

delivery of pesticides and herbicides in plants as well as in hormonal wastewater treatment. CR formulation is superior to its counterpart and results in a higher yield and better crop quality. Such a formulation also finds use in active-agent herbicides, pesticides, and plant growth regulators. The potential application of a layered single-metal hydroxide, particularly zinc-layered hydroxide, as the host for the preparation of a nanohybrid compound with a tunable CR property containing two herbicides simultaneously has been demonstrated. In this context, a nanohybrid containing both herbicides (4-(2,4-dichlorophenoxy) butyrate [DPBA] and 2-(3-chlorophenoxy) propionate [CPPA]) labeled as ZCDX was found a suitable host for the CR formulation of two herbicides, namely DPBA and CPPA, simultaneously. The monophasic, well-ordered zinc-layered hydroxide nanohybrid containing two herbicides, CPPA and DPBA, was found to be composed of a higher loading of DPBA compared to CPPA between the zinc-layered hydroxide inorganic interlayers, with percentage contributions of 83.78% and 16.22%, respectively. The release rate of both CPPA and DPBA was found to be different, suggesting that the anionic guest molecules' sizes and the interactions between the host and guest could control the release kinetics. Researchers reported a functional hybrid nanocomposite based on the intercalation of two herbicides' anions (2,4-dichlorophenoxy acetate and 4-chlorophenoxy acetate) with zinc–aluminum-layered double hydroxide. CR formulations of nanocomposites such as 4-chlorophenoxy acetate–zinc–aluminum-layered double hydroxide and 4-dichlorophenoxy acetate–zinc–aluminum-layered double hydroxide were reported. Researchers reported manganese carbonate core-shell nanoparticles loaded with pre-emergence herbicide pendimethalin programmed to release smartly based upon the requirements. Researchers have reported nanosilver and titanium dioxide nanoparticle applications in management of plant diseases (Rao and Paria, 2013). Fungicidal efficiency of sulfur nanoparticles against two phytopathogens has been reported: *Fusarium solani* (isolated from an infected tomato leaf, responsible for early blight and Fusarium wilt diseases) and *Venturia inaequalis* (responsible for the apple scab disease) (Soni and Prakash, 2012). Pheromones are naturally occurring volatile semiochemicals and are considered ecofriendly biological control agents. Pheromones immobilized in a nanogel exhibited high residual activity and excellent efficacy in an open orchard (Bhagat et al., 2013). Environment-friendly management of fruit flies involving pheromones for the reduction of undesirable pest populations, responsible for decreasing yield and crop quality, has been reported. The development of nanocomposites is a new strategy to improve physical properties

of polymers, including mechanical strength, thermal stability, and gas barrier properties (Kumar and Krishnamoorti, 2010). The most promising nanoscale size fillers are montmorillonite and kaolinite clays. Graphite nanoplates are currently under study. In food packaging, a major emphasis is on the development of high barrier properties against the migration of oxygen, carbon dioxide, flavor compounds, and water vapor. Decreasing water vapor permeability is a critical issue in the development of biopolymers as sustainable packaging materials. The polymer composites incorporating clay nanoparticles are among the first nanocomposites to emerge on the market as improved materials for food packaging. Nano-layer structure of clays increases the path of diffusion of gases or other substances that penetrating significantly improve the polymer's barrier properties. The nanoscale plate morphology of clays and other fillers promotes the development of gas barrier properties. Several examples are cited. Challenges remain in increasing the compatibility between clays and polymers and reaching complete dispersion of nanoplates (Pandey et al., 2013). Challenges remain in processing of these nanodispersions and in maintaining stability over longer durations. Commercial products (e.g. ImpermR, AegisR or DurethanR) are included into two general categories: regular and high load. Regular products have nanoclay loading in the 2-4% range and high load 5-8%. Regular load products bring 2 times barrier improvement for oxygen and water vapour. The food contact materials based on metal/metal oxide nanoparticles use especially Nano-Silver, Nano-Titanium, Nano-Aluminium and Nano Zinc Oxide. Nano-Silver particles can significantly reduce bacteria and insure safer, fresher and tastier food (Boholm and Arvidsson, 2014). Nano-Titanium is used in filtration systems in fridges and vacuum cleaners. Nano-Aluminium enables to improve properties of the foil surface, for instance to develop anti-adhesive coating or black coating of baking foil which does not reflect heat in an oven. Nano ZnO is used as a non-organic antibacterial agent, which does not discolour nor does not need ultra-violet light to be activated. Products based on metal or metal oxide nanoparticles used for food contact materials are already in the market, e.g. food containers, cutting boards, refrigerators, kitchenware and tableware, aluminum foil or plastic wrap. Recently a method has been reported combining a processing technique of modified emulsion templating and freeze drying; the resulting powder composites are stable, highly porous and form nanodispersions when added to water. The technique has been demonstrated with the antimicrobial agent Triclosan (Liu et al., 2009). There has been considerable research into the use of nanosized quantum dots (QDs) to detect foodborne pathogens. These semiconductor nanocrystals have been used as fluorophores

for cellular imaging, as they possess superior properties to conventional fluorophores. QDs have been coupled with specific antibodies to facilitate detection of organisms, including the parasites *Cryptosporidium parvum* and *Giardia lamblia* and the bacteria *Mycobacterium bovis*, *Escherichia coli* O157:H7, *Listeria monocytogenes*, *Salmonella*, and *Shigella*. Indeed, a modified cellphone has been used as a detection system for *E. coli*. Toxins, including shiga-like toxin, cholera toxin, and ricin, have been detected using a QD protocol (Billington et al., 2014).

NANOTECHNOLOGY AND AGRI-ENVIRONMENT

The use of pesticides and fertilizers to improve food production leads to an uncontrolled release of undesired substances into the environment. Recent decades have revealed the high environmental costs associated with industrial scale chemical-intensive agriculture, including biodiversity loss, toxic pollution of soils and waterways, salinity, erosion and declining soil fertility. Effect of carbon nano materials on pesticide residue in zucchini, corn, tomato and soybean has been investigated by Torre-Roche et al. It was found that pesticide residue uptake by the above plants was reduced in presence of carbon nanotubes. Today, nanotechnology represents a promising approach to improve agricultural production and remediate contaminated soil and groundwater. Researchers reported the recent applications of nanotechnologies in agro environmental studies, with particular attention to the fate of nanomaterials once introduced in water and soil (Gruere et al., 2014). They showed that the use of nanomaterials improved the quality of the environment and helped detect and remediate polluted sites; however, only a small number of nanomaterials demonstrated potential toxic effects (Parda Saradhi, 2014). Carbon/ fullerene nanotechnology is a rapidly growing area of research which finds use in plant, medicine and engineering. Carbon nanotubes (single-wall carbon nanotubes and multi-wall carbon nanotubes) in many cases can penetrate the seed coat and plant cell wall which depends on their size, concentration and solubility. The size of carbon nanotubes alone is of great significance in agriculture and biotechnology, the penetration of carbon nanotubes into the plant system can bring changes in metabolic functions leading to an increase in biomass and fruit/ grain yield (Serag et al., 2013). The impact of iron nanoparticles on terrestrial plants revealed that orange–brown complexes/ plaques, formed by root systems of all plant species from distinct families tested, were constituted of nanoparticles containing iron. Further, the formation of iron nanoparticles/ nanocomplexes

was reported as an ideal homeostasis mechanism evolved by plants to modulate uptake of desired levels of ionic iron (Husen and Siddiqi, 2014). Copper is an essential element in the cellular electron-transport chain, but as a free ion it can catalyze production of damaging radicals. Researchers showed using synchrotron microanalyses that common wetlands plants, as *Phragmites australis* and *Iris pseudoacorus*, transformed copper into metallic nanoparticles in and near roots with evidence of assistance by endomycorrhizal fungi when they are grown in contaminated soil in the natural environment (Manceau et al., 2008). Converting carbon dioxide to useful chemicals in a selective and efficient manner remains a major challenge in renewable and sustainable energy research. Silver electrocatalyst converts carbon dioxide to carbon monoxide at room temperature; however, the traditional polycrystalline silver electrocatalyst requires a large overpotential. A nanoporous silver electrocatalyst enables electrochemical reduction of carbon dioxide to carbon monoxide with approximately 92% selectivity at a rate (that is, current) over 3,000 times higher than its polycrystalline counterpart under moderate overpotentials of <0.50 V. The improved higher activity is a result of a large electrochemical surface area and intrinsically higher activity compared with polycrystalline silver (Rou et al., 2014). Growing and harvesting organic nanoparticles from plants represents an important step in the development of plant-based nanomanufacturing (Xia et al., 2010). It is a significant improvement on the exploitation of plant systems for the formation of metallic nanoparticles. An enhanced system for the production of English ivy adventitious roots and their nanoparticles by modifying GA7 Magenta boxes and identifying the optimal concentration of indole-3-butyric acid for adventitious root growth was developed, it represents a pathway for the generation of bulk ivy nanoparticles for translation into biomedical applications (Burris et al., 2011). Recent research has demonstrated that the adventitious roots of English ivy are responsible for the production of an adhesive compound composed of polysaccharide and spherical nanoparticles 60-85 nm in diameter (Xia et al., 2011). The recent advances brought into methodology for biological and eco-friendly synthesis and characterization of herbal and medicinal plant-mediated nanoparticles were reported (Thul et al., 2013; Chauhan et al., 2012).

NANOBIOTECHNOLOGY IN AGRI-FOOD PRODUCTION

Nature is a great teacher, and nanotechnology applications in agriculture can be successful if natural processes are simulated in greater scientific sophistication/articulation for successful implementation. For example, the goal might be to

Antibodies attached to fluorescent nanoparticles to detect chemicals or foodborne pathogens
Antimicrobial and antifungal surface coatings with nanoparticles
Biodegradable nanosensors for temperature, moisture and time monitoring
Cellulose nanocrystal composites as drug carrier
Delivery of growth hormones in a controlled fashion
Electrochemical nanosensors to detect ethylene
Lighter, stronger and more heat-resistant films with silicate nanoparticles
Modified permeation behaviour of foils
Nanocapsulated flavour enhancers
Nanocapsule infusion of plant based steroids to replace a meat's cholesterol
Nanocapsules for delivery of pesticides, fertilizers and other agrichemicals more efficiently
Nanocapsules to deliver vaccines
Nanocapsules to improve bioavailability of nutraceuticals in standard ingredients.
Nanochips for identity preservation and tracking
Nanoclays and nanofilms as barrier materials to prevent spoilage and oxygen absorption
Nanocochleates (coiled nanoparticles) to deliver nutrients more efficiently without affecting colour or taste
Nanoemulsions and nanoparticles for better availability and dispersion of nutrients
Nanoencapsulation of nutraceuticals for better absorption, better stability or targeted delivery
Nanoparticles to deliver DNA to plants (targeted genetic engineering).
Nanoparticles to selectively bind and remove chemicals or pathogens from food
Nanosensors for detection of animal and plant pathogens
Nanosensors for monitoring soil conditions and crop growth
Nanosize powders to increase absorption of nutrients
Nanotubes and nanoparticles as gelation and viscosifying agents
Single molecule detection to determine enzyme/substrate interactions
Vitamin sprays dispersing active molecules into nanodroplets for better absorption

Tab. 1 *Examples of potential applications of nanotechnologies in Agrifood sector*

make soils more capable in order to improve efficient nutrient use for greater productivity and better environmental security (Haghighi and Pourkhaloe, 2013). In a recent article in the journal *Nature Materials*, a researcher at the Cavendish Laboratory of Cambridge University urged her material scientist colleagues to consider agriculture not as a “feedstock with an essentially uncontrollable composition,” but as “a rich and diverse category of materials”, many of them “nanostructure composites, in which self-assembly may play a key role (Athene, 2004). Nanobiotechnology opportunities include food, agriculture and energy applications. Kraft, Nestle, Unilever and others are employing nanotech to change the structure of food – creating “interactive” drinks containing nanocapsules that can change colour and flavour (Kraft) and ice creams with nanoparticle emulsions (Unilever, Nestle) to improve their texture. Others are inventing small nanocapsules that will smuggle nutrients and flavours into the body (what one company calls “nanocuticals”). As noted earlier, nanotechnology has the potential to revolutionize agricultural and food (agrifood) production as illustrated in Tab. 1. Potential applications of the technology include controlled nutraceutical delivery systems for food; on farm applications to deliver drugs or pesticides to livestock or crops; and smart-sensing devices for agri-

culture environment interactions (Huang et al., 2009). Nutrient management with nanotechnology must rely on two important parameters, ie, ions must be present in plant-available forms in the soil system, and since nutrient transport in soil-plant systems relies on ion exchange (eg, NH_4^+ , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , Zn^{2+}), adsorption-desorption (eg, phosphorus nutrients) and solubility-precipitation (eg, iron) reactions, nanomaterials must facilitate processes that would ensure availability of nutrients to plants in the rate and manner that plants demand (Cao et al., 2011). Nanobiotechnology provided industry with new tools to modify genes and even produce new organisms (Knauer and Bucheli, 2009). This is due to the fact that it enables nanoparticles, nanofibers, and nanocapsules to carry foreign DNA and chemicals that modify genes (Torney et al., 2007). In addition, novel plant varieties may be developed using synthetic biology (a new branch that draws on the techniques of genetic engineering, nanotechnology, and informatics). In a recent breakthrough in this area, researchers completely replaced the genetic material of one bacterium with that from another transforming it from one species to another (Galbraith, 2007). Using a medicinally rich vegetable crop, bitter melon, researchers demonstrated the accumulation of carbon-based nanoparticle Fullerol ($\text{C}_{60}(\text{OH})_{20}$) in tissues and cells of root, stem, petiole, leaf, flower and fruit at particular concentrations, as the causal factor of increase in biomass yield, fruit yield, and phytomedicine content in fruits. Fullerenes are a relatively new group of compounds and represent a class of sphere-shaped molecules made exclusively of carbon atoms. Since their discovery in 1985, many aspects of both fullerene and its analogues have been intensively studied to reveal their physical and chemical reactivity, as well as potential use in biological systems (Injac et al., 2013). Fullerol treatment resulted in increases of up to 54% in biomass yield and 24% in water content. Increases of up to 20% in fruit length, 59% in fruit number, and 70% in fruit weight led to an improvement of up to 128% in fruit yield (Kole et al., 2013). Further, contents of two anticancer phytomedicines, cucurbitacin-B and lycopene, were enhanced up to 74% and 82%, respectively, and contents of two antidiabetic phytomedicines, charantin and insulin, were augmented up to 20% and 91%, respectively (Kresma, 2007). Chemists have successfully made DNA crystals by producing synthetic DNA sequences that can self-assemble into a series of three-dimensional triangle-like patterns. When multiple helices are attached through single-stranded sticky ends, a three-dimensional crystal is formed. This technique helps in improving important crops by organizing and linking carbohydrates, lipids, proteins, and nucleic acids to this crystal (Zeng et al., 2009). Chemically coated mesoporous silica nanoparticles help in delivering DNA and chemicals into isolated plant cells, these are various ways in

which nanoparticles enhance drug delivery, and these include encapsulation against immune response, tissue penetration, target selectivity and specificity, delivery monitoring, promoting apoptosis, and blocking pathways (Chandolu and Dass, 2013). The coating triggers the plant to take the particles through the cell walls, where the genes are inserted and activated in a precise and controlled manner, without any toxic side or after effects. This technique has been applied to introduce DNA successfully to plants, including tobacco and corn plants (Park et al., 2008). An International Federation on Organic Agriculture Movements Position Paper on the Use of Nanotechnologies and Nanomaterials in Organic Agriculture rejected the use of nanotechnology in organic agriculture (IFOAM 2011). However, Nano Green Sciences Inc. sells a nanopesticide that they claim is organic (GMO Report 2009). Canada has banned nanotechnology in organic food production. An amendment was added to Canada's national organic rules banning nanotechnology as a "Prohibited Substance or Method".

NANOREMEDIATION AND WATER PURIFICATION

Nanotechnology has played a very important role in developing a number of low-energy alternatives in remediation, among which three are most promising: 1) protein-polymer biomimetic membranes; 2) aligned-carbon nanotube membranes; and 3) thin-film nanocomposite membranes. Nanoremediation methods entail the application of reactive nanomaterials for transformation and detoxification of pollutants (Tratnyek and Johnson, 2006). These nanomaterials have properties that enable both chemical reduction and catalysis to mitigate the pollutants of concern (Zhang and Elliott, 2006). For nanoremediation *in situ*, no groundwater is pumped out for above-ground treatment, and no soil is transported to other places for treatment and disposal (Otto et al., 2008). Many different nanoscale materials have been explored for remediation, such as carbon nanotubes and fibers, enzymes, various noble metals [mainly as bimetallic nanoparticles (BNPs)] and nanoscale zeolites (Manikandan and Subramanian, 2014), nanostructures like titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles and nanowires offer large surface to volume ratio to attract higher probability of the organic molecules to come in contact with the metal oxide molecules residing on the surface of the nanoparticles metal oxides. Nanotechnology can be applied simultaneously to remove the harmful effects of highly toxic organic pesticides and increasing the fertility of the soil through photocatalysis. An attracti-

ve part of photocatalysis is that the end products are carbon dioxide that escapes into the atmosphere, water and mineral salts that are added for the fertility of the soil. Photocatalysis degradation process has also gained popularity in the area of wastewater treatment. Of these, nanoscale zero-valent iron (nZVI) is currently the most widely used (Theron et al. 2008 and Zhang 2003). Macro-scale zero-valent iron (ZVI) has been recognized as a good electron donor with a property to release electrons in aquatic environments. ZVI has been used as a reactive material in subsurface permeable reactive barriers to degrade groundwater pollutants since the early 1990s. ZVI is very active in transforming halogenated compounds, polychlorinated hydrocarbon pesticides and dyes (Mueller et al., 2012). Nanotechnology can also be used to clean ground water e.g. the use of aluminum oxide nanofibres (Nano-Ceram) can remove viruses, bacteria and protozoan cysts from water (Thorn-ton, 2010). Nanocheck, a commercial lanthanum nano-particle product that absorbs phosphates from aqueous environments, is utilized for cleaning fish ponds and swimming pools effectively (Senturk et al., 2013). Water purification using nanotechnology exploits nanoscopic materials such as carbon nanotubes and alumina fibers for nanofiltration (Cohen-Tanugi and Grossman, 2012). Nanofiltration is a relatively recent membrane filtration process used mostly to remove solids, including bacteria and parasites, in surface and fresh groundwater. The solar-powered system uses nanofiltration membranes to treat the local brackish (saline) water, resulting in high-quality desalinated irrigation water. The first field application was reported in 2000 (Zhang, 2005). Nanoparticles have been shown to remain reactive in soil and water for up to 8 weeks and can flow with the groundwater for > 20 m. In one study, Zhang (2003) produced a 99% reduction of TCE within a few days of injection. Trichloroethylene (TCE) is a halogenated aliphatic organic compound which, due to its unique properties and solvent effects, has been widely used as an ingredient in industrial cleaning solutions and as a “universal” degreasing agent. TCE, perchloroethylene (PCE), and trichloroethane (TCA) are the most frequently detected Volatile Organic Chemicals (VOCs) in ground water. Nanomaterials have shown great potential in a wide range of environmental applications due to the extremely small particle size, large surface area, and high reactivity. Nanoscale iron–manganese binary oxide was an effective sorbent for removal of arsenic (III) and arsenic (V) from both synthetic and actual field groundwater (Kong et al., 2013). Calcium–alginate polymer is an excellent choice as an entrapment medium as it is nontoxic and has little solubility in water. The use of nanoscale zero-valent iron (diameter 10–90 nm with an average value of 35 nm) entrapped in calcium–alginate

beads showed great promise for aqueous arsenic treatment (Bezbaruah et al., 2014). A water-cleaning product for swimming pools and fishponds called “Nano-Check” (Altair Nanotechnologies, Reno, NV, USA) uses 40 nm particles of a lanthanum-based compound which absorbs phosphates from the water and prevents algae growth. Lanthanum oxide nanoparticles were utilized to scavenge phosphate from microbial growth media for the use of targeted nutrient starvation as an antimicrobial strategy (Gerber et al., 2012). The effect was shown on *Escherichia coli*, *Staphylococcus carnosus*, *Penicillium roqueforti*, and *Chlorella vulgaris* (Li et al., 2014). Nanotechnology can be used to clean ground water. The US company Argonide (Sanford, FL, USA) is using 2 nm diameter aluminum oxide nanofibers (NanoCeram) as a water purifier. Filters made from 2 nm diameter aluminum oxide nanofibers (NanoCeram) can remove viruses, bacteria, and protozoan cysts from water. Nanoscale iron oxide particles are extremely effective at binding and removing arsenic from groundwater. GeohumusR, a product of Geohumus International is a soil enhancer with water storage capacity based on nanotechnology, which can be also used as a mineral repository in agriculture. It has a larger water storage capacity than previous wetting agents and a product lifetime of 3–5 years. GeohumusR is a high-efficiency polymer that consists of a water storing hybrid material, volcanic rock flour and plant available colloidal silicate. Nanoscale Fe(oxy)hydroxide phases are among the most common natural mineral nanoparticles formed by precipitation from solution after oxidation of aqueous ferrous Fe (Van der Zee et al., 2003), although Fe is an essential element for growth in nearly all species, an abundance of free chelating Fe has been linked to DNA damage, lipid peroxidation, and oxidative protein damage in vivo (Valko et al., 2005). Particle coating, surface treatments, surface excitation by ultraviolet radiation, and particle aggregation can modify the effects of particle size, suggesting that some nanoparticles could exert their toxic effects as aggregates or through the release of toxic chemicals (Nel et al., 2006). The inevitable release of engineered silver nanoparticles (AgNPs) into aquatic environments has drawn great controversy over antibacterial silver: implications for environmental and sustainability assessments toxicity and safety (Boholm and Arvidsson, 2014). Although aggregation and transformation play crucial roles in the transport and toxicity of AgNPs, how the water chemistry of environmental waters influences the aggregation and transformation of engineered AgNPs is still not well understood (Yu et al., 2013). The iron nanoparticles as catalysts are reported (Stein et al., 2011) in reaction catalysis such as asymmetric transfer hydrogenation of ketones, alkene, alkyne hydrogenation, carbonyl reductions, and hydroge-

nation of several functional groups such as aldehydes, ketones, imines, and amides, and breakdown of organic contaminants such as trichloroethene, carbon tetrachloride, dioxins, and PCBs (Polychlorinated biphenyl) to simpler carbon compounds which are much less toxic (Rangheard et al., 2010). Nanoscale iron oxide particles can effectively bind and remove arsenic from groundwater and can help to develop potable water problems in the developing world (Otto et al., 2008). The European Commission requested EFSA (Question number: EFSAQ-2007-124a) to conduct an initial scientific opinion of the risks arising from nanoscience and nanotechnology in food and feed with respect to human health, safety and environmental quality. EFSA which started the process in November 2007 requested from industry the following information:

- Data on the safety of nanomaterials used in food and feed.
- Environmental studies performed on nanotechnologies and nanomaterials used in food and feed.
- Food and feed applications and products containing or consisting of nanomaterials.
- Methods, procedures and performance criteria used to analyse nanomaterials in food and feed.
- Other data of relevance for risk assessment of nanotechnology and nanomaterials in food and feed.
- Risk assessments performed on nanomaterials used in food and feed.
- Toxicological data on nanomaterials used in food and feed.
- Use patterns and exposure to humans and environment.

NANOTECHNOLOGY FOR AQUACULTURE AND FISHERIES

Aquaculture plays an important role in global food production through genetic improvement of plants and animals along with cellular level delivery of genes and drug molecules to specific sites in plants and animals (FAO 2011). Aquaculture is the fastest growing food-producing sector in the world, the world's fastest growing area of animal production is the farming of fish (Defra, 2009), crustaceans and mollusks and the highly integrated fish farming industry may be among the first to incorporate and commercialize nanotech products (Lead and Wilkinson, 2006). According to the FAO there were 45.7 million tonnes of aquaculture production in 2000 and it is growing at a rate of more than 9% per year. With a strong history of adopting new technologies, the highly integrated fish farming industry may be among the first to incor-

porate and commercialize nanotech products expanding and intensifying as novel tool for aquaculture and fisheries development in almost all regions of the world (Rather et al., 2011). The global population is increasing, thus, the demand for aquatic food products is also increasing. Production from capture fisheries has leveled off and most of the main fishing areas have reached their maximum potential (Subasinghe et al., 2014). Nanotechnology has a wide usage potential in aquaculture and seafood industries (FAO, 2011). The shelf life of fish and shellfish may be improved with the use of antibacterial nano-coatings, and transparent polymer films that can help exclude oxygen from around the food product. Nanosensors on the food packaging can also be used to report the deterioration of the fish or shellfish. A public engagement programme is needed to ensure public confidence in the food uses of nanotechnology by the industry. Little is known about the effect of nanoparticles on aquatic organisms (Handy, 2012). There is an immense opportunity to use the nanoparticles to deliver nutraceuticals in fish feed and neutrogenomics studies (Can et al., 2011). Moreover, various nanoformulations of feed help to maintain better consistency and taste of feed (Rather et al., 2011). For fish health in aquaculture, nanotechnological applications include antibacterial surfaces in the aquaculture system, nanodelivery of veterinary products in fish food using porous nanostructures, production from heterotrophic microalgae through transesterification, nanosensors for detecting pathogens in the water, nanopurified water could be used for irrigation and fish culture (Zhang et al., 2013). Scientists from the Russian Academy of Sciences have reported that young carp and sturgeon exhibited a faster rate of growth upon iron nanoparticle feeding furthermore a nanoselenium-supplemented diet could improve the final weight, relative gain rate, antioxidant status as the glutathione peroxidase activities and muscle selenium concentrations of crucian carp (*Carassius auratus gibelio*) (Zhou et al., 2009), moreover, nanoselenium was found more effective than organic selenomethionine in increasing muscle selenium content (Zoho, 2009). Further, the growth and performance of the fish which were experimented, were found higher at nanolevel delivery of these nutraceuticals (Rather et al., 2013). Direct use of silver nano-particles in water to treat a fungal disease has been found toxic to young trout, but a water filter coated with silver nanoparticles prevented fungal infections in rainbow trout farmed indoors (Johari et al., 2013). Not surprisingly, a great deal of government funded research in nanosensors aims to detect minute quantities of biowarfare agents such as anthrax or chemical toxins to counter terrorist attacks on US soil as well to warn soldiers on a battle field of possible risks. For example, the US government's "SensorNet" project attempts

to cast a net of sensor across the entire United States that will act as an early warning system for chemical, biological, radiological, nuclear and explosive threats (Handi et al., 2011; Rather et al., 2011). Pretreatment of rare earth oxide nanoparticles with phosphate in a neutral pH environment prevented their biological transformation into urchin shaped structures and profibrogenic effects. Nanocochleates are unique lipid-based supramolecular assemblies composed of a negatively charged phospholipid and a divalent cation. Nanocochleates, 50 nm cylindrical (cigarlike) nanomaterials, can be used to deliver nutrients such as vitamins, lycopene, and omega fatty acids more efficiently to cells, without affecting the color or taste of food. Researchers have met with moderate success at developing nanoencapsulated vaccines against the bacterium *Listonella anguillarum* in Asian carp (Rajesh et al., 2008), and white spot syndrome virus in shrimp (Rajesh et al., 2009). Nanoparticles have promise for improving protection of farmed fish against diseases caused by pathogens. Chitosan nanoparticles are promising carriers for an oral plasmid DNA vaccine. The major advantages of encapsulating agrochemicals and genetic material in a chitosan matrix include its ability to function as a protective reservoir for the active ingredients, protecting the ingredients from the surrounding environment while they are in the chitosan domain, and then controlling their release, allowing them to serve as efficient gene delivery systems (Kashyap et al., 2015). For example, oral administration with chitosan/ pDNA induced an antibody immune response in fish against *Vibrio parahaemolyticus* (OS4) (Li et al., 2013; Myhr et al., 2011).

NANOTECHNOLOGY IN ANIMAL PRODUCTION/REPRODUCTION AND ANIMAL NANOFEED APPLICATIONS

Many diverse opportunities for nanotechnology exist to play an important role in food production as well as in livestock production (Mura et al., 2014). The potential uses and benefits of nanotechnology are enormous (Verma et al., 2012). Several types of nanostructures and NPs have been developed and have revolutionized the approach to animal sciences. In particular, nanotechnologies were applied to the development of novel drug delivery systems and nanosensors for the diagnosis and treatment of diseases. Emerging evidences indicate that nanotechnology may represent a promising approach to develop new and specific products for animal nutrition (Ross et al., 2004). Although there are not many studies on this topic, many advantages can be obtained by applying this technology to animal production (Scott, 2005),

and to improvement of reproductive performance in beef and dairy cattle (Sutovsky et al., 2013). Reproduction management is an important part of the sustainable production of livestock. It has become evident that advances in farm animal reproduction have become increasingly dependent on advance scientific research in addition to an understanding of the physiological processes involved in reproduction. The use of assisted reproductive techniques (ART) has helped owners to produce offspring from valuable farm animals that were considered infertile using standard breeding techniques. Recently in some of these fields remarkable progress has been made. Implanting tracking devices in animals is nothing new - either in pets, valuable farm animals or for wildlife conservation. Injectable microchips are already used in a variety of ways with the aim of improving animal welfare and safety - to study animal behaviour in the wild, to track meat products back to their source or to reunite strays with their human guardians. In the nanotech era, however, retrofitting farm animals with sensors, drug chips and nanocapsules will further extend the vision of animals as industrial production units. None the less, imperfections are remaining and sustained efforts will be required to optimize existing and invent new technologies (Verma et al., 2012). Microfluidic biochips are being used to segregate male sperm from female eggs for sex selection for animal breeding. Microfluidic devices can not only sort sperm and eggs, but also bring them together in a way that mimics the movement of natural reproduction. This technique would make mass production of embryos cheap, quick and reliable (Studnicka et al., 2009); this study evaluated a nanoparticle-based magnetic purification method that removes defective spermatozoa (~30% of sample) from bull semen and improves sperm sample viability and fertilizing ability in vitro and in vivo. Nanotubes linked to nutrients can be administered to animals and released in specific sites, thus allowing the maintenance of high levels for a long time; this approach should avoid the degradation of nutrients and increase their availability (Ross et al., 2004). Sodium selenite NPs coated with metacrylate copolymers, sensitive to variations of pH, were orally administrated to ruminants and the improvement of selenium absorption was evaluated (Romeo-Perez et al., 2010). Silver NPs and Cu-montmorillonite NPs were used as feed additives to increase the average daily weight gain of pigs (Fondevila et al., 2009; Tong et al., 2007). With funding from the US Department of Agriculture (USDA), Clemson University researchers are feeding bioactive polystyrene nanoparticles that bind with bacteria to chickens as an alternative to chemical antibiotics in industrial chicken production. The FAO has estimated a contamination of 25% of worldwide cereals stockpile by mycotoxins each year with an enor-

mous economic effect (Jelinek et al., 1989; Lindemann et al., 1993; Kim et al., 2012). Regarding this topic, nanoabsorbents composed of magnesium oxide and embedded by silica nanoparticles has been used as effective adsorbent agents as a way to remove aflatoxins from wheat flour (Luo et al., 2004; Masoero et al., 2007; Moghaddam et al., 2010). Shi et al. (2009) reported the use of a modified montmorillonite to decrease the toxicity in feeds of chicks.

NANOFOOD

The term ‘nanofood’ describes food which has been cultivated, produced, processed or packaged using nanotechnology techniques or tools, or to which manufactured nanomaterials have been added (Joseph and Morrison, 2006). In the food processing industries, a few of the most common usages of nanobiotechnology in quality monitoring of food products may be enumerated as nanosensors/ nanobiosensors and bacteria identification; furthermore this technology provides barriers to oxygen and carbon dioxide, thus protecting food quality. The nanosensors can be utilized to detect the presence of insects or fungus accurately inside the stored grain bulk in storage rooms. Researchers suggested models for use of nanobiotechnology, either on a standalone basis or through complementarity with the existing technologies (Sastry and Rao, 2013). Cellular “injection” with carbon nanofibers containing foreign DNA has been used to genetically modify golden rice. Many natural foods contain nanoscale components and their properties are determined by their structure (Dingman et al., 2008). Research into naturally occurring nanostructures in foods is mainly designed to improve the functional behavior of the food (Momin et al., 2013). These have been eaten safely for generations; future generations of humanity will be able to eat any food, no matter how rich; sugar, salt, fat, cholesterol — all the things we love but have to consume in moderation now will have no restrictions on them in future. All food will be nutritious; the sole criterion for choosing meals will be taste. Nanotechnology also holds out the promise of ‘interactive’ foods able to change their nutritional profile in response to an individual’s allergies, dietary needs or food preferences. The purpose of nanofood is to improve food safety, enhance nutrition and flavor, and cut costs. Although nanofood is still in its infancy, nanoparticles are now finding application as a carrier of antimicrobial polypeptides required against microbial deterioration of food quality in the food industry (Cao et al., 2008). Nanofood has, in fact, been part of food processing for centuries, since many food structures naturally exist at the nanoscale.

Currently, the number of food products using nanotechnology of any kind is relatively small. Most of the nanotechnology is still only a promise for enabling new food products: some or many years in the future (Chen et al., 2014). Nanotechnology may revolutionize the food system and has the potential to influence the science of food in a positive way, as it could generate innovation in food texture, taste, processability, and stability during shelf life (Rao, 2009). The benefits of nanofood, for instance, include health-promoting additives, longer shelf lives or new flavor varieties. Researchers examined the encapsulation and controlled release of active food ingredients using nanotechnological approaches (Huang et al., 2009). The dairy industry utilizes three basic micro-sized and nano-sized structures (casein micelles, fat globules, whey proteins) to build all sorts of emulsions (butter), foams (ice cream and whipped cream), complex liquids (milk), plastic solids (cheese), and gel networks (yogurt) (Semo et al., 2007). In fact, dairy technologies not just a microtechnology but also a nanotechnology has existed for a long time. The present research has been focused on modifying food substances to produce nanoparticles that have a different function from the original substance. Early examples from the patent literature and marketing brochures are a number of oxides, such as titanium dioxide and silicon dioxide. TiO_2 is in the top five of NPs used in consumer products, accounting for 70% of the total production volume of pigments and consumed annually at about 4 million tons worldwide, the former has conventionally been used as a color and the latter as a flow agent in foods. Nano-emulsions can encapsulate functional ingredients within their droplets, which can facilitate a reduction in chemical degradation. Nanolamination is a technique for protecting the food from moisture, lipids and gases (Chen et al., 2006). Examples of nano-ingredients and manufactured nanomaterial additives include nanoparticles of iron or zinc, and nanocapsules containing ingredients like co-enzyme and lipids (Magnuson et al., 2011). Food industries argue the addition of micro and nanocapsules to processed foods that will improve both the availability and delivery of nutrients, thereby enhancing a food's nutritional status (Kuzma and VerHage, 2006). For example, a recent study claimed that the encapsulation in nanoemulsions of curcumin, the phytochemical found in tumeric and claimed to have antitumor and anticarcinogenic properties, increased the bioavailability of this compound (Wang, 2007) and hydrophobically modified starch formed micelles encapsulated curcumin (Huang et al., 2010). Dairy products, cereals, breads and beverages are now fortified with vitamins, minerals, probiotics, bioactive peptides, antioxidants and plant sterols (Kumar and Rai, 2009). Some of these active ingredients are now being added to foods as

nanoparticles or at particles of a few hundred nm in size (Shefer and Shefer, 2003). Active ingredients including vitamins, preservatives and enzymes have recently been added to foods in microscale capsules. For instance, many of the commonly used Omega-3 food additives are micrometres in size, such as the 140-180 micron microencapsulated tuna fish oils, which are used by Nu-Mega Driphorm to fortify Australian bread (Mozafari et al., 2006). A coating of starch colloids filled with antimicrobial substance, such that if microorganisms grow on the packaged food they will penetrate the starch releasing the antimicrobial agent. Reports on nanofoods are covered by the popular media. Octenyl succinic anhydride- ϵ -polylysine has the potential to become a bifunctional molecule that can be used as either surfactants or emulsifiers in the encapsulation of nutraceuticals or drugs or as antimicrobial agents. Lipid-based nanoencapsulation systems enhance the performance of antioxidants by improving their solubility and bioavailability, in vitro and in vivo stability, and preventing their unwanted interactions with other food components (Mozafari et al., 2008). The main lipid-based nanoencapsulation systems that can be used for the protection and delivery of foods and nutraceuticals are nanoliposomes, nanocochleates, and archaeosomes. Nanoliposome technology presents exciting opportunities for food technologists in areas such as encapsulation and controlled release of food materials, as well as the enhanced bioavailability, stability, and shelf-life of sensitive ingredients. The application of nanoliposomes as carrier vehicles of nutrients, nutraceuticals, enzymes, food additives, and food antimicrobials was reported (Mozafari et al., 2008). Nanotechnology can provide manipulation of food polymers and polymeric assemblages to provide tailor-made improvements to functional food quality and food safety (Momin et al., 2013). Further, foods among the nanotechnology-created consumer products coming onto the market include a brand of canola cooking oil called Canola Active Oil (Shemen Industries, Tel Aviv, Israel), a tea called Nanotea (Qinhuangdao Taiji Ring Nano-Products Co., Ltd., Hebei, People's Republic of China), and a chocolate diet shake called Nanoceuticals Slim Shake Chocolate (RBC Life Sciences Inc., Irving, TX, USA). The canola oil contains an additive called "nanodrops" designed to carry vitamins, minerals, and phytochemicals through the digestive system and urea. Experts envision numerous nanoparticulate agroformulations with higher bioavailability and efficacy and better selectivity in the near future. Multidisciplinary approaches could potentially improve food production, incorporating new emerging technologies and disciplines such as biochemical biology integrated with nanotechnologies to tackle existing biological bottlenecks that currently limit further develop-

ments. European Food Safety Authority (EFSA) in its opinion on the potential risks arising from nanotechnologies on food and feed safety uses term engineered nano materials (ENM). An engineered nanomaterial is any material that is deliberately created such that it is composed of discrete functional and structural parts, either internally or at the surface, many of which will have one or more dimensions of the order of 100 nm or less. The safety of a given compound engineered in a food should not automatically apply to a nanoversion of the compound, due to possible novel properties and characteristics (Rico et al., 2011), interaction of nanoparticles with edible plants and their possible implications in the food chain. The term "engineered" as used in this opinion is equivalent to the term "manufactured" as used in other reports. Insufficient scientific data prevents FDA from extending GRAS (generally recognized as safe) status of an ingredient to its nanosized version. A significant segment of the public does not want its food "engineered" – bio, nano, GM or otherwise (Kahan et al., 2008).

Reason 1: Toxicity risks of nanofoods and nano agrochemicals remain very poorly understood. The current scientific evidence of the risks associated with nanomaterials is sufficient to warrant a precautionary approach to their management. However significant knowledge gaps remain, presenting a barrier to the development of effective regulation to manage nanofoods and nano agrochemicals.

Reason 2: Nanomaterials are not assessed as new chemicals. Existing regulations do not treat nanomaterials as new chemicals. If a chemical has been approved in larger particle form, the new use of the substance in nanoparticle form does not trigger any requirement for new or additional safety testing (Cushen et al., 2012). This has been recognized by the United Kingdom's Royal Society and Royal Academy of Engineering as a critical regulatory gap (Coles and Frewer, 2013). They recommended that all nanomaterials be assessed as new chemicals (U.K. RS/RAE 2004).

Reason 3: Current methods for measuring exposure are not suitable for nano. Existing regulations are based on the mass of the material as a predictor for expected exposure rates. This approach is completely inappropriate for nanomaterials as the toxicity can be far greater per unit of mass (Reijnders, 2006). Scientists have suggested that nanoparticle surface area or the number of nanoparticles is a more valid metric for measurement of nano exposure (Nel et al., 2006; SCENIHR 2006).

Reason 4: Current safety testing is not suitable for nano. Even if a nanomaterial triggered new safety testing, current test guidelines are inadequate for nanomaterials as they do not assess key properties that influence nanotoxicity. These include: shape, surface, catalytic properties, structure, surface charge,

aggregation, solubility and the presence or absence of 'functional groups' of other chemicals (Magrez et al., 2006; Nel et al., 2006). Nanomaterials must also face full life-cycle assessment, which existing regulation does not require.

Reason 5: Many safety assessments use confidential industry studies. Past assessments of nanomaterials safety by the European Scientific Committee on Cosmetics and Non-food Products and the United States Food and Drug Administration have relied on proprietary company studies (Innovest, 2006). There is often no requirement for the safety of nanomaterials to be assessed by independent nanotoxicologists or for the results and methodology of this safety testing to be made public.

CONCLUSION AND PERSPECTIVES

Coming nanotechnologies in the agricultural field seem quiet promising. However, the potential risks in using nanoparticles in agriculture are not different than those in any other industry. Through the rapid distribution of nanoparticles to food products – whether it be in the food itself or part of the packaging – nanoparticles will come in direct contact with virtually everyone. The editors of *Nature* estimated that any technology takes some 20 years to emerge from the laboratory and be commercialized. Technological innovation has played an important role in shaping the development and characteristics of the agri-food system over the past century and more (Goodman et al., 1987). The emergence of the new biotechnologies of food production since the 1980s — such as genetic engineering, tissue culture and other cellular and genetic level techniques — have been identified as the basis of a new technological paradigm, and as framing the restructuring of contemporary agri-food systems. In the agricultural sector in particular, this has variously been referred to as a new 'bioindustrial paradigm' (Goodman and Wilkinson, 1990; Wilkinson, 2002b), a 'genetic-corporate paradigm' (Scrini, 1995; 2007), or more generally in terms of a shift from a Green Revolution to a Gene Revolution form of agricultural production (Chauhan et al., 2012). Since successive waves of technology, from tractors and combine harvesters to herbicides and GM crops, agriculture have moved ever closer towards an industrial ideal in which agricultural production more closely mirrors the factory system and agricultural labourers are left under-paid, under-employed and unemployed. Nanotechnology in agriculture might take a few decades to move from laboratory to land, especially since it has to avoid the pitfalls experienced with biotechnology. As we are still in the relatively early stages of research and commercialization of nanotechnology, there is considerable

nable potential for civil society groups, workers' unions, farmer and producer organizations, environmental and consumer groups, to challenge and shape the development and implementation of this technology, and to thereby support alternative applications, regulatory regimes, and techno-economic paradigms of development. With the production of engineered nanoparticles we are confronted with a new class of materials that have novel properties compared to bulk material. Information describing the health risk of engineered nanoparticles is only evolving and many questions are still open. For this to happen, sustained funding and understanding on the part of policy planners and science administrators, along with reasonable expectations, would be crucial for this nascent field to blossom. The opportunity for application of nanotechnology in agriculture is prodigious. Research on the applications of nanotechnology in agriculture is less than a decade old. Nevertheless, as conventional farming practices become increasingly inadequate, and needs have exceeded the carrying capacity of the terrestrial ecosystem. We have little option to explore nanotechnology in all sectors of agriculture. It is well recognized that adoption of new technology is crucial in accumulation of national wealth (Knauer and Bucheli, 2009). As the excitement of nanotechnology began to grow, the initial approach to address the potential toxicity of engineered nanomaterials was to assume that these novel materials will behave like their bulk counterparts. A strong dismissive tone regarding potential hazard reigned supreme. It was apparent that material scientists were guiding safety assessment in the early stages of this field. Inevitably, biologist and toxicologist became involved and took a new leadership role in the safety evaluations of nanomaterials. Unfortunately, out of the gate there were missteps. There is an urgent need to develop human resources with an understanding of the complexities of the agricultural production system to serve nanotechnology applications in agriculture successfully. By and large, agricultural education has not been able to attract sufficient numbers of brilliant minds the world over, while personnel from kindred disciplines might lack an understanding of agricultural production systems (Brock et al., 2011). Instruction programs in agricultural nanotechnology, if initiated, might fill this void by fulfilling the twin goals of attracting brilliant learners and developing a body of skilled farm-focused personnel.

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RIASSUNTO

La nanotecnologia è una tecnologia emergente e può rappresentare un'opportunità importante per la comunità scientifica e le imprese. Essa si basa sullo sviluppo di "nanomateriali" che includono materiali naturali, accidentali, o ingegnerizzati, contenenti particelle (non legate, aggregate o agglomerate) in cui il 50% o più in numero e distribuzione, hanno una dimensione esterna nel range 1-100 nm. I nanomateriali posseggono nuove proprietà, come maggiore forza, caratteristiche ottiche avanzate, proprietà antimicrobiche e superconduttività. Attualmente esistono applicazioni in campi diversi, ma ci aspettiamo che la nanotecnologia diventerà una forza economica trainante per lo sviluppo della moderna agricoltura e nel settore alimentare. Le nanotecnologie, infatti, sono in grado di utilizzare in modo più efficiente acqua, pesticidi e fertilizzanti; inoltre possono essere sviluppati nuovi metodi di produzione per sostituire gli impianti di produzione esistenti e riformulare nuovi materiali e sostanze chimiche con prestazioni migliorate con conseguente minore consumo di energia, di materiali, ridotto danno per l'ambiente, e per una bonifica ambientale. In questo lavoro verranno analizzati i recenti progressi nello sviluppo di prodotti nanoagrochimici e le applicazioni delle nanotecnologie in campo agroambientale, per la produzione agroalimentare, per le nanobonifiche e depurazione delle acque, per l'acquacoltura e la pesca, per la produzione/ riproduzione animale, per lo sviluppo di nano-cibo e per l'alimentazione animale.

ABSTRACT

Nanotechnology is an emerging technology and can represent an important opportunity for the scientific and business community. It is based on the development of "nanomaterials" that include natural, incidental, or manufactured materials containing particles (unbound, aggregated or agglomerated) where 50% or more of them, in number and size distribution, have an external dimension in the range 1-100 nm. Nanomaterials exhibit novel properties such as increased strength, enhanced optical features, antimicrobial properties, and superconductivity. Actually exist different applications in different fields but we expect that nanotechnology will become a driving economic force for the development of modern agriculture and in the food sector. Nanotechnology in fact can enable plants to use water, pesticides and fertilizers more efficiently; furthermore novel methods of production can be developed to replace existing production plants and to

reformulate new materials and chemicals with improved performances resulting in lower consumption of energy and materials, reduced damage to the environment, and for environmental remediation. In this work recent advances on the development of nanoagrochemicals, and applications of nanotechnology in agri-environment, agri-food production, nanoremediation and water purification, aquaculture and fisheries, animal production/ reproduction, nanofood and animal nanofeed will be analyzed.

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