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Advanced applications of nanotechnology in agriculture: an overview

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Authors' Contribution **S. Younas**, **H. Asghar** and **I. Shaukat** wrote the introduction, nanotechnology and agriculture, nano-encapsuled fertilizers; **S. Riaz** and **M. Zaib** wrote liquid nano-fertilizers, engineered nanoparticles, gold nanoparticles, nano-encapsulate pesticides; **M. Ishaq, A. Jamshaid, Z. Tariq** and **S. H. Hadri** worked on the development of nano-encapsulated pesticides with different materials and biosensors

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ABSTRACT

As population of world is increasing at an enormous rate, so this increase in population exerts pressure on farmers to increase food production from available area of agriculture. Conventional methods used to increase food production like formation of genetically modified plants as well as use of fertilizers such as urea fertilizer have large number of disadvantages. In order to increase food quantity and quality, nanotechnology is being preferred now a days. Nanotechnology involves Nano encapsulation of agro chemicals such as fertilizers and pesticides so that their accurate and desired amount is released in plants when needed. This nano encapsulation prevents toxicity which is caused by excessive use of these chemicals when these are directly applied to plants. Nano sensor is another application of nanotechnology, which is used to detect pathogen attack on plants. Diagnosis and treatment of the disease at Nano scale is acquiring a lot of attention these days. Inspite of all that nanoparticles can cause chemical as well as physical poisonousness and phytotoxicity to plants affecting their development. Even then, Scientists are expecting that in future, use of nanotechnology in agriculture will be helpful to solve all the problems that are related to food shortage.

Keywords: Urbanization, nano-encapsulated fertilizers, nano-encapsulated pesticides, nano-microcapsules, biostimulator.

INTRODUCTION: The process of Agriculture which is also called as farming is basically a science in which food is produced by using the ability of plants to convert inorganic energy to organic compounds. In the agriculture certain other food compounds are also produce by raising the livestock. Agriculture is the basic corner stone of food production in most of the developing countries. Agriculture food production is basic driver of economy of a country (Sekhon, 2014). In 1950, global population was about 2.5 billion in number which has grown up to 7.2 billion in the year 2014. It is estimated that world's population will increase up to 9.6 billion by 2025 (Grillo *et al.*, 2016). Food and Agriculture Organization (FAO) has forecasted that annually 200 million tons of meat will be required by 2050 in order to fulfill the food requirements of growing population. This rapid growth in population intensifies the food demand produced through agriculture means. This increase in food demand exerts pressure on farmers to increase the growth of crops which are used for animal feed (Sekhon, 2014). In the developing countries there is high rate of urbanization which has also reduced the area for agriculture. Satellite images of earth have also shown that Earth is running out of fertile land and in future food production will be inefficient to satisfy needs of growing world's population (Naderi and Danesh-Shahraki, 2013). About 13.5% of the world's population in 2012-2014 is suffering from undernourishment. Mortality caused by food shortage is estimated to be greater than due to different diseases like tuberculosis, AIDS and malaria in total (Grillo *et al.*, 2016). In order to fulfill the food requirements of large population with limited agriculture resources it is necessary to increase the yield of food production from same area of agricultural land (Khati *et al.*, 2018).

Conventional techniques used to increase food yield: There is urgent need of developing effective strategies that could help in increasing agricultural productivity (Grillo *et al.*, 2016). There are many methods which can be used to increase the yield and quality of agricultural food. Genetically modified plants (GMPs) are one of alternative method use to increase yield of food in the land available for cultivation. GMPs are not accepted worldwide because they have altered genetic makeup and because of human health and environmental concerns (Arora *et al.*, 2012). In order to increase food yield large number of fertilizers such as urea fertilizers, herbicides and pesticides are being used. Phosphorus and nitrogen are the main constituents of the fertilizers. Efficiency of nitrogen fertilizers is 20-50% and that for phosphorus fertilizers is 10-25% so there is a need to make food production more efficient (Naderi and Danesh-Shahraki, 2013). There are certain disadvantages associated with use of chemicals such as pesticides, herbicides and fungicides. This results in bad effects on human health, on domestic animals and also causes soil and water pollution (Mousavi and Rezaei, 2011). When nitrogen phosphorus fertilizers are applied in excessive amount then these fertilizers can affect the growth of plant, decreases organic matter present in soil and also they can move to ground water where excessive nutrient causes eutrophication, water contamination and also affect aquatic life (Naderi and Danesh-Shahraki, 2013).

Nanotechnology and agriculture: Nanotechnology can be used to solve all the problems related with agricultural food quality and quantity. Nanotechnology being an emerging field, opens up wide range of opportunities in different fields like electronics, safety and security, energy conservation, medicine, pharmaceutical industry and also plays a significant role in agriculture area (Ragaei and Sabry, 2014). Agro chemicals can be prepared in Nano-formulation for supplying accurate and desired amount of fertilizers and pesticides to plants which result in crop improvement. Application of biotechnology in agriculture is important (Khan *et al.*, 2017) Nano sensor is another application of Nano biotechnology which is used to detect any disease produced in plant so that it can be identified and cured. For example silver nanoparticles are used for detection and diagnosis of pathogens in plants. Several nano-devices have also made which are being used for genetic manipulation of plants. With the help of these devices foreign DNA can be injected inside of plant cells to make plants insect resistant or herbicide resistant (Sekhon, 2014). Gold nanoparticles are specifically use for the bombardment of foreign DNA into plant cells because they easily take up DNA and are not toxic to plants and they do not harm them (Arora *et al.*, 2012). Nano-technology is also used for processing of food, storage of food and increasing shelf life of processed food. Nano biotechnology is also used to improve animal health, poultry production and animal breeding (Sekhon, 2014).

Nano technology particularly focuses on the use of nanoencapsulated pesticides that aims at increasing solubility of active ingredients and then their release in targeted manner preventing their premature degradation (Ragaei and Sabry, 2014). Another important application of Nano biotechnology is nano-sensor. Network of wireless Nano sensors help in real time monitoring of crop growth and field conditions like moisture content of soil, pests, viruses, temperature, crop nutrient status, weeds and soil fertility etc (Ditta, 2012). Nowadays, Nanotechnology is used for the disease management in plant. Engineered Nanoparticles (e.g. metalloids, nanomaterial and metallic oxide nanoparticles) and lipid derived nano-sensors are used to eliminate plant diseases and observe nutrient deficiency (Karny *et al.*, 2018).

Nano-encapsulated fertilizers Fertilizers have a crucial role in the betterment of crop yields, yet connate inabilities of conventional fertilizer treatments may result in drastic economic and ecological consequences. Almost half of the nitrogen supplied to the plants in the form of the fertilizer is lost to air, water, and other channels, resulting in negative environmental effects such as nitrates leaching into aquatic ecosystem and discharge of nitrogen oxides into the atmosphere. Usage of phosphorus fertilizers is evenly discouraging, a huge concern taking into account the fact that its runoff exasperates eutrophication in marine ecosystems (Mastronardi *et al.*, 2015).

Regarding sustainable agriculture, the application of productive nanotechnology in agriculture is considered as one of the propitious approaches for fundamentally increasing crop yield and to feed the world's fast-growing population. Despite of the interest taken by the agricultural experts towards advancement and use of nanomaterial-related fertilizers, there is a lack of directly-related research in this field (Liu and Lal, 2015). Nanomaterial or nanoparticles can procure time-controlled, estimated, target-specific, automated, and multifunctional abilities to fertilizers (Wang *et al.*, 2016)

Liquid nano-fertilizers: Ekinci, et al. in 2014 carried out experiments on cucumber plant (*Cucumis sativus* A-21F_1) in two years. Ferbanat and Nanonat are liquid nanofertilizers. Ferbanat is composed of amino acids, natural biological substances, vitamins, micro hamates and micro floras. These components are in appropriate agricultural values to improve the existence of the crops produced. Moreover, Nano Nat is a source of mineral and vitamins for the crops which is used to bring about chemical dressing. For this purpose, 30-50% nanonat, with elements in it, is used with phosphorus, calcium, potassium, magnesium and biological nitrogen. Ferbanat is used as a biostimulator against soil microorganisms and stress, for the new generation plants. These liquid Nano fertilizers significantly affected the fruit weight, total yield, fruit length, yield per plant, and dry matter statistically. In both the years, the control gave the lowest value of yield (Ekinci *et al.*, 2014).

Engineered nanoparticles: Engineered nanoparticles (ENPs), such as mesoporous silica nanoparticles (MSNs) can be used to deliver proteins or enzymes that may be helpful for biochemical analysis and genome modifications. Other types of ENPs, such as quantum dots (QDs) or gold nanoparticles (Au NPs) can be used to deliver plasmid having a GFP gene and efficient recombinase enzyme into plant tissues, resulting in effective genome editing. Compared to the conventional delivery techniques, this NP-facilitated methodology can be carried out easily and is very much sensitive (Wang *et al.*, 2016).

Gold nanoparticles: In an experiment to study the Gold-nanoparticles (AuNPs), five experimental groups of the plant *Brassica juncea* were sprayed with different concentrations of Gold-nanoparticles. With increasing concentration of Gold-nanoparticles that were applied, the bio-accumulation of AuNPs was recorded to be increased when calculated by atomic absorption spectroscopy. In the seeds sprayed with 25 ppm of AuNPs, percent germination was recorded to be maximum i.e. 97%. While it was only 80% in the control seeds. This may be because seed capsule now has enhanced permeability. Gold-nanoparticles have an antagonistic effect on the ethylene, causing an increased number of *Brassica* leaves. The AuNPs-treated seedlings also exhibited greater height and stem diameter, as compared to the control. Treatment with Gold-nanoparticles also affected the biochemical markers such as increased chlorophyll, more CO_2 fixation, and higher level of hydrogen peroxide (H_2O_2) (Arora *et al.*, 2012).

Nano encapsulated pesticides: In agriculture, pesticides are used for controlling insects and to minimize the loss caused by the damage to the crops by the insects (Ramadass and Thiagarajan, 2017). Studies have revealed that there are 20-40% losses in global agricultural production due to damage by pests (Grillo *et al.*, 2016). The use of traditional strategies in agriculture like integrated pest management are insufficient. Furthermore, the use of conventional chemical pesticides causes adverse effects on human beings and animals (Ragaei and Sabry, 2014). Pesticide poisoning can lead to abnormalities in fetus, cancer, female infertility, and many problems in immune, nervous and endocrine systems (Grillo *et al.*, 2016). Excessive pesticide usage in agriculture leads to incorporation of toxic materials in ground and surface water. So, ultimately water supplies get contaminated (Chaturvedi, 2014). Therefore, there is need of pesticides that can be employed efficiently and more safely (Grillo *et al.*, 2016).

Nanoencapsuled pesticides are the novel products targeting pests more effectively in smaller concentrations. Active ingredients are encapsulated in polymer material allowing them to be enclosed in protective matrix that protects sensitive core material from physical factors like light or air (Chaturvedi, 2014). Nanopesticides are more advantageous than conventional pesticides because efficiency of active ingredients is increased, also reduces the hazard to the human health and environment safety profiles are enhanced (Mohd Firdaus *et al.*, 2018).

Development of new pesticides: Nano-encapsulation is the process in which substances are coated by various materials in nano range. Substances being coated or encapsulated material are commonly known as core material, the fill or filler, or internal phase, for example pesticides. Materials used for encapsulation are referred to as coating, external phase, membrane or shell, for instance Nano capsules (Auffan *et al.*, 2009).

To encapsulate, different nanomaterial that have been used already includes inorganic porous nanomaterial, polymer based nanomaterial, layered double hydroxides, solid lipid nanoparticles, Nano clays. These nanomaterial that can either be used as carrier material or pesticides exhibiting excellent properties like thermal stability, permeability, stiffness, biodegradability. Active ingredients encapsulated within Nano carrier material and uniformly spreads over the surface of soil or on leaves, are readily ingested by chewing insects. Insects also absorbs it by physiosorption process through cuticular lipid layer as a result of which water protection barrier of insects breaks causing death of insect from desiccation. Nanopesticides larger surface area results in greater affinity to susceptible species thus helps in pest control. Active materials are being protected from premature degradation and also get released in controlled manner by using these nano-carrier materials (Nuruzzaman *et al.*, 2016).

Huang suggested that different polymer materials that are humidity sensitive, light sensitive, enzyme sensitive, pH-sensitive, and thermo sensitive can be used to prepare Nano-microcapsules for pesticide delivery. Nanopesticides formulated using these materials can detect environmental responses and then causes pesticide release in targeted manner. Because of their ability of responding to external stimuli, these intelligent microcapsules have gained considerable attention (Huang *et al.*, 2018).

Encapsulation with polymer based materials: Polymer based materials can be used to encapsulate active ingredients. For example, Polymer Nano composites in which Nano fillers or nanoparticles being dispersed in matrix form polymer. Nano capsules that are used for encapsulating active ingredients generally have core-shell arrangement in which shell is made of polymer material while liquid core contains dissolved active substances. Pesticide formulations are loaded on inner core which may have polymeric matrix absorbing active ingredients. Nano spheres are also being used as Nano carrier system. Active compounds here are distributed uniformly and embedded in polymer material (Ezhilarasi *et al.*, 2013). Nano gels are composed of hydrogel particles dispersed in aqueous solution through chemical and physical cross linking polymers can also be used (Kabanov and Vinogradov, 2009).

Encapsulation with lipid-based nanomaterial: Lipid-based nanomaterial are being used for encapsulation of active ingredients that are hydrophobic, lipophilic and hydrophilic in nature. Hydrophobic active ingredients dispersion in aqueous solutions and bioactive compounds absorption through insect's cuticle is facilitated by them. Example includes Nano liposomes and solid lipid nanoparticles. Nano liposomes are actually vesicles composed of lipid bilayer having watery interior. Phospholipids present in aqueous solution form basis of colloidal structure (Mozafari, 2010). Solid Lipid Nanoparticles are composed of constituents like Lipids (solid at physiological temperatures), emulsifiers, surfactants and water. These nanostructure substances are either crystalline or semi-crystalline. Lipids being used here can be fatty acids, triglycerides, waxes, steroids stabilized by emulsifiers (Potta *et al.*, 2011).

Encapsulation with other materials: Porous inorganic nanomaterial can be used for encapsulation of bioactive compounds. For example, mesoporous silica nanoparticles in which deposition of pesticides is done by suspending them in solution of pesticides followed by evaporation of solvent (Popat *et al.*, 2012) Layered Double Hydroxides (LDHs) are synthetic and natural material composed of metal hydroxide layers that are positively charged can be used for encapsulation (Bi *et al.*, 2014). Clay-Based Nanomaterial's, for example Nano clays are being used for development of Nano carrier materials as well. Nano clays refers to material that is finely grained and belong to class of minerals occurring naturally as hydrous silicate or aluminium silicates (Majeed *et al.*, 2013). Many other Materials can be used for Nano encapsulation such as noisome, nano-zeolite, carbon nanotubes, polymersomes, dendrimers etc (Nuruzzaman *et al.*, 2016).

Formulation of Nano-encapsulated Pesticide: Formulation of pesticide include combination of different materials like active ingredients, stabilizers, solvents and surface active ingredients. Different nanoformulations are available include micro emulsions, Nano emulsions and Nano suspensions (Nuruzzaman *et al.*, 2016).

Micro emulsions are pesticides translucent and transparent dispersions in oil or water and to solubilize them, certain additives like surfactants are added (Langevin, 1991). Nano emulsions also called as ultrafine emulsions or mini-emulsions consists of two immiscible liquid phases. One liquid phase exists as droplets of smaller spherical size that are dispersed in second liquid phase. Less Surfactant is used here as compared to micro emulsions (Kah and Hofmann, 2014). Nano suspensions refers to solid nanoparticles dispersion in liquid solution. It is colloidal dispersion in sub-micrometer range in which particles of drug get stabilized by polymer or surfactant or sometimes by both (Chingunpituk, 2011). This technology increases pesticides bioavailability by facilitating the dispersion of poorly soluble pesticides (Nuruzzaman *et al.*, 2016).

Nano biosensors: Nano biosensors are the sensors consisting of immobilized bio receptor probes for the detection of target analyte molecules. Nano biosensors not only enhances the research opportunities but also act as a potential instrument in the monitoring of biological and physiochemical changes in soil and gives an electrical signal which can be easily determined by humans (Singh and Prasad, 2017). These are the devices designed for the detection of biological or chemical component with Nano scale sensitivity by giving a digital electronic signal. Nano biosensors are reported as mini-laboratories with high potencies for monitoring seasonal and temporal changes in precision agriculture (Subramanian and Tarafdar, 2011). These detect a range of analytes including pathogens, pesticides, environmental pollutants, glucose, urea, metabolites etc.

Nano biosensors usually have three components including a probe, a transducer and a detector. Probes could be any biologically sensitive component such as enzymes, lectins, cells, tissues, receptors, amino acids, molecular imprints etc. which are either directly obtained from biological components or are agonist molecules. These detect the biological change and transmit signal to next component named as a transducer. The transducer then measures the physical change that occurs at probe-analyte interaction site and convert this change into an electrical signal. The detector then perceives the signal and transmit it to microprocessor for amplification, after this data is analyzed and displayed in the form of output (Kaushal and Wani, 2017).

A research reported the first nanowire field biosensor based on transistor which was able to detect DNA methylation in the form of electronic signal, thus avoiding PCR amplification or bisulphite treatments which were used previously for methylated DNA detection. In the same way, Nano biosensors having protein molecules as a probe can sense the presence of special proteins. The ultra-sense detection of protein and DNA molecules play a vital role in the detection of biomarkers, plant microbes, mineral deficiencies in plants and for to differentiate one kind of plant species from the other one (Maki *et al.*, 2008).

Microorganisms produce a number of beneficial and devastating compounds for human beings such as alcohol produced by anaerobic respiration of bacteria. These pathogens cause the rotting of food and results in the production of foul odor which sometimes cannot be detected by humans and thus enhances the food poisoning. So, for these reasons rapid detecting bio elements are required which for to detect microbes in water supplies, food goods and raw food contents. Rapid detecting bio elements also saved time and cost of laborious immunoassays and microbial testing (Ditta, 2012). Latest, Nano biosensors are introduced which can rapidly detect metabolites and IgG (Dasgupta *et al.*, 2017).

By the quantitative measurement of differential oxygen consumption of bad and good microbes in the soil, Nano sensors help a lot in diagnosing the soil diseases caused by fungus, viruses, bacteria and other microorganisms. This measurement involves two sensors_impregnated with bad and good microbes respectively and then these are dipped in a soil solution and differential oxygen consumption of these two sensors are detected. By comparing the oxygen consumption data, the suitable organism for the soil can be determined. Forzani manufactured a device known as noncontact sensor to sense heavy metals in water. In this device a silicon chip is fabricated with an array of electrode rods separated from each other by a few nanometers distance. When Nano sensors are placed in a soil solution then the heavy metal ions in the solution deposit on silicon chip between electrode pairs. This deposition of ions forms a bridge between electrode rods enabling quantum jump conductance in them and thus detection of metal ions.

Nano sensors linked with zeolites also enhance the status of sustainable agriculture. As zeolites enable efficient plant growth by improving the value and efficiency of fertilizer and also by improving the infiltration and retention of water, so by linking Nano sensors with zeolites the release of nutrients and water in plants and soil can be monitored (Singh and Prasad, 2017).

Nano-sensors for disease management: The effective diagnosis and management of plant diseases has fundamental importance for food production, many plant-derived products, and for the sustainability of natural environment. Financial cost on conventional plant pathogen management is very high. The emergence of wide range pathogens and cultural context is critical. To make the successful disease-control strategies, policy makers and farmers tend to communicate and engage (Almeida, 2018).

Nanotechnology now a days is being used for the (Agrawal and Rathore, 2014) disease management in plants. Diagnosis and treatment of the disease at nano scale is acquiring attention these days. Engineered Nanoparticles (NPs) like metalloids, nanomaterial and metallic oxides have activity in elimination of plant diseases. For example, Ag, Zn and Cu NPs are toxic to microorganisms directly (Elmer *et al.*, 2018). Lipid derived Nanosensors are used to observe malnutrition level in diseased plants. These nanoparticles are lipid soluble. So, these Nano-particles can easily penetrate from membranes (Karny *et al.*, 2018). Wade H. Elmer described a new way to manage the plant diseases. According to them, engineered nanoparticles can be used for this purpose. The most used nano-particles are of Ag, Cu and Zn. These nanoparticles act as nano-sensors and also have fungicidal and bactericidal properties to enhance plant health. Other nanoparticles of B, Mn, Cu and silicon have appeared to function in host defense system as fertilizers. These NPs are more competent against pathogens than commonly used fertilizers.

Problems associated with the use of nano-biotechnology in agriculture: Most recently and commonly used engineered Nano particles are classified into five subsequent classes: zerovalent, metal oxides, quantum dots, nano-polymers and carbonaceous nanoparticles. These engineered nanoparticles can stick to roots of plants and they can cause chemical as well as physical poisonousness to plants. Nanoparticles injected to plant cells can also leach to soil and they can cause agricultural land contamination which can also contaminate and spoil food chain (Handy and Shaw, 2007).

In a study, phytotoxicity caused by five different varieties of nanoparticles (MWCNTs, zinc, zinc oxide, alumina and aluminum) on germination of seeds and roots progression of six higher plants (rye-grass, rape, radish, corn, lettuce and cucumber) was examined. Germination of seeds were not exaggerated except for reticence of Nano zinc on ryegrass and Nano zinc oxide on corn plant at a concentration of 2000mg/L. Inhibition of the growth of roots varies among different plants and nanoparticles. Nano zinc and Nano zinc oxide suspensions at concentration of 2000mg/L fired the elongation of roots of different tested plants. Low level of Nano cerium oxide reduced the soybean pods size and growth of plant. Nano-cerium oxide enter into roots of plants and are important in a process of nitrogen fixation performed by soybean crops. When amount of nano-cerium oxide is higher in soil then soybean crops are incapable to perform nitrogen fixation.

It has been also observed that very high meditation of Nano silica silver can produce chemical injuries to the plants such as cucumber leaves. Some plants which are grown hydroponically are also affected by myriad synthetic Nano materials, increasing disquiets concerning the long term effects of these synthetic materials on food supply (Lin and Xing, 2007).

CONCLUSION: Nanotechnology will suitably enhance agricultural inputs and will ensure the safety of human beings and environment by decreasing byproducts that will ultimately improves the agricultural productivity. Much anticipated applications of nanotechnology include detections of pathogens using Nano sensors and monitoring of the plant health. Furthermore, most of the exertions are oriented for the reduction of negative influence of different agrochemical products on human health. Besides limited implementations, nanotechnology will revolutionize the future precision agricultural methodology. Nanotechnology integrated with different emerging technologies like chemical biology would confront the biological problems that cause hindrances in further development.

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